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PROCEEDINGS

THE SEVENTH JAPANESE-GERMAN WORKSHOP ON WASTE WATER AND SLUDGE TREATMENT

Date :
December 11 and 12,1997
Place :
Heian Kaikan, Kyoto, Japan

WATER QUALITY CONTROL DEPARTMENT
PUBLIC WORKS RESEARCH INSTITUTE
MINISTRY OF CONSTUCTION

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PROCEEDINGS

THE SEVENTH JAPANESE-GERMAN WORKSHOP ON WASTE WATER AND SLUDGE TREATMENT

Synopsis:

As an activity within the Japanese – German Cooperation in the field of the environmental protection technology, the seventh Workshop on Waste Water and Sludge Treatment was held on December 11 and 12, 1997 at Heian Kaikan, Kyoto, Japan.

In total, 14 papers were presented from the German Delegation and 21 papers were presented from the Japanese Delegation. There were 11 sessions ;1)The topics were Phosphorus Removal from Wastewater, 2)Reuse of Sludge Ash as Construction Material, 3)Monitoring, Sludge Management, 4)Cost Reduction, 5)Groundwater Preservation and Membrane, 6)Reuse of Wastewater Resources, 7)Environment Preservation, 8) Combined Sewer Overflow Control, 9)Disinfection and THM Precursors, 10)N and P Removal, 11)Toxic Substance Removal.

Key Words : Proceedings, The Seventh Japanese-German Workshop, Waste Water and Sludge Treatment, Municipal Waste Water Field, Industrial Waste Water Field

Foreword

"The Seventh Japanese-German Workshop on Waste Water and Sludge Treatment" was held on Dec. 11 and 12, 1997 at Heian Kaikan, Kyoto, Japan. From the standpoint of Japanese side, this was the first time to be organized jointly with the municipal waste water field which Ministry of Construction manages, and the industrial waste water field Ministry of International Trade and Industry does. We are totally satisfied with the joint workshop and hope to continue the style.

Workshop had been usually held at Tsukuba, when it was opened in Japan. It was opened for the first time outside Tsukuba because some of German delegations attended the COP3 about the Control of Green House Gas effect and related events in Kyoto in the same time.

The both sides exchanged valuable information each other at the Workshop. There were excellent presentations and active discussions. Technological exchange and friendship were very successful and fruitful.

We would like to express our heartily appreciation to the delegations of both countries, especially to the head of German delegation, Dr. Heidborn, Div. Regional Aspects of Technologies, Federal Ministry of Education, Science, Research and Technology (BMBF), for his great leadership to the successful Workshop.

This proceeding contains full papers presented in the Workshop. The contents of the proceeding represent a state of arts and progress of wastewater treatment technology in both countries. We are convinced that the proceeding will be valuable not only for the delegation members but also for the engineers concerned in both countries.

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AIST	: Agency of Industrial Science and Technology
BMBF	: Federal Ministry of Education, Science Research and Technology
GSJ	: Geological Survey of Japan
HIPD	: Hydrospheric Environmental Protection Department
JSWA	: Japan Sewage Works Agency
MITI	: Ministry of International Trade and Industry
MOC	: Ministry of Construction
NIES	: National Institute for Environmental Studies
NIMC	: National Institute of Material and Chemical Research
NIRE	: National Institute for Resources and Environment
ONRI	: Osaka National Research Institute
PWRI	: Public Works Research Institute
RTDD	: Research and Technology Development Division
WQCD	: Water Quality Control Department
WRPC	: Water Re-use Promotion Center

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Schedule of the Workshop and Attached Program

December 10, 1997 — **Study Tour**
Kissyou-in Waste Water Treatment Plant
(Kyoto)
Industrial Waste Water Treatment Plant of ASAHI Beer factory
(Suita, Osaka)

December 11, 1997 — **Workshop**
Heian Kaikan(Kyoto)

December 12, 1997 — **Workshop**
Heian Kaikan(Kyoto)

Joint Communique

The Seventh Japanese – German Workshop on Waste Water and Sludge Treatment

Heian Kaikan, Kyoto, Japan, December 11-12, 1997

1. As an activity within the Japanese – German Cooperation in the field of the environmental protection technology, the seventh Workshop on Waste Water and Sludge Treatment was held on December 11 and 12, 1997 in Heian Kaikan, Kyoto, Japan.

2. The German Delegation was headed by Dr. Heidborn, Head, Div. Regional Aspects of Environmental Technologies, Federal Ministry of Education, Science Research and Technology (BMBF) and was composed of one delegate from Technical Uni. of Aachen, one delegate from Technical Univ. of Darmstadt, one delegate from Technical Univ. of Dresden, two delegates from Technical Univ. of Munich, three delegates from Univ. of Hanover, one delegate from BMBF Project Agency for Waste Management and Remediation of Abandoned Hazardous Site, Federal Environmental Agency, one delegate from BMBF Project Agency for Water Technology Research Center Karsruhe, one delegate from Waste Water Association Obere Iller, one delegate from Herrenknecht GmbH, and one delegate from Preussag Noell.

3. The Japanese Delegation was composed of Municipal Waste Water Field and Industrial Waste Water Field. Municipal Waste Water Field headed by Dr. Kyosai, Director, Water Quality Control Dep., Public Works Research Institute (PWRI), Ministry of Construction (MOC), was composed of one delegate from Osaka Sangyo Univ., one delegate from Kyushu Univ., five delegates from PWRI, one delegate from National Institute for Environmental Studies, two delegates from Japan Sewage Works Agency, and five delegates form cities of Tokyo, Nagoya, Kyoto, Osaka, and Fukuoka. Industrial Waste Water Field headed by Dr. Miyazaki, Director, Hydrospheric Environmental Protection Dep., National Institute for Resources and Environment (NIRE), Agency of Industrial Science and Technology, Ministry of International Trade and Industry (MITI), was composed of five delegates from NIRE, one delegate from Geological Survey of Japan, two delegates from National Institute of Material and Chemical Research (NIMC), one delegate from Osaka National Research Institute, one delegate from city of Osaka, and one delegate from Water Re-Use Promotion Center.

4. Opening addresses were given by Dr. Miyazaki, Dr. Kyosai, Dr. Heidborn, Mr. Ishikawa, Director, Sewerage and Sewage Purification Dep., City Bu., MOC, and Mr. Takeuchi, Assistant Director, Water Generation Policy Office, Environmental Protection and Industrial Location Bu., MITI.

5. The chairmanship was shared by Dr. Tominaga, NIRE, Dr. Kyosai, Dr. Miyazaki, Dr. Heidborn, Prof. Kusuda, Kyusyu Univ., Dr. Tanaka, NIMC, Dipl.–Ing. Fuhrmann, BMBF Project Agency, FZK, Prof. Seyfried, Univ. Hannover, Mr. Nakamura, PWRI, Prof. Niessner, Technical Univ. Muenchen, Dr. Suwa, NIRE, and Dr. Masuoka, NIMC.

6. In total, 14 papers were presented from the German Delegation and 21 papers were presented from the Japanese Delegation (Municipal Waste Water Field : 11 papers, Industrial Waste Water Field : 10 papers). The topics were Phosphorus Removal from Wastewater, Reuse of Sludge Ash as Construction Material, Monitoring, Sludge Management, Cost Reduction, Groundwater Preservation and Membrane, Reuse of Wastewater Resources, Environment Preservation, CSO Control, Disinfection and THM Precursors, N and P Removal, and Toxic Substance Removal.

7. A study tour was held on December 10 at Kissyou–in Waste Water Treatment Plant, Kyoto city, and industrial waste water treatment plant of ASAHI Beer factory, Suita city.

8. Both sides agreed that this exchange of research and development was very worthwhile. The eighth Workshop is proposed to be held in Germany in the year 2000.

Shunsoku Kyosai	Akira Miyazaki	Juergen Heidborn
Head	Head	Head
Japanese Delegation of Municipal Waste Water Field	Japanese Delegation of Industrial Waste Water Field	German Delegation

Opening Address

"Research for the Environment Programme of the Federal Government"

Dr. J. Heidborn

421 (B)
Dr. Heidborn

Bonn, 22th of November 97
T. 3541

Research for the Environment
Programme of the Federal Government
(1998 - 2001)

I. ***Introduction:***

The programme „Research for the Environment" was decided by the Federal Government at the beginning of September 1997. It will cover the federal policy in this field from 1998 to 2001 and was worked out commonly by the ministries for Environment and for Research and Technology.

This programme is considered as a frame which is filled out by two main chapters:

1) „Engineering the Environment Regionally and Globaly"
and
2) „Sustainable Management"

Both including state promotion for various sectors like

a) on first hand environmental engineering in rural and urban areas, in Biosphere, in Hydro-, Cryo- and Atmosphere, in the climat system and in Global Change,
b) on second hand in integrated environmental technology (those are environmental protection integrating measures in industry) and in end of the pipe cleaning-up-technologies for waste management, for abandoned sites, waste water and polluted air.

A third chapter is dealing with „Environmental Education".

II. Basic aims and definitions:

A new central element in the Federal Government's strategy is the creation of concepts for a sustainable development of regions. This new, area-related approach will seek solutions both for national and also global environmental problems.

This new research approach requires the definition of environmental goals, which are then the starting point for concepts as a basis for future action. They have the goal of a precautionary avoidance of harmful stresses caused by environmentally inappropriate use or engineering. The measures are focused on the environment as a human habitat.

The research indicating approaches towards sustainably dealing with the regions in which we live, work and spend our leisure, needs a solid knowledge base which must be continuously extended. We seek to understand the basic functions and processes of the biosphere, atmosphere, the general climate system as well as the overall system of the earth. An important goal of the support measures for environmental research is to obtain orientational knowledge for environmentally acceptable behaviour and to recognize in good time the risks of environmental change.

Sustainable management implies that the forces of the social market economy must be harnessed in the service of sustainable development and means that damage to the ecosystem must be avoided on a small and large scale, over time and space, quantitatively and qualitatively. On the other hand, sustainable management means learning from nature. From a better understanding of ecosystem functions the "eco-efficiency" of man-made products and production processes can be improved above all by conserving energy and resources and their ecological compatibility (consistency) can be increased by a recycling economy.

The national goals of sustainable managment are:

1. uncoupling of economic growth from additional polluting environmental exploitation,
2. reduction of costs for environmental protection and
3. strengthening the competitive position of the German environmental industry.

This means the entire innovation potential of the economy and society must be activated.

On the basis of what has already been achieved, Germany has good prospects of consolidating its position in environmental protection by a further approach towards sustainable management and thus in the long term of improving both its attractiveness as an industrial site and future competitive opportunities in which environmental standards will gain significance. With this environmental research programme, the Federal Government intends to create incentives for the search for and realization of solutions on the way towards environmentally appropriate management and to initiate specific measures for promoting this process.

III. Production - integrated environmental protection (i.e. clean technologies)

Environmental pollution is mainly manifested by material extraction and inputs so that the slowing down and minimization of material flows are among the central goals of product- and production-integrated environmental protection.

The subject of research and technological development in **product**-integrated environmental protection are approaches for avoiding emissions during manufacture as well as in the use and consumption of products, for reusing or recycling products as well as for the dematerialization and slowing down of material cycles.

The Federal Government considers that in addition to the direct promotion of production integrated environmental production **free-market incentives** are also necessary (free-market incentives mean, for example release of taxes, special fees on polluters and pressure for selfcommitments of producers) Those measures shall support the ecological optimization of products and production techniques in order to contribute to an economically successful reduction of material and energy conversion rates, to increasing material and resource productivity, to closing the material cycles and minimizing pollutant inputs. The government thus aims at an increasing **uncoupling of economic growth from environmental pollution**.

IV. Water research and -technology

The main goal is to protect natural water resources and to assure a sustainable use of them. Therefore sustainable ways of consumption and technical innovations are

required. The protection of resources and control of sustainability of water management or water economics is enabled by the development of extensive and integrated water quality standards. Cost-efficiency and implementation into a marketable proposition of new developments is of fundamental importance also for the global competitivity of German water-industries.

During the last two decades the **biological water quality** of German Rivers improved continiously which includes the eastern part of Germany since 1990. Nowadays a kind of a steady state is reached, where no more improvements can be observed. On the other hand there are lots of reports about the appearance of several anthropocentric contaminants and hazardous substances in natural aqueous systems.
Some reasons for the stand still are: morphological aspects of river systems were neglected; contaminants appear by non point sources; low but chronic concentrations of contaminants have occured.

measures:
- Development of extensive water quality standards, that lead to practical instructions in dealing with natural water resources
- Examination of the appearance of health relevant hazards and organisms in water cycle

In Germany the **drinking-water** is produced to 72 % out of groundwater. There are problems with the impact of hazardous substances, espacially airborne chemicals or substances with origin in agricultural land use.

measures:
- Build up of a test facility for subsurface remediation for large-scale experiments of different remediation and cleanup technologies (e. g. VEGAS)
- Development of cost effective in situ bioremediation technologies
- Development of sustainable strategies for drinking-water supply (withdrawing of groundwater according to the self regeneration ability of the resources; low energy and low chemical demanding conditioning processes; utilization of drinking-water sludge)

German **municipal waste water** treatment policy requires the application of new physical and biotechnological processes. The developments will be focused on hygienic safety, disposal of waste water sludge and cost effectivness.

measures:
- Development of eco efficient waste water treatment devices
- Selective treatment of rainwater and waste water
- Decreasing the cost of operation and investment

Measures in **industrial waste water** management are not only restricted to the modification of existing production processes or to develop new ones. They also take into account that future products have to be environmental sound and do not pollute the environment especially do not contribute to non point sources.

measures:
- Closing loops of process water and reduzing fresh water demand of industrial production
- Development and use of high technologies for selective recovery of usable wastes
- Substitution of water poluting products; especially mass products like pesticides, fertilizers and others

The examination of the quality of natural water resources requires new **analytical methods** and special risk assessment techniques.

measures:
- Development of analytics that are related to environmental and health effects caused by pollutants
- field screening methods; remote sensing apparatus.

Session 1

Joint Research

[Phosphorus Removal from Wastewater]

" Performance and Microbial Structure of Two Bench-scale Plants for N- and P- Elimination"
Dipl. – Biol. M. Eschenhagen -11

"Performance of Biological Phosphorus and Nitrogen Removal Process with Immobilized Nitrifiers and its Model Development "
Y. Suzuki -25

"New Experiences of the Fullscale Application of Biological N-and P-Removal in Germany - Problems with Filamentous Bacteria and Scum "
Prof. Dr. C. F. Seyfried -36

[Reuse of Sludge Ash as Construction Material]

"Evaluation Method for the Construction Material Made of Sewage Sludge - Technical Standard and the Leaching Test Method "
M. Ozaki -63

"Impact of Sewage Sludge Ashes on Brick Manufacturing - Technical Aspects and Environmental Compatibility
Dipl.-Ing. B. Wiebusch -75

Performance and microbial structure of two bench-scale plants for nitrogen and phosphorus elimination

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ABSTRACT

The performance and the composition of the microbial community have been examined in two bench-scale reactors for nitrogen and biological phosphorus elimination. One was a fluidized-bed biofilm reactor for nitrification arranged as the ultimate treatment step subsequent to BOD and biological P elimination, the other one a series of anaerobic, anoxic and aerobic tanks, respectively, for combined nitrogen and phosphorus elimination. Both reactors were subjected to shock loads caused by the addition of fecal matter to the inflow of a full-scale domestic waste water treatment plant. The microbial composition was analysed by means of oligonucleotide probes. The performance of both reactors was high, and despite of the quite different mode of operation, the microbial composition in terms of major taxonomica groups not displayed significant differences. There were no very significant successional changes in the 10 months operational period. Irrespective to the efficient P elimination, the gamma Proteobacteria which include the genus *Acinetobacter* not were present at high cell numbers.

ABBREVIATIONS

CFU	Colony forming units
DAPI	4′,6-Diamidino-2-phenylindol-dihydrochlorid
FLUOS	5,(6)-Carboxyfluorescein-N-hyroxysuccinimidester
MPN	Most probable number
HGC	Gram-positive bacteria with a high Guanin and Cytosin content of the DNA
TNB	Total number of bacteria

INTRODUCTION

Within the scope of the joint German-Japanese Research project on wastewater and sludge which is sponsored by the BMBF, investigations have been performed on two bench-scale plants for biological phosphorus and nitrogen elimination.

One of the plants consists of anaerobic and aerobic tank and the last tank is a fluidized- bed reactor. The performance of this nitrification reactor has been investigated at different levels of the water residence time and concentration of the carrier material, respectively. The other plant is composed of an anaerobic, an anoxic and an aerob tank, respectively, succeeded by a clarifier. The feed for the experimental plant is diverted from the aerated grit chamber of a domestic waste water treatment plant.

The research goal was to analyze the microbial community of the nitrifying biofilm and to characterize the microbial composition of the suspended growths of the plant for combined P and N elimination as a function of the composition of the wastewater, for instance through addition of night soil. The influence of load surges likewise has been examined.

For the investigation of the microrganisms, both classical methods such as plate count (CFU) and most probable number (MPN) and molecular biological methods have been used. The classical methods are restricted as to the conclusions to be drawn from the analytical results because of the selection pressure exerted on the structure of the microbial community by the composition of the culture media. Microbial species that are easily to cultivate are stimulated

as to their growth rate. This results in a severe and unrealistic shift in the species composition of the microbial population. Furthermore, the total number of cells normally is underestimated by up to three orders of magnitude. Even if optimal (i.e. very special) culture media were used, only 1 to 15% of the total number of bacteria (direct count) have been recorded (WAGNER et al.1993).
With the in situ hybridization by means of rRNA-targeted oligonucleotide probes a method is available which makes an in situ-identification of the microbial populations possible. The special advantage of this method is that rRNA has the highest proportion in the total concentration of RNA of the microbial cell, that this content is high if the cells are active, that it is available with at a high number of copies. For the identification of the bacteria it is important that segments of the rRNA molecules exist that are highly conservative, i.e. common to the same major group of bacteria, and other which are variable and thus may be specific to a lower taxonomic unit like a species or a strain. Thus the specifity spectrum of the probes which are recently available is very broad, from universal probes which identify all Eubacteria (or, alternatively, all Archaebacteria including the methanogens) to probes which are specific at the species and subspecies level.
We have made an attempt to analyze microbial composition of both the activated sludge and the biofilms on the supporting material in the nitrification reactor.

METHODS

Arrangement of the experimental plant.
The fluidized bed nitrification reactor has been arranged as the final step subsequent to the tanks for the elimination of organic carbon and of phosphorus (Fig. 1, Plant No1).
The aeration was performed by means of punched PVC tubes supplied by a compressor. The nitrification reactor is filled with the supporting material supplied by the Japanese partner. The properties of the material are evident from Table.1.

Table 1: Properties of the carrier material

Material	polypropylene tubules
Density	$1{,}025 g \cdot cm^{-3}$
Length of a tubule	5mm
Diameter	4mm
Surface	$121 mm^2$
Number of tubules per unit volume	$1160 \cdot l^{-1}$
Specific surface per unit volume	$1{,}41 m^2 \cdot l^{-1}$

Plant No 2 presents the arrangement of the reactors for the biological P and N elimination. The mixed liquor is held in suspension by means of stirrers in the anaerobic and anoxic tank. The dissolved oxygen concentration was adjusted to a level of 2 to 3mg/l. Whereas the anaerobic and the anoxic tank have been completely mixed, the aeration tank was a cascade consisting of cells in series.

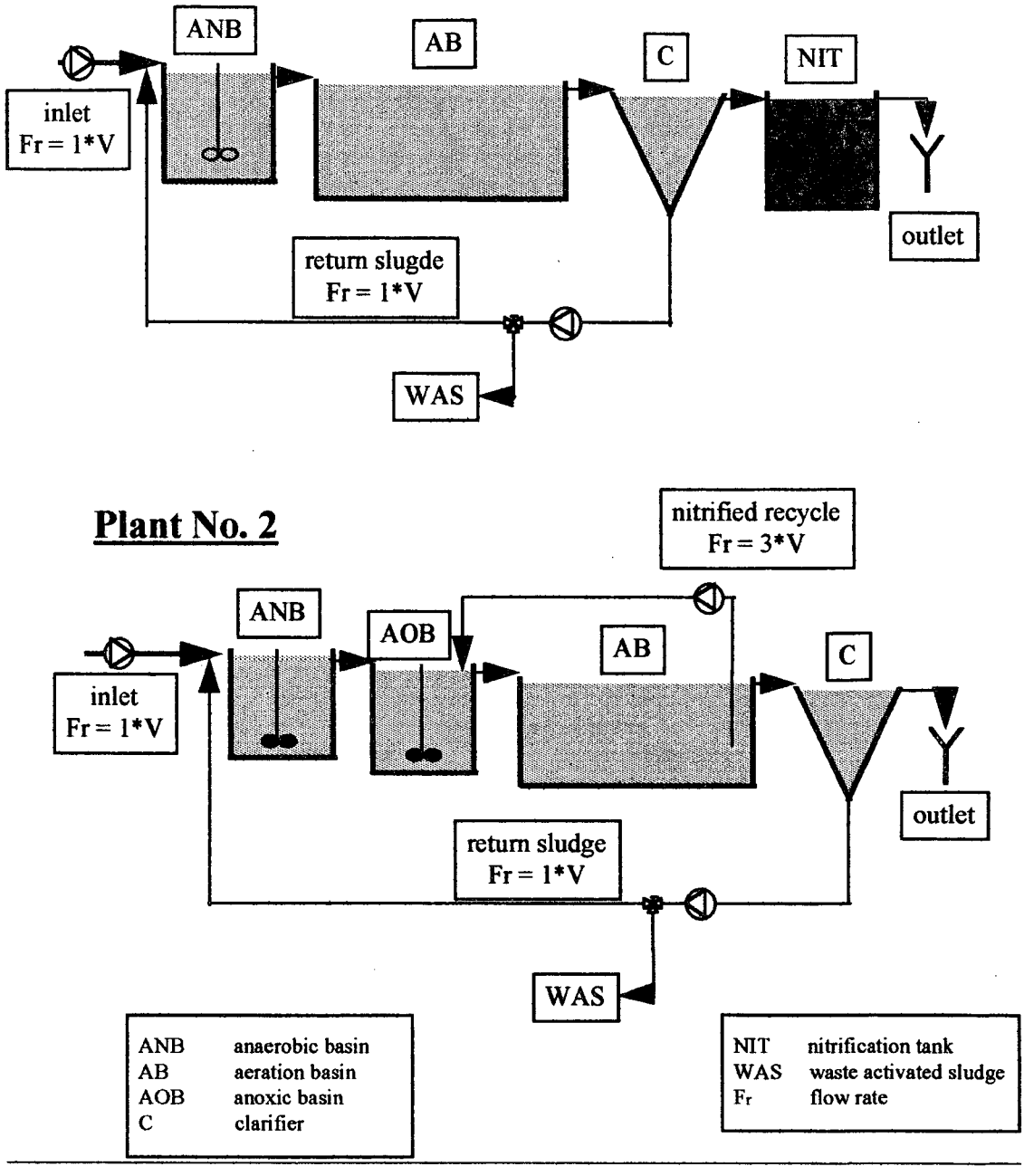


Fig.1: Bench-scale plant for nitrogen and biological phosphorus elimination

Microbiological examination

In both bench-scale plants, the microbial communities have been investigated by means of in situ hybridization with oligonucleotide probes.

For the sampling of the bacteria, 10 biofilm carriers taken from one tank have been transmitted into phosphate buffered saline (130mM NaCl and 10mM $NaHPO_4/NaH2PO_4$, pH 7,4).

The biofilm was detached and homogenized by means of sonication (USD30,Emich Ultraschall GmbH, Berlin). The cells were separated at 13.000 rpm and preserved as follows:

Cell fixation, in situ hybridization

Cell fixation, in situ hybridization. The samples were fixated with fresh prepared paraformaldehyde solution (3,7%) for 1-3 h at 4°C or with 50% absolute ethanol for the investigation of Gram-positive cells. After fixation the cells were washed with PBS (130mM NaCl, 10mM Na_2HPO_4/NaH_2PO_4, pH 7,4) and treated with equal parts of PBS and icy-cold absolute ethanol. The samples were stored at -20°C. These biofilm samples were spread on the wells of gelatin coated slides [0,1% gelatin, 0,01% $CrK(SO_4)_2$,Marienfeld, Bad Mergentheim, FRG]. They were air-dried and subsequently dehydratized by successive passages through 50%, 80%, 98% ethanol (at each concentration for 3min). Upon each of the panels on glass slides, 8µl of the hybridization buffer [0,9M NaCl, 10mM Tris-HCl-solution, 0,01% SDS, formamid concentration depending on the probe] and 1µl of the oligonucleotide probe with a concentration of 20-50ng ml^{-1}were added. The slides were incubated in a moisture chamber for 1,5 hours at 46 °C in a horizontal position. Subsequently, the hybridization mixture was rinsed with washing buffer which had a temperature of 48 °C and the slide was transfered into a vial with washing buffer of the same temperature. After 20 min, the slide was withdrawn, carefully rinsed with destilled water, and air dried.
The probes used for the investigation of the microbial communities are presented in Table 2.

Table 2: Oligonucleotide probes for the investigation of the biofilms and activated slugde

Specifity	**Probe**	**Sequence (5′ - 3′)**	**References**
Eubacteria	EUB	5′-GCTGCCTCCCGTAGGAGT	Amann et al. 1990
NON-Eubacteria	NEUB	5′-CGACGGAGGGCATAATCA	Amann et al. 1990
α-subclass of Proteobacteria	ALF1b	5′-CGTTCGYTCTGAGCCAG	Manz et al. 1992
β-subclass of Proteobacteria	BET42a	5′-GCCTTCCCACTTCGTTT	Manz et al. 1992
γ-subclass of Proteobacteria	GAM42a	5′-GCCTTCCCACATCGTTT	Manz et al. 1992
Cytophaga-Flavobacterium group	CF	5′-TGGTCCGTGTCTCAGTAC	Wagner et al.1994
Gram-positive bacteria with a high G+C-content	HGC	5′-TATAGTTACCACCGCCGT	Wagner et al.1994
Nitrosomonas spec.	NEU	5′-CCCCTCTGCTGCACTCTA	Wagner et al.1995
Nitrosomononas C-56, N. europaea, N. eutropha, Nitrosococcus mobilis	Nsm156	5′-TATTAGCACATCTTTCGAT	Mobarry et al. 1996
Nitrosolobus multiformis, Nitrospira briensis, Nitrovibrio tenuis	Nsv443	5′-CCGTGACCGTTTCGTTCCG	Mobarry et al. 1996
Nitrosomononas C-56, N. europaea, N. eutropha	Nso1225	5′-CGCGATTGTATTACGTGTGA	Mobarry et al. 1996
Acinetobacter spec.	ACA23	5′-ATCCTCTCCCATACTCTA	Wagner et al. 1994
Paracoccus spec.	PAR651	5′-ACCTCTCTCGAACTCCAG	Neef et al. 1996

Competitor oligonucleotide probes

Competitor for probe	**Probe**	**Sequence (5′ - 3′)**	**References**
Beta	Cgam	5′-GCCTTCCCACATCGTTT	Amann et al. 1990
Gamma	Cbeta	5′-GCCTTCCCACTTCGTTT	Stahl et al. 1991
NEU	CTE	5′-TTCCATCCCCCTCTGCCG	Wagner et al. 1995

These probes had been labelled with the fluorescence stain Cy3 (absorption maximum at 554 nm, emission maximum at 570 nm).

For the probes specific to the beta and the gamma-subclass as well as to *Nitrosomas sp.* (NEU) competitor probes have been used to improve the specificity of the hybridization, i.e. to block unspecific binding sites. These probes have not been laballed with a fluorescence marker.
For the determination of the total cell number, the slides were stained with DAPI (4',6-Diamidino-2-phenylindol-dihydrochlorid) at a final concentration of $1 \mu g \cdot ml^{-1}$.The staining with DAPI (Merck) was performed subsequent to the in situ hybridization with 40µl DAPI upon each panel for 15min at room temperature in the dark. The slides were mounted in Citifluor AF1 (Citifluor Ltd., London, UK). For the microscopical examination, an epifluorescence microscope was used. Combinations of specific filters were used for DAPI (exciter D 360/40, dichroic mirror 400 DC LP, emission filter D 460/50) and for Cy3 (exciter HQ 535/50, dichroic mirror Q 565 LP, emission filter HQ 610/75). At first the hybridized cells were counted, subsequently those stained with DAPI in order to avoid bleaching of Cy3 during DAPI examination.

Confocal laser scanning microscopy (CLSM)
In order to examine the three-dimensional distribution of the microorganisms, the CLSM appeared to be promising. On principle, the preparation with a microbial film/activated sludge floc is scanned by means of a laser beam. The photographs were produced by means of CLSM, Leica TCS 4D. The resulting optical sections are available in a digitalized form. In order to be able to use different fluorescent dyes simultaneously, the following filters have been used:

Excitation wavelength	Emission detector
647 nm	LP665
568 nm	LP530
568 nm	LP590
488 nm	BP-FiTC

The biofilms had been hybridized with a specific probe labelled with Cy3 and with EUB 338 labelled with FLUOS.

RESULTS AND DISCUSSION

Bench-scale plant for biological phosphorus elimination and a fluidized bed reactor for nitrification (Plant No1)
The volume loading of the activated sludge tank arranged in front of the nitrification reactor was so high that there occured still no nitrification. To examine the NH_4 elimination in the fluidized-bed reactor, the hydraulic residence time and the concentration of the carrier material have been varied. Fig. 2 presents the NH_4 elimination as a function of both variables. Irrespective to the high variation of the data a trend is evident as to the increase in the NH_4 elimination with a higher concentration of the supporting material (full lines). Simultaneously, the NH_4 elimination decreases with an increasing volume loading (dotted lines). At very low volume loadings, this correlation is not significant, but this low range also is unimportant for a practical application.
A carrier concentration of 70% by volume corresponded to an average areal of 0,632 gNH_4-$N/m_F^2 \cdot d$ (m_F:.effective surface of carrier) and an NH_4N-elimination of more than 93%.

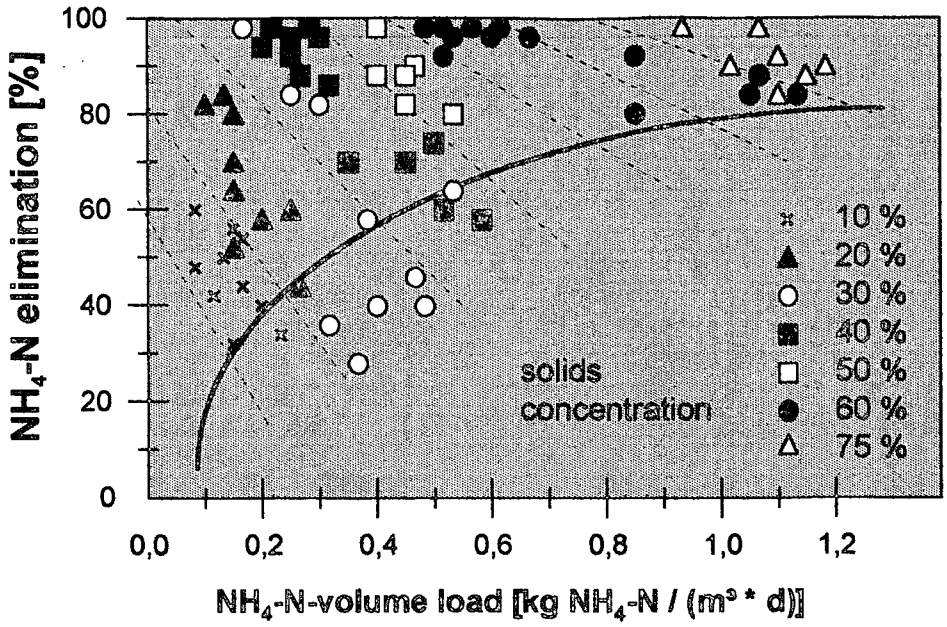


Fig. 2: NH_4-N elimination in relation to the ammonia volume loading and the concentration of carrier material

In Fig. 3, the NH_4-N effluent concentration (at a hydraulic residence time of 1,8h and a carrier concentration of 70% is presented. The effluent concentrations obtained in the experiments are far below the German effluent standard of 10mg/l NH_4-N. If the ammonia concentration in the inflow sharply increased due to the addition of fecal matter from a scavenging service, the standard for ammonia in the outflow could not be met.

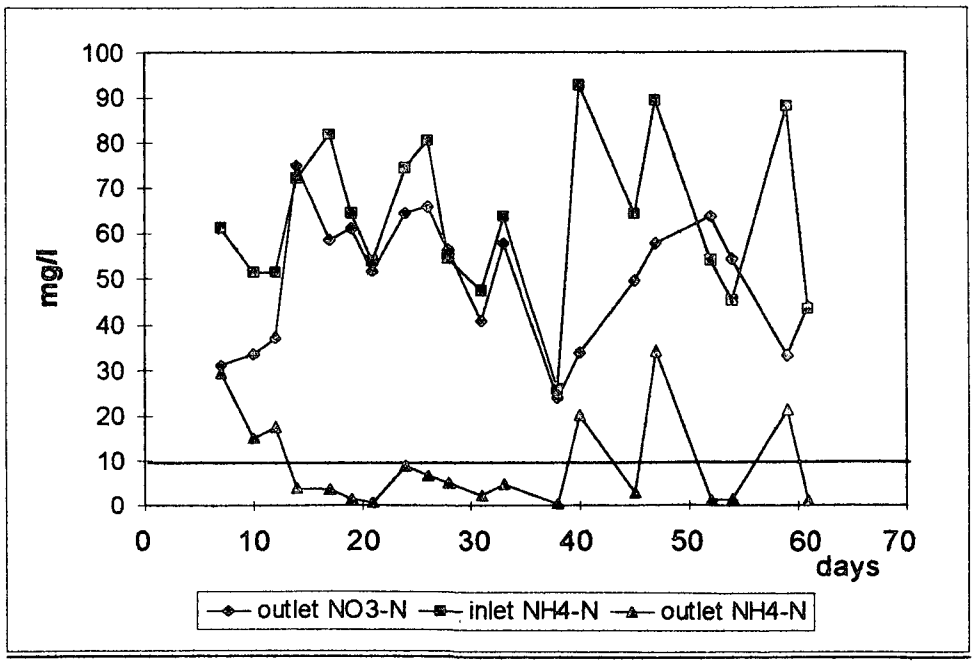
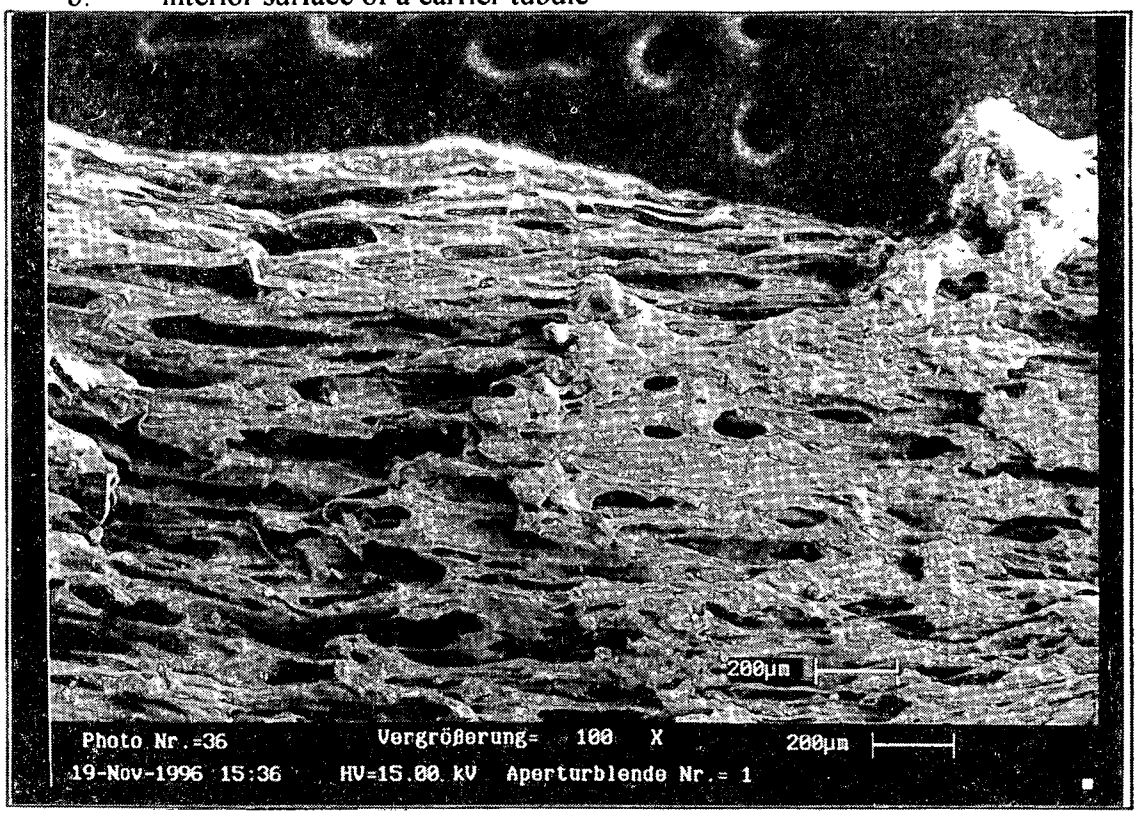
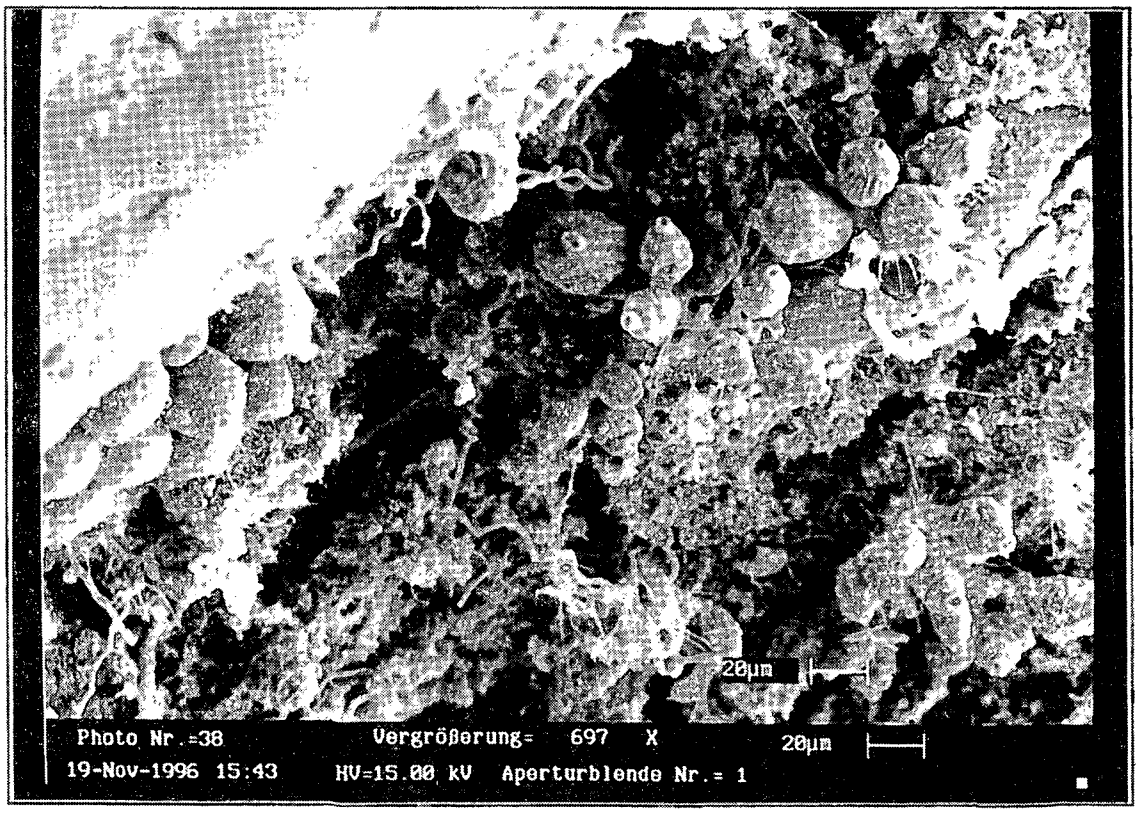


Fig. 3: Ammonium oxidation in the nitrification reactor with a carrier concentration of 70%

Fig. 4: Scanning electron microscope
a: carrier material without biofilm
b: interior surface of a carrier tubule



a



c

b

Properties of the carrying material

The material used in our experiments has a high coefficient of roughness. Thus, enough area is available to the bacteria to grow to an optimum biomass concentration. Only if the thickness of the biofilm is low, there is a direct relationship of the biofilm surface to the specific surface of the carrying material. If the thickness is high, this no longer is valid, but the internal surface of the biofilm now likewise is relevant. Unlike the outer surface of the tubules on which only a very thin biofilm could be maintained, the lumen was protected from shear forces. There must have been step concentration gradients of dissolved oxygen and ammonia from the mouths towards to the central part of the lumen. The microscopical examination revealed dense growths of stalked peritrich ciliates in the lumen (Fig.4). This indicates that the molecular diffusion of oxygen and ammonia to the microbial films in the lumina may have been forced through the „bioturbation", i.e. the microcurrents generated by the peristom currents of the peritrichs. As related to the size of the microbial cells in the biofilm and the thickness of the Prandtl boundary layer, these microcurrents may be relevant to the oxygen and ammonia flux and, thus, to the performance of the reactor.

In the experimental period with the highest concentration (75%) of the carrier material, the shearing forces caused by the increased number of collisions between the tubules were very high. This resulted in the formation of a thin and compact biofilm. The high hydraulic stress may also have been efficient as a stimulant for the microbial synthesis of extrapolymeric substances which stabilize the biofilm (LAZAROVA et al 1994).

Microbiological investigations

The composition of the microbial community grown on the carrier material in the nitrification reactor was examined by means of in situ identification with rRNA-targeted oligonucleotide probes. This method already has been approved in studies on biofilms (AMANN et al. 1992, MANZ et al 1993, ROTHEMUND, 1995). Besides a probe of low specifity in order to cover all *Eubacteria*, group-specific probes were used to identify alpha-, beta- and gamma-Proteobacteria, the *Cytophaga-Flavobacterium* group and for Gram-positive bacteria with a high G+C content of the DNA. In addition, we used genus-specific probes in order to get information on the proportion of ammonia and nitrite-oxidizing bacteria as well as a probe for *Paracoccus* as a principal representative of the denitrifiers.

The cell numbers obtained by means of the probes were related to the number detected after staining with DAPI.

As several of the bacterial species mainly exhibited growth in clusters, these samples could only be examined after some modification. The clusters could not be efficiently disintegrated by ultrasonication. Thus the probe for the beta subclass of the Proteobacteria, which covers also the nitrifiers, was used with exclusion of the clusters. In addition, the clusters were enumerated on the basis of their coverage per microscopic field of vision. This was only used as a relative method. Two of the 7 special probes for nitrifiers (Neu23a, Nsm156) likewise exclusively hybridized with clusters. Thus they were quantified also on the basis of the coverage per field of vision. Over the whole experiment (10 months), the *Eubacteria*-specific probe (EUB 338) detected 60% to 80% of the total number of cells found with DAPI (Fig. 5). The proportion of alpha Proteobacteria ranged between 3% and 23% of the DAPI cell number and on the average amounted to 10%. The proportion of cells of the *Cytophaga-Flavobacterium* group likewise was about 10% of the DAPI number. The Gram-positive bacteria with a high G+C-content normally were present with lower cell numbers. If they were examined on small pieces of the biofilm, the absence of clusters/aggregates and a rather homogenous distribution of the cells became evident. The proportion of the gamma Proteobacteria was still lower and normally much below 10%. The beta Proteobacteria achieved the highest proportion (about 10% to 40%) in the DAPI cell number. This however, does not include the cells in the clusters detected with the probe for beta bacteria. Thus, the real number of nitrifier has been still higher, about 15%-55% (Fig. 6). The formation of clusters is a typical property of ammonia

oxidizing bacteria, in particular, *Nitrosomonas* (MOBARRY et al. 1996, WAGNER et al. 1995, 1997). As is evident from Table 2, this genus can be examined both by probe Neu23a and by Nsm156. However, both of these probes cover still other genera.

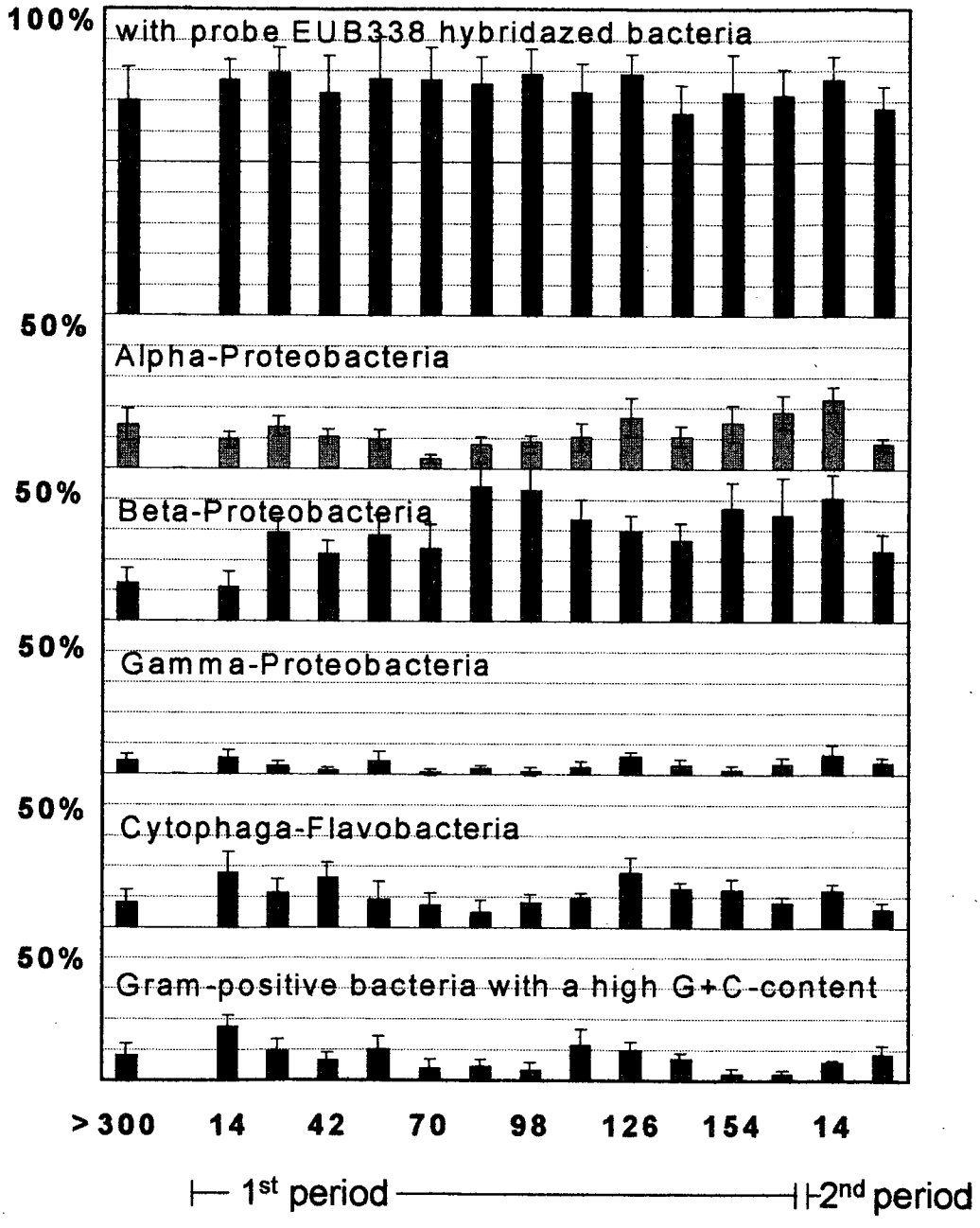


Fig. 5: Microbial community received by in situ hybridization with oligonucleotide probes in dependence of the biofilm age (in days)

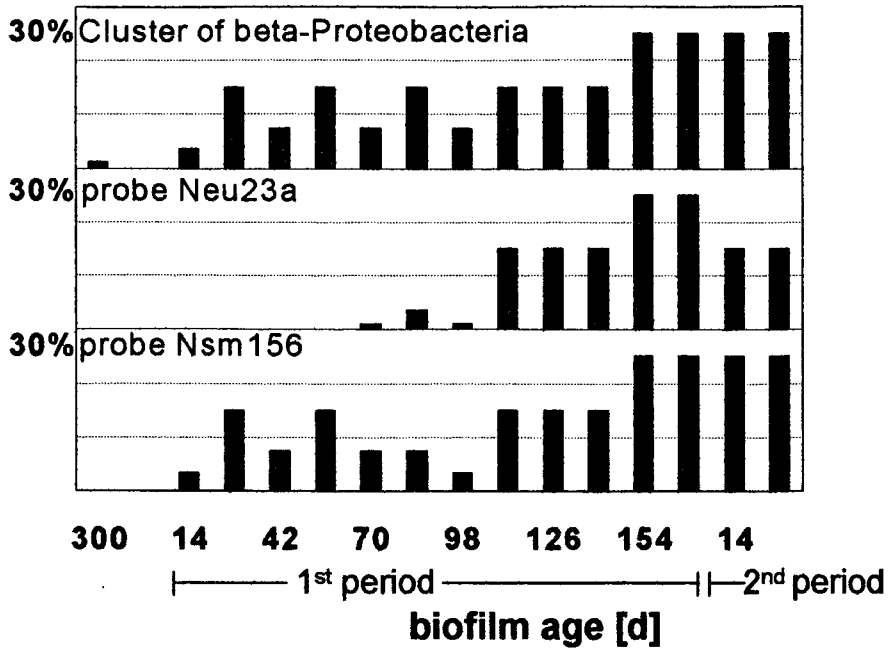


Fig. 6: Proportion of cluster of the beta-proteobacteria in the total number of bacteria

As is evident from Fig. 7, the number of colony forming units (CFU) in the inflow to the nitrification reactor was much lower than the total count with DAPI. This had to expected in view of the selectivity of the culture media. On the other hand, there was a substantial decrease in the CFU from the inflow of the nitrification reactor to its outflow. This means that the performance with concern to the fecal bacteria was high. The elimination amounted to 98% CFU. Probably this may, inter alia, be attributed to the dense colonization of the interior of the tubulues by filter-feeding protozoa (peritrich ciliates). The concentration of coliforms likewise was reduced by two to even three orders of magnitude. The reduction in the total number of bacteria (DAPI counting) was much less than the decrease in the number of fecal indicators and can be explained by the growth of bacteria which have not been present in the sewage but are characteristic of water bodies. The reduction in the direct count (DAPI) so far has been measured in sewage treatment plants only in rare cases, but BRÜCKER et al. found in process reservoirs for the polishing of effluents from the Dresden sewage treatment plant a decrease which was very similar to our data. The highest reduction in the CFU achieved in our experiments was 99,97%. This indicates that the reactor meets very high standards microbial in terms of microbial pollution.

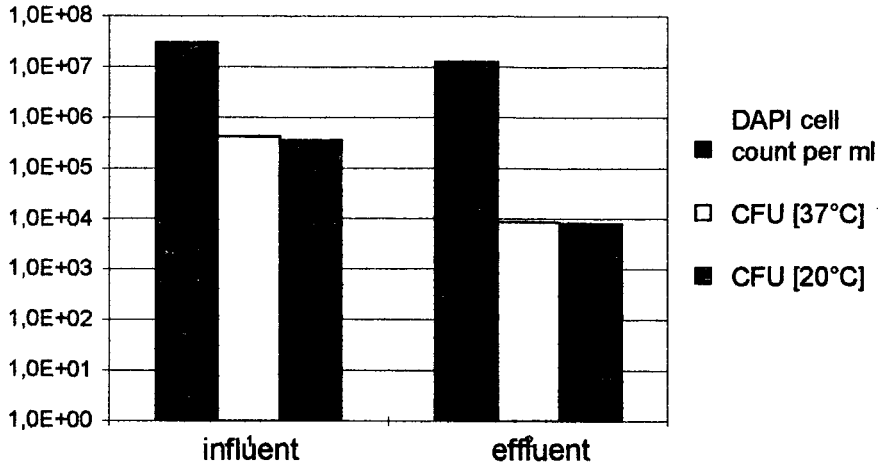
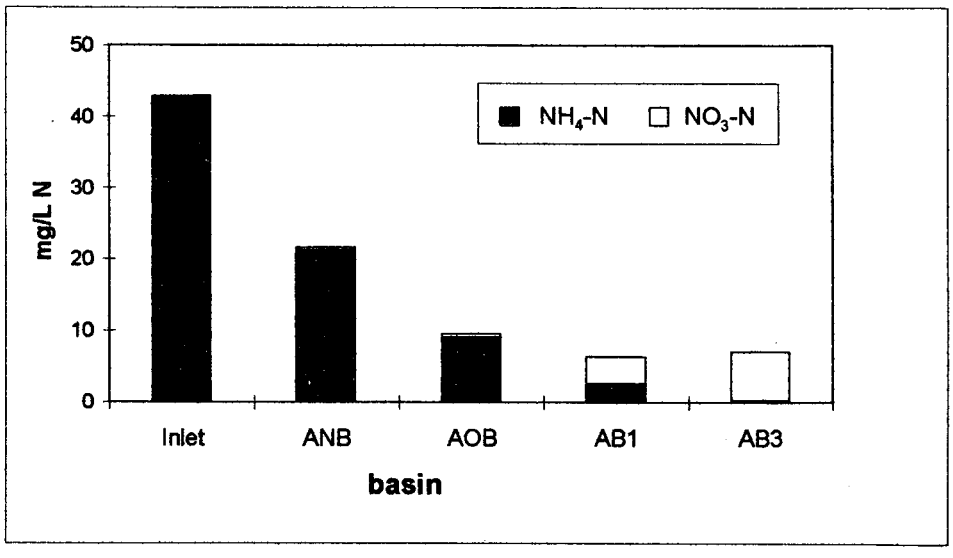


Fig. 7: Elimination of bacteria in the nitrification reactor

The bench-scale plant for phosphorus and nitrogen elimination (Phoredox Plant, Plant No2).
This is operated on the basis of the Phoredox process. In the six months experimental period the operational conditions were as follows:

Sludge loading: 0,15 kgBOD/kg Dry weight·day
Volume loading: 0,55 kgBOD/m^3·d
Sludge age: 16 d

Under these conditions, the N elimination (respect to total N) amounted to 89% and the P elimination to 87% (Fig. 8).



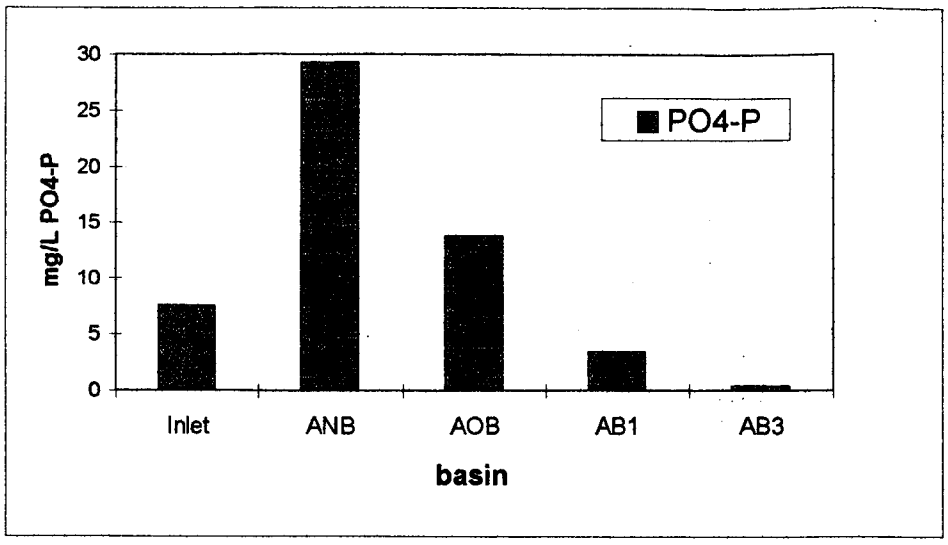


Fig. 8: Phosphate and dissolved inorganic nitrogen elimination in bench-scale plant No 2. (arithmetic means from June to October)

Microbiological investigations: Despite of the quite different operational conditions, there were no significant differences in the composition of the microbial community (at the level of major taxonomical groups) between the two experimental plants. There were also no significant successional changes over the whole period of 10 months. This probably indicates a high stability. With an average of 30%, the beta Proteobacteria contributed the largest portion in the total cell count. They were followed by the *Cytophaga/Flavobacterium* group with 18%. The gamma Proteobacteria among which also ranks the genus Acinetobacter only had a proportion of 5-15% in the total cell count. This indicates that other taxa of the bacteria may have been more relevant to the P elimination in our plant. Despite of a quite different level of sludge loading (0,12 - 0,35 kg BOD/kg Dry weight * day) in both bench-scale plants the composition of the major taxonomic groups of bacteria was approximately identical. As Fig. 9 indicates, there was possibly a correlation between P release and the proportion of the *Cytophaga/Flavobacterium* group.

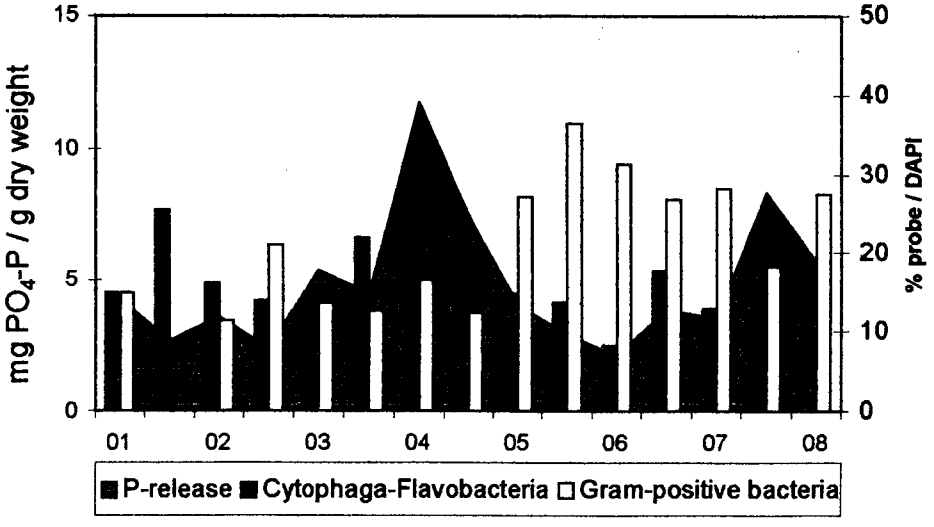


Fig. 9: The occurence of the Gram-positive bacteria and the *Cytophaga-Flavpbacterium* group as compare to the P-release

SUMMARY AND CONCLUSIONS

The efficiency of a fluidized-bed nitrification reactor with polypropylene tubules as carrier material was analyzed with concern to variations in hydraulic load and in biofilm surface. The preceding step comprised BOD and P elimination in an activated sludge system. A second bench-scale plant, operated for comparison, fully was an activated sludge system. The performance of the fluidized-bed nitrification reactor was high: with volume loadings of ammonia nitrogen higher than 0.6 kg/m^3*d and a solids concentration equal to or higher than 60%, a minimum elimination of 65 to 80% has been achieved. In many cases it was even higher than 95%. The fluidized-bed nitrification reactor was characterized by a very thin and compact microbial film on the outer side and a well developed community of bacteria and bacteria-feeding protozoa in the lumen of the tubules. The capacity of this reactor to eliminate fecal bacteria was very high. The composition of the microbial community of the biofilms as examined with rRNA targeted oligonucleotide probes showed a high amount of nitrifier corresponded with a high elimination rate of ammonia.
Depite of shocks loadings(to the inflow of the grit chamber) with night soil, the composition of the microbial community was comparatively stable in terms of the total number of Eubacteria as a proportion of the total cell count over the whole operational period of 10 months. This was, though to a little lower extent, also true of the numbers of the major taxonomical groups. The beta Proteobacteria by far were the most abundant, followed by the alpha Proteobacteria, the *Cytophaga-Flavobacterium* group or the Gram-positive bacteria with a high G+C content. The gamma Proteobacteria which include the genus Acinetobacter had the lowest cell numbers.

ACKNOWLEDGEMENT

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PERFORMANCE OF BIOLOGICAL PHOSPHORUS AND NITROGEN REMOBAL PROCESS WITH IMMOBILIZED NITRIFIERS AND ITS MODEL DEVELOPMENT

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ABSTRACT

A simulation model was developed for a combined activated sludge and biofilm process which was developed in Japan to achieve nitrogen and phosphorus removal without extending existing treatment facilities. The process consists of an activated sludge process of three zones (anaerobic, anoxic and aerobic) and a biofilm process in the form of a fluidized bed in the aerobic zone. Firstly, a biofilm model was developed by modifying an existing model, using the experimental results of the fluidized bed process. Secondly, the biofilm model was incorporated into the IAWQ Activated Sludge Model No.2 with the addition of a mechanism of transferring detached biofilm to the activated sludge. The model was evaluated with pilot plant data.

The balances of potassium and magnesium, which were taken up by phosphorus accumulating bacteria as counter ions of the polyphosphate, were also investigated in sludge treatment processes of wastewater treatment plants .

KEYWORDS

Wastewater treatment, Nitrogen and phosphorus removal, Activated Sludge, Biofilm, Immobilization, Model, Potassium balance

INTRODUCTION

Nationwide application of nitrogen and phosphorous removal to publicly owned wastewater treatment (POWT) plants is an urgent issue in Japan. However, most of the large cities have already built their POWT plants as relatively high loaded activated sludge processes, and they do not have additional space for retrofitting the existing plants to the nitrogen and phosphorous removal processes because these plants are located in densely populated areas.

The application of immobilized microorganisms has been investigated to reduce the volume of the biological reactor. For nitrification, the suspended growth systems require long solids retention time (SRT), and thus a large reactor volume. On the other hand, in the process using immobilized nitrifiers requires the SRT of the activated sludge need not be considered, because the nitrifiers are attached to the immobilization media.

A pilot plant of a three-zone biological nitrogen and phosphorus removal process with immobilized nitrifiers (BNPRI process) has been running now for more than 3 years, and shows

highly efficient nitrogen and phosphorus removal. A design method and operational strategy for this process are required, but no simulation model exists for this process at present. An attempt was made, therefore, to construct a simulation model for the process by incorporating a biofilm model to an activated sludge model.

At the same time, the balances of potassium and magnesium, which are the counter ions of polyphosphate formed in phosphorus accumulating bacteria, are investigated in sludge treatment processes of two wastewater treatment plants, because they are important elements when excess sludge is applied to farm land as fertilizer.

This paper describes how the simulation model for the BNPRI process was developed and how the model can predict the experimental results. Also, the balances of potassium and magnesium in sludge treatment processes of wastewater treatment plants are shown.

PROCESS DESCRIPTION

BNPRI process

Fig. 1 shows the outline of the BNPRI process, which has anaerobic, anoxic and aerobic cells with immobilization media in the aerobic cells. Nitrogen removal is possible even though the reactor volume is the same as that of the conventional activated sludge process and the aerobic SRT is short for nitrifiers, because nitrifiers can grow on the media in the aerobic cells. The media are kept in the each aerobic cell by a screen.

Immobilization media

The characteristics of the media used for the immobilization of nitrifiers are listed in Table 2. The media can be easily fluidized in the aeration tank with air diffusion. The volume ratio of the media to the reactor must be lower than 40 % to prevent sedimentation of the media on the bottom of the reactor.

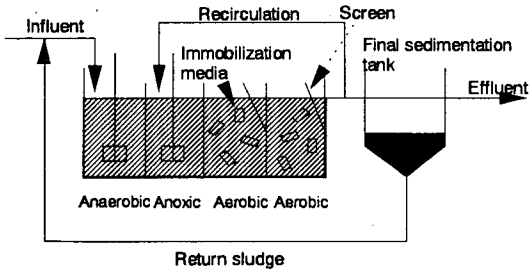


Fig. 1 Outline of three-zone biological nitrogen andphosphorus removal process with immobilized nitrifiers

TABLE 1 Characteristics of Immobilization Media

Material	: Polypropylene
Specific gravity	: 1.025 g/cm^3
Configuration	: Empty cylinder (diameter : 4 mm, length : 5 mm)
Specific surface area when packed densely	: 1410 m^2/m^3
Specific gravity when packed densely	: 0.271g/cm^3

METHODS

Two kinds of experiments were conducted for the model development, one to investigate the nitrification efficiency of the biofilms formed on the media with different substrate loads (Miyata et al., 1994) (Experiment 1), and the other was the pilot plant experiment of the BNPRI process (Experiment 2).

Potassium and magnesium balances were measured in sludge treatment processes of two wastewater treatment plants performing biological phosphorus removal. One treatment plant

(plant A) is equipped with centrifuges for excess sludge thickening, and the other (plant B) has a gravity thickener for primary and excess sludge. In plant B, coagulant is added to the end of aeration tank at the ratio of 1 mol Fe / mol (T-P in the primary effluent) for the supplement of biological phosphorus removal.

Experiment for nitrification efficiency of biofilm formed on media (Experiment 1)

The nitrification efficiency of the biofilms formed on the media was investigated using the apparatus shown in Fig. 2 without the existence of activated sludge. Three reactors (A, B and C) which differed in influent concentration were operated with four different hydraulic retention times (Run 1 to 4) as shown in Table 2. When a steady state was reached after about one month of treatment in each run, batch experiments were conducted to obtain the maximum nitrification rate and the maximum organic matter removal rate in order to evaluate of the mass of the nitrifiers and the heterotrophs on the media.

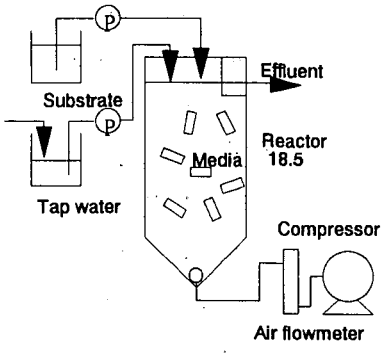


Fig. 2 Experimental apparatus (Experiment 1)

TABLE 2 Conditions for Experiment 1

	Influent water quality (g/m^3)			
Reactor	BOD	TOC	T-N	NH_4-N
A	0.3	5	25	25
B	12.5	20	27.5	25
C	125	120	25	3

	Run 1	Run 2	Run 3	Run 4
HRT(h)	8	4	2	1
Qin (m^3/d)	0.0554	0.111	0.222	0.444

Pilot plant experiment (Experiment 2)

The performance of the BNPRI process was investigated using a pilot plant supplied with settled municipal wastewater. Table 3 shows the size and the conditions of the pilot plant. The media in the first aerobic cell were removed in some cases.

In addition, two kinds of batch tests and one continuous flow experiment were conducted. In one of the two batch tests the change of denitrification rate with time was measured to determine the readily biodegradable COD (RBCOD) concentration according to the method of Scheer and Seyfried (1994). The other batch test measured the maximum nitrification rates of the activated sludge and the biofilm on the media to evaluate the mass of nitrifiers. The continuous flow experiment was carried out to determine the maximum growth rate of nitrifiers under the water quality conditions of the municipal wastewater according to the method described in Activated Sludge Model No. 1 (Henze *et al.* 1986).

TABLE 3 Conditions of Pilot Plant Experiment

	Anaerobic	Anoxic	Aerocic1	Aerocic2
Volume of cell	$2.5m^3$	$2.5m^3$	$2.5m^3$	$2.5m^3$
Inflow rate	: 30 m^3/d			
Return sludge ratio	: 0.5			
Recirculation ratio of nitrified mixed liquor	: 1.5			
Solids retention time	: 14d			
Aerobic solids retention time	: 7d			
Volumetric ratio of media in aerobic cell	: 40%			

MODELING PROCEDURE

The procedure of modeling the BNPRI process consisted of two steps. The first step was modeling the biofilm formed on the media, for which the results of Experiment 1 were used. The second step was modeling the BNPRI process, in which the biofilm model developed was incorporated in the Activated Sludge Model No. 2 (Henze et al., 1994). The data of Experiment 2 were used for the model development.

A simulation software, AQUASIM developed by P. Reichert (1994), was used for the simulation in this research.

Modeling of biofilm process

The biofilm model in this research employed the concept of the model developed by Wanner and Gujer (1984). The detachment mechanism of the biofilm, however, was investigated separately based on the results of Experiment 1, assuming four types of detachment mechanisms.

The components used in this model were based on the Activated Sludge Model No. 2, however, the slowly biodegradable COD was divided into two parts, soluble (S_S) and particulate (X_S), because some part of the slowly biodegradable COD is actually soluble and it can diffuse into the biofilm. Particularly the organic substrate in Experiment 1 was defined as the soluble slowly biodegradable COD because it was composed of high molecular organic matter such as dextrin and peptone.

The expression of the biological processes and most of the parameter values in the Activated Sludge Model No. 2 were used in this model, except for the nitrogen content in the slowly biodegradable COD, the hydrolysis rate constant, the yield coefficient for heterotrophs and the maximum specific growth rate of nitrifiers; these were obtained from the results of Reactor A and C in Experiment 1. The saturation coefficient for S_S in the hydrolysis process was introduced in this model, because S_S is soluble and the hydrolysis mechanism is different from that of X_S.

The intensity of the mixing in the reactor was strong, therefore, the resistance of the substrate transport in the liquid phase was not considered.

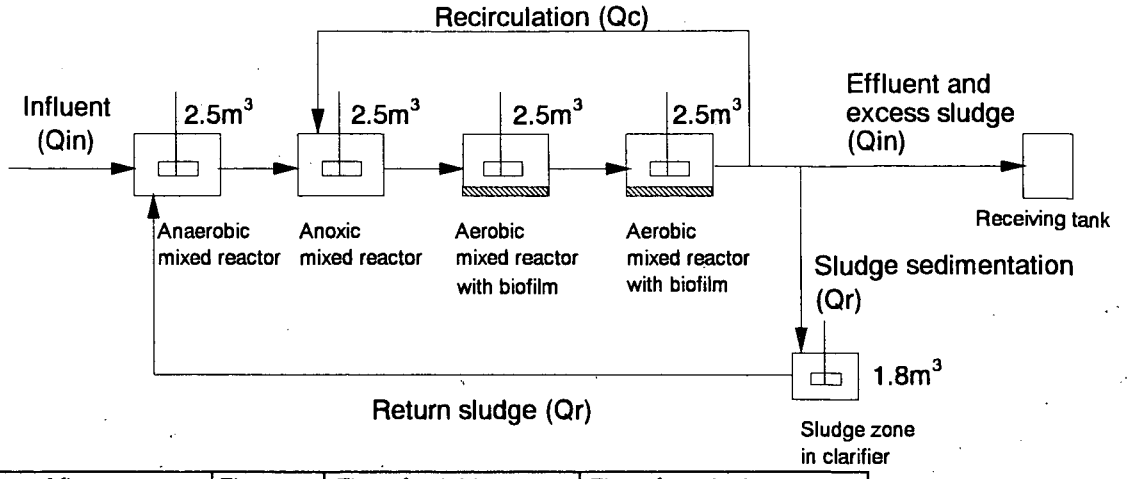
Modeling of BNPRI process

The structure of the model is shown in Fig. 3. It consists of six compartments, four of which represent the aerobic, anoxic and aerobic cells of the reactor. The biofilm model developed is incorporated in the aerobic cells. The sludge zone in the clarifier is also defined as a reactor because biological reactions can take place in this zone. Excess sludge is separated from the treatment process at the line between the second aerobic cell and the clarifier, and it runs away together with the effluent.

RESULTS

Biofilm model

Biofilm detachment rates are shown in Fig. 4. However, the detachment rate at every biofilm depth must be formulated, because a biofilm has thickness and the concentration of each species may not be uniform through the depth. Four assumptions were made for the detachment mechanism as shown in Fig. 5.



Name of flow	Flow rate (L^3/T)	Flux of soluble matter (M/T)	Flux of particulate matter (M/T)
Recirculation	Qc	Qc C	QcX
Sludge sedimentation (or return sludge)	Qr	Qr C	(Qin+Qr-Qex) X
Effluent and excess sludge	Qin	Qin C	Qex X

C: concentration of soluble matter (M/L^3)
X: concentration of particulate matter (M/L^3)

Fig. 3 Structure of the model of BNPRI process

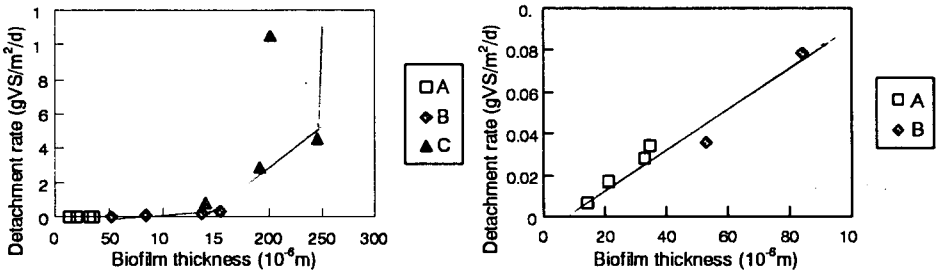


Fig. 4 Biofilm detachment rate

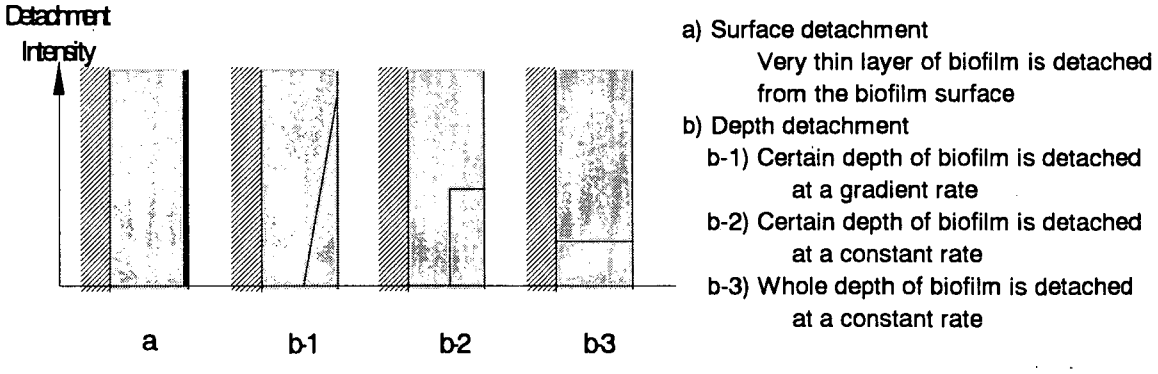


Fig. 5 Assumptions of biofilm detachment mechanisms

The values of the parameters and the molecular diffusion coefficients are listed in Table 4 and Table 5 respectively.

With the assumptions and the values above, treated water quality and biofilm thickness were calculated for the reactor B of Experiment 1, and the results are shown in Fig. 6. As for the

biofilm thickness and the COD concentration in the effluent, each model with a different detachment mechanism could simulate the experiment results well. However, concerning the NH_4-N concentration, only the model with the detachment mechanism of b-3 (whole detachment at a constant rate through the film) could calculate the high concentration of NH_4-N in Run 4.

TABLE 4 Parameter Values

Conversion Factors

Nitrogen:		
Soluble material:		
i_{NSS} N content of slowly biodegradable substrate S_S	**0.1**	$g_N g^{-1}_{COD}$

Stoichiometric Constants

Heterotrophic organisms X_H		
Y_H Yield coefficient	**0.8**	$g_{COD} g^{-1}_{COD}$

Kinetic Constants

Hydrolysis:		
r_h = Hydrolysis rate constant	**1.5**	d^{-1}
K_S = Saturation coefficient for soluble slowly biodegradable COD (S_S)	**4.0**	**$g_{COD}m^{-3}$**
Heterotrophic organisms:		
b_H = Rate constant for lysis	**0.10**	d^{-1}
K_{NH4} = Saturation coefficient for ammonium (nutrient)	**0.05**	$g_N m^{-3}$
Nitrifiers:		
μ_{AUT} = Maximum growth rate	**0.25**	d^{-1}
b_{AUT} = Decay rate	**0.05**	d^{-1}
K_{NH4} = Saturation coefficient for ammonium	**0.20**	$g_N m^{-3}$
K_{ALK} =Saturation coefficient for alkalinity	**0.10**	$mole_{HCO3}m^{-3}$
Biofilm:		
Xf = Biofilm concentration	**25,000**	gVS/m^3

TABLE 5 Molecular Diffusion Coefficient

Symbol	Substrate	Diffusion coefficient (m^2/d)	
		in Water	in Biofilm
D_A	Acetate	1×10^{-4}	0.8×10^{-4}
D_{ALK}	Alkalinity	1×10^{-4}	0.8×10^{-4}
D_F	S_F	6×10^{-5}	4.8×10^{-5}
D_S	S_S	1×10^{-5}	0.8×10^{-5}
D_{NH4}	NH_4	1.6×10^{-4}	1.3×10^{-4}
D_{NO3}	NO_3	1.2×10^{-4}	1.0×10^{-4}
D_{O2}	O_2	2.2×10^{-4}	1.8×10^{-4}
D_{PO4}	PO_4	1.5×10^{-4}	1.2×10^{-4}

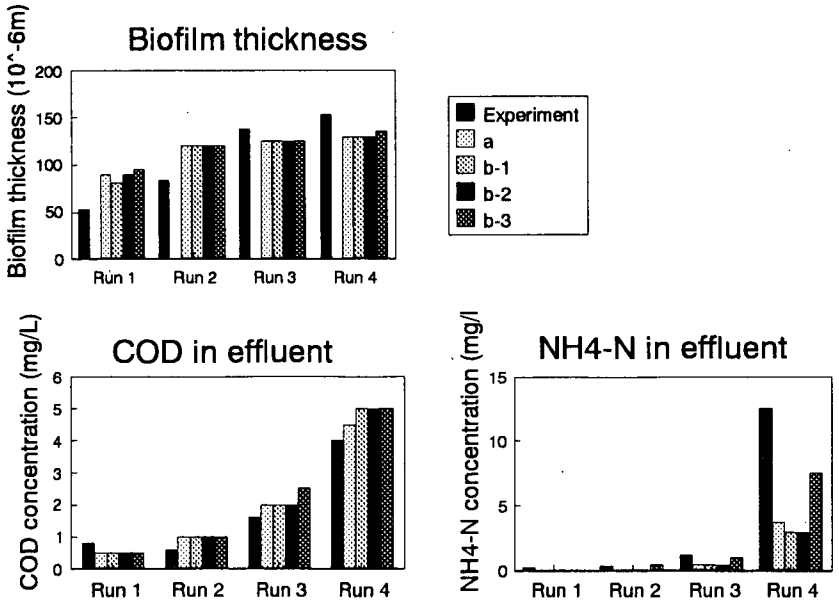


Fig. 6 Simulation results with four detachment mechanisms (Reactor B of Experiment 1)

Biomass distributions in the biofilm calculated with each detachment mechanism for Run 4 of Reactor B are shown in Fig. 7. When the detachment mechanisms were **a** (surface detachment), **b-1** and **b-2** (certain depth detachment), nitrifiers could exist throughout the biofilm, which caused the higher nitrification rates and the low NH_4-N concentration in the effluent. On the other hand, with the detachment mechanism of **b-3**, nitrifiers could not exist in the upper layer of the biofilm, which resulted in the lower nitrification rate and the higher NH_4-N concentration in the effluent.

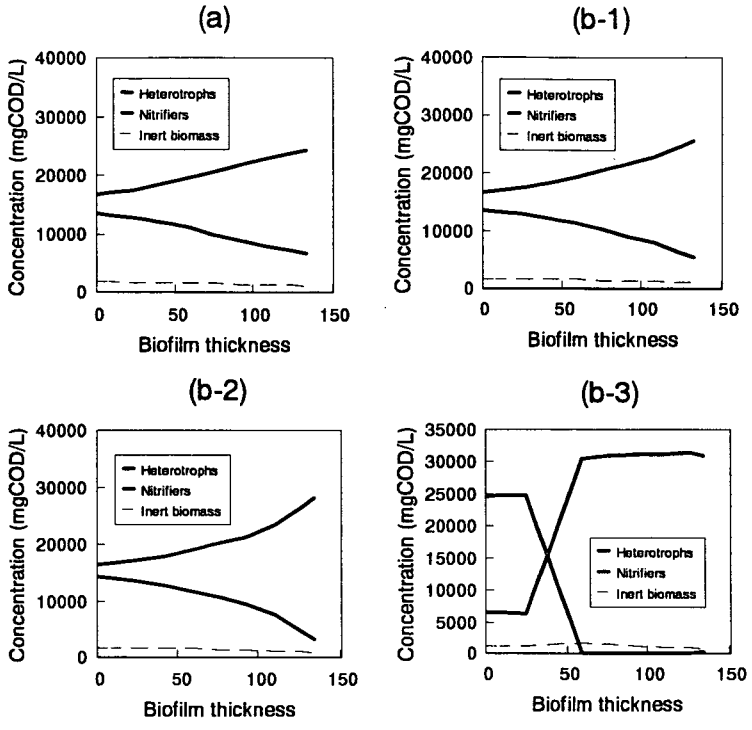


Fig. 7 Distributions of biomass in biofilms (Run 4 of Reactor B)

Model of BNPRI process

The RBCOD concentration and the acetate concentration in the influent were 60% and 46% of the soluble COD concentration in the influent respectively. The maximum specific growth rate of nitrifiers was calculated to be 0.25 d^{-1} at 20°C.

Parameter fitting was carried out mainly for the hydrolysis process using the experiment data of 20°C during the period without rainfall. The results of the fitting are shown in Fig. 8 for the water quality, and in Fig. 9 and Fig. 10 for the biomass concentration. The parameter values which differed from the biofilm model are listed in Table 6.

Table 6 Parameter Values used in Model

Conversion Factors

Nitrogen:	
Soluble material:	
i_{NSS} N content of slowly biodegradable substrate S_S	**0.04** $g_N\ g^{-1}_{COD}$

Stoichiometric Constants

Heterotrophic organisms X_H	
Y_H Yield coefficient	**0.63** $g_{COD}\ g^{-1}_{COD}$

Kinetic Constants

Hydrolysis:	
r_h = Hydrolysis rate constant	**6** d^{-1}
K_X = Saturation coefficient for particulate COD (X_S)	**0.05** $g_{COD}g^{-1}_{COD}$

The model could express the water quality well. As for the activated sludge, the high value of poly-phosphate concentration was expressed well, but the calculated nitrifier concentration was lower, which might be caused by higher the temperature of the preceding term of Experiment 2.

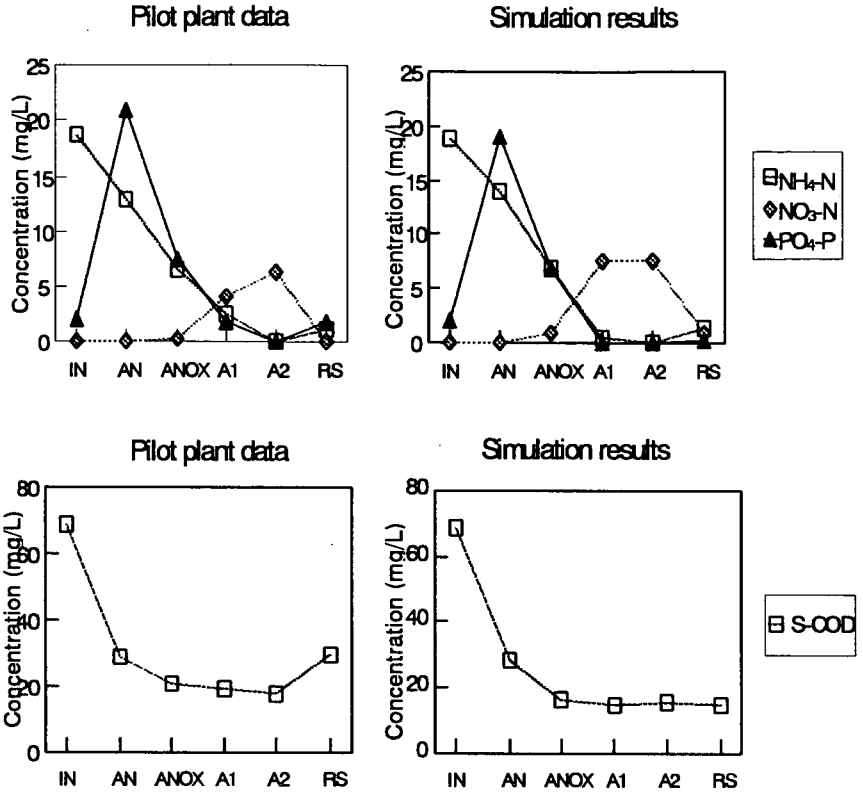


Fig. 8 Calculation results of water quality after parameter fitting

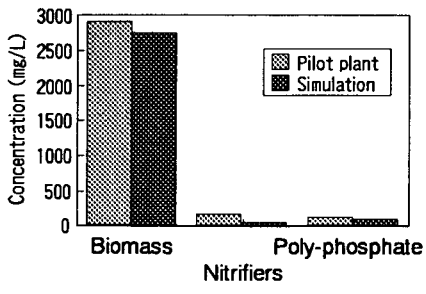


Fig. 9 Calculation results of biomass concentration in activated sludge after parameter fitting

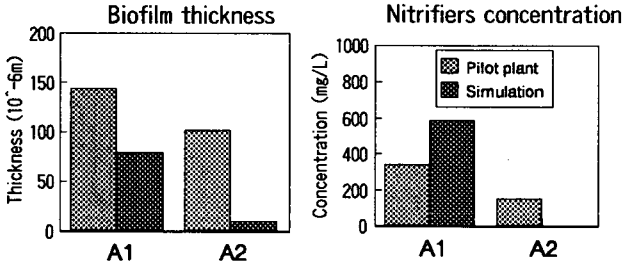


Fig. 10 Calculation results of thickness and nitrifier concentration of biofilm after parameter fitting

As for the biofilm, there were differences between the experiment values and the calculated values; the calculated values were lower for the biofilm thickness and higher for the nitrifier concentration in the first aerobic cell. This might be caused by underestimating the heterotroph growth in the biofilm or by overestimating the detachment rate of the biofilm.

If the former assumption is true, a possible reason could be that the particulate slowly biodegradable COD (P-SBCOD) is not treated as a substrate for the biofilm because the processes of attachment and hydrolysis of P-SBCOD at the biofilm surface are not considered. Little is known about the mechanisms of these two processes, and so the mechanisms must be clarified to

improve the model. There is also a possibility that the detachment rate of the biofilm in Experiment 2 is lower than that in Experiment 1. Further investigation is needed concerning the detachment rate of the biofilm.

Model evaluation

The model fitted above was evaluated using the pilot plant data of 20°C during the period with much rainfall. The influent concentration was diluted by successive rainfall, therefore, the treatment condition was quite different from that of Fig. 8 through 10. In this case, the media in the first aerobic cell were taken out from the plant.

The results of the simulation are shown in Fig. 11 for the water quality and in Fig. 12 for the biomass concentration. The relatively low nitrate concentration in the first aerobic cell and the high concentration in the second aerobic cell were calculated well, which means this model accurately simulated the high nitrification rate of the biofilm and the low nitrification rate of the activated sludge.

The calculated phosphorus concentration in the anaerobic cell also showed good agreement with the pilot plant data, but the effluent phosphorus concentration was lower than the real value. The reason for this might be that the pilot plant had not reached the steady state even though the calculated value was of the steady state.

The thick biofilm in spite of the diluted influent was not expressed at all by the model. It seems that biofilm does not lose its attachment strength easily after the reduction of organic load. Further research is needed on the attachment mechanism.

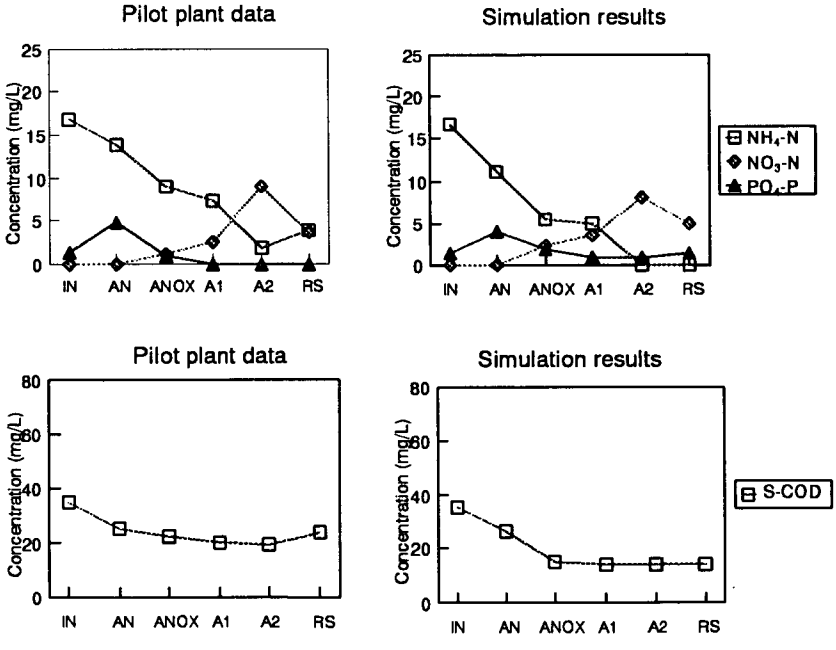


Fig. 11 Calculated water quality in the case of diluted influent with parameter values fitted for normal influent

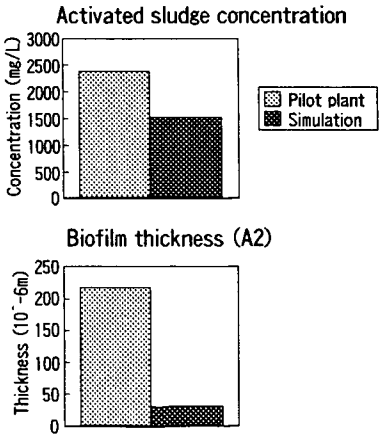
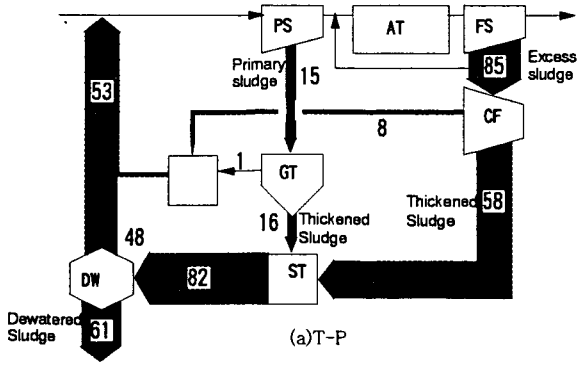


Fig. 12 Calculated biomass concentration in the case of diluted influent with parameter values fitted for normal influent

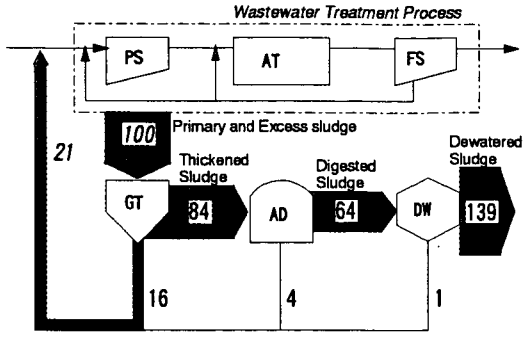
Balances of potassium and magnesium in wastewater treatment plants

Potassium and magnesium balances in wastewater treatment plant (A) which is equipped with

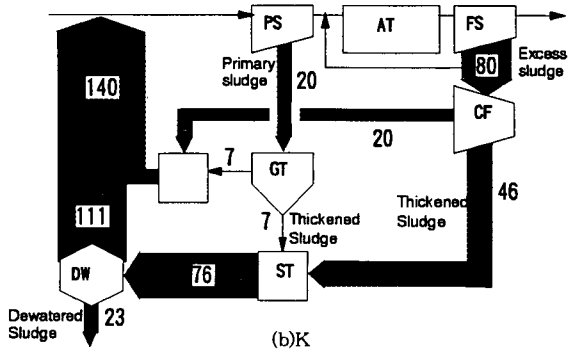
a centrifuge for excess sludge thickening and those in plant (B) with a gravity thickener for primary and excess sludge were investigated. Fig. 13 and Fig. 14 show the balances in plant (A) and in plant (B) respectively.



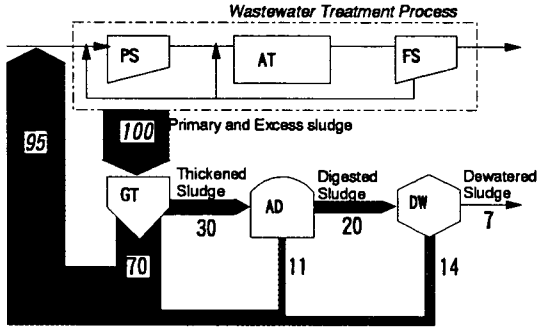
(a)T-P



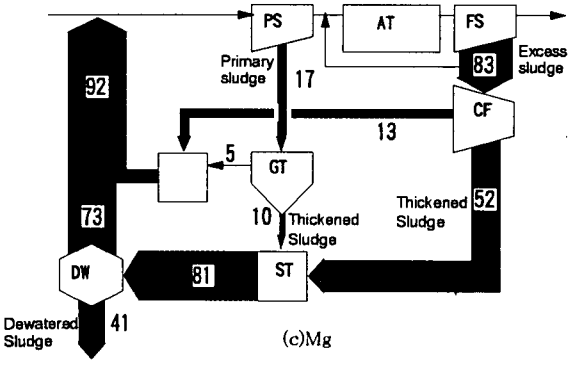
(a)T-P



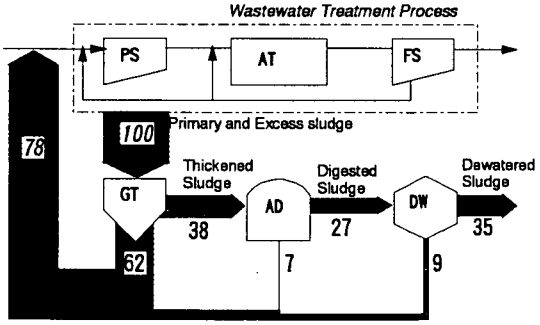
(b)K



(b)K



(c)Mg



(c)Mg

Fig.13 Balances of T-P, K and Mg in Plant A
(eqipped with CF for excess sludge thickening)
(Content in primary and excess sludge : 100)

Fig. 14 Balances of T-P, K and Mg in Plant B
(GT for primary and excess sludge. Coagulant is added before FS)
(Content in primary and excess sludge : 100)

PS : primary sedimentation tank
AT : aeration tank
FS : final sedimentation tank
CF : centrifuge
GT : gravity thickener
ST : storage tank
DW : dewatering machine
AD : anaerobic digester

In plant (A), T-P, K and Mg was withdrawn from the wastewater treatment process contained in the excess sludge, and effectively recovered in the thickened sludge after centrifugal process. However, stored in the storage tank, most of K and Mg was released to water phase and returned to inflow after dewatering. Quick separation of sludge and water can be thought essential for the recovery of K and Mg in the sludge.

In plant (B), because coagulant is added to the wastewater treatment process supplementary, phosphorus withdrawn from the wastewater treatment process stayed in the sludge even after several sludge treatment processes. On the other hand, most of K and Mg was released to water phase in the gravity thickener. Hydrolysis of polyphosphate seems to take place in the thickener, though phosphorus is not released combined with coagulant.

From these results, it can be said that short retention time under anaerobic condition is important to recover K and Mg in sludge.

CONCLUSION

A simulation model for the three-zone biological nitrogen and phosphorus removal process with immobilized nitrifiers was developed, which combined the activated sludge model and the biofilm model with the additional mechanism of transferring detached biofilm to the activated sludge. The biofilm model was developed first by investigating the mechanism of biofilm detachment. Then the biofilm model was incorporated in the activated sludge model, and parameter fitting was carried out with the pilot plant data. The model expressed the results of the pilot plant experiment well, but some improvement is needed to improve the simulation of the thickness of the biofilm on the media.

A survey of the balances of potassium and magnesium in wastewater treatment plants with biological phosphorus removal process was conducted, and it indicated that short retention time of excess sludge under anaerobic condition is essential for the recovery of K and Mg.

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New experiences of the fullscale application of biological N- and P-removal in Germany - problems with filamentous bacteria and scum

C.F. Seyfried, D. Dittrich, C. Helmer, W. Hinrichs, S. Knoop

Abstract

An overview of the current status of the application of the enhanced biological phosphorous removal (BIO-P) in the German speaking area is given. In practice the design and construction of BIO-P plants generally rely on dimensioning and modeling based on data which partly result from experiments with pure or enhanced cultures under defined conditions. This leads to the fact that BIO-P processes are already used on a large technical scale, although their fundamental microbiological processes have not been fully understood yet. In the following the temperature influences on the biocenosis and the development of filamentous bacteria in wastewater treatment plants operating Bio-P processes are described.

1. Introduction

The need of many waste water treatment plants to upgrade over the next years to obtain a stable advanced waste water treatment including phosphorous removal, led to extensive research to describe this process. The enhanced biological phosphorous removal (BIO-P) gets particular significance thanks to its environmental friendliness. For this reason the status of this process technology was researched closely in sewage treatment plants by a stock taking of the BIO-P in the German speaking area (Scheer et al, 1996).

First tendencies concerning the realisation of the BIO-P process should be indicated by the results of a stock taking.

The conversion of the wastewater treatment plants to advanced waste water treatment meant to changes of the environmental conditions. These changes of the environmental conditions led to different biocenosis. In former times bulking sludge was one of the operation problems and today besides the bulking sludge stable foams on the surfaces of the aeration basins are observed often.

In the following a research to define some selection criteria for the growth of filamentous bacteria, especially *M.parvicella*, and a possibility to reduce the problems with scum are presented.

2. Enhanced biological phosphorus removal in the German speaking area

In the spring of 1994 as the stock-taking was completed (Scheer et al. ,1996) 125 sewage treatment plants operating an enhanced biological phosphorus removal (BIO-P) were registered. Distribution of treatment plants operated with BIO-P in Germany is shown on Figure 1. As can be seen from this diagram, the distribution in Germany varies according to

the federal states: especially noticeable is the high density of treatments using this technique in Lower Saxony and North Rhine-Wesphalia. Partly the reason is that the ISAH in Hanover and the ISA in Aachen are centers of the Bio-P research in Germany.

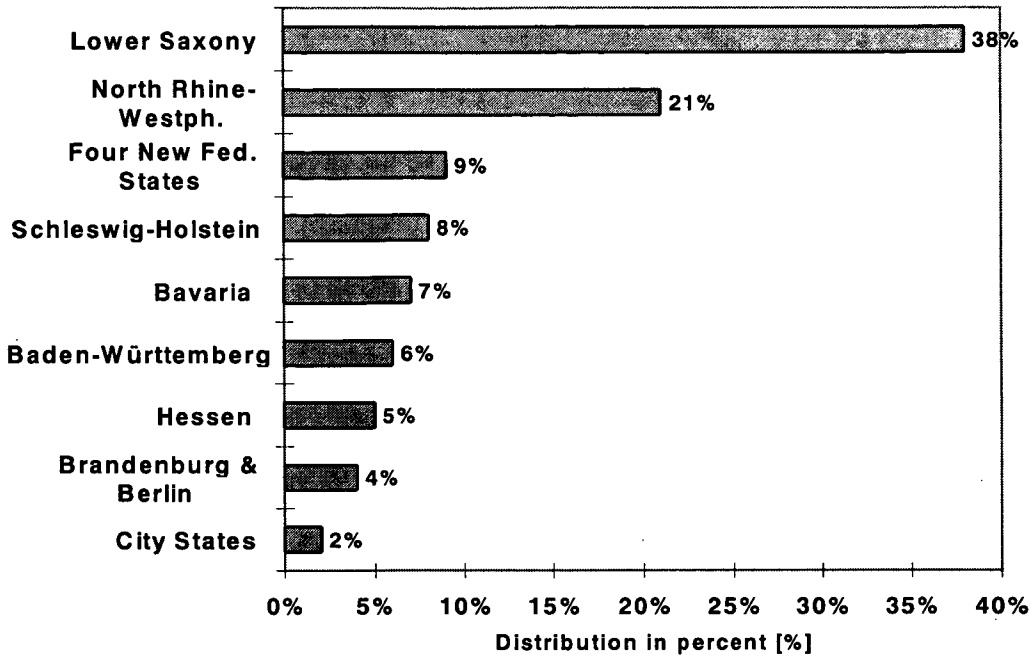


Figure 1: Distribution in Germany of the sewage treatment plants operating with enhanced biological phosphorus removal according to the federal states (in percent)

The stock taking in the German speaking area also shows that in Germany the dimensioning strategies for the estimation of the anaerobic volume essentially bases on the anaerobic contact time. This means that a suitable contact time for the activated sludge in the tank is necessary, this time is referred to the dry weather flow and respecting the sludge flow of the recycle. Boll (1988) recommends a contact time of about 0.75 to 1 hour for favourable conditions and 1 to 2 hours for unfavourable conditions. The anaerobic contact time also has direct influence on the sludge loading regarding the aerobic and anoxic basins, which can lead to different microbial communities. The following figure gives an overview of the commonly applied anaerobic contact times in the wastewater treatment plants considered in the stock taking (Scheer and Seyfried, 1996)

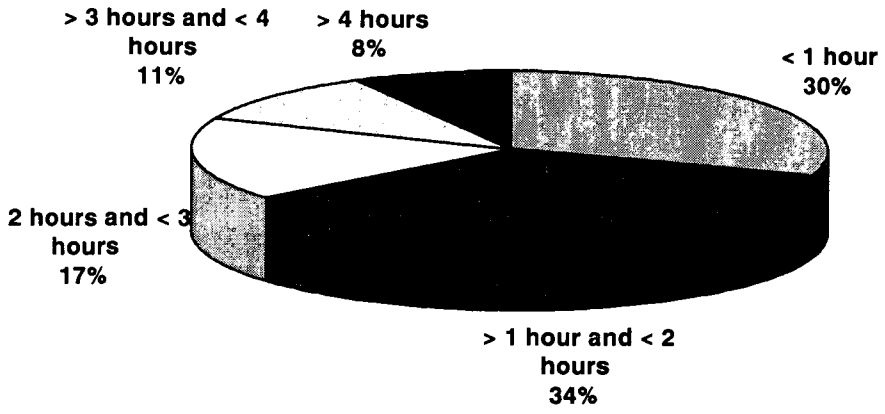


Figure 2: Distribution of applied anaerobic contact times in percent

3. Low temperature effects on phosphorus release and uptake by microorganisms in BIO-P plants

In spite of the spread wide use of BIO-P systems there are still uncertainties about the groups of organisms taking part in the process and about the underlying metabolism. As activated sludge consist of mixed populations with a changing combination of bacterial species, the determination of the involved microorganisms proves exceedingly difficult. Therefore in practice the planning and construction of BIO-P plants generally rely on dimensioning and modeling based on data which partly result from experiments with pure or enhanced cultures under defined conditions. This leads to the fact that BIO-P processes are already used on a large technical scale, although their fundamental microbiological processes have not been fully understood, yet. Occurring difficulties in full scale plants are therefore hard to relate to a certain cause and the optimization of BIO-P continues to be a problem.

The influence of temperature on mixed microbial populations in BIO-P plants is also unclear. In northern-hemisphere countries minus temperatures are common during winter months and a low waste water temperature can be of significance for the plant's efficiency. The aim of an undertaken research (Helmer and Kunst, 1997) was to characterize the BIO-P process in respect of polyphosphate storing organisms involved and their metabolism at different temperatures. The investigations focus on the question of whether or not under low temperature conditions (5-10°C) the microbiological models are correct based on *Acinetobacter sp.*.

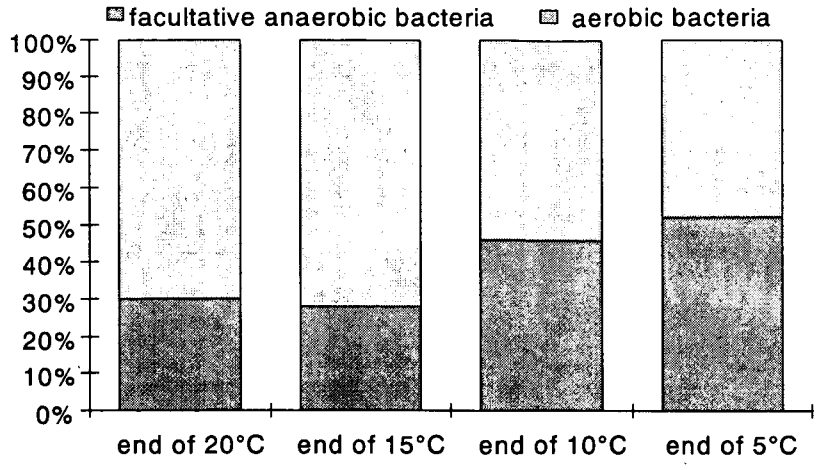


Figure 3: Amount of aerobic and facultative anaerobic bacteria on the total number of isolates at different temperatures

Summarizing the results of the population studies a lowering of operating temperature to 10°C and then to 5°C resulted in a noticeable selection of facultative anaerobic microorganisms in the activated sludge (Fig. 3). Their number increased from 28% at 15°C to 51% at 5°C. The development of the large group of facultative anaerobic bacteria is probably due to the reduced nitrification at lower temperatures. With no nitrate production the anoxic zone became additional anaerobic during these temperature phases, so organisms must overcome longer anaerobic periods compared to 15°C and 20°C.

The results of this research show that the existing models can only correctly describe BIO-P processes when applied on tests at operating temperatures of 20 to 15°C with a dominant amount of aerobic microorganisms. As the facultative anaerobic bacteria are able to gain energy through fermentation in the anaerobic zone, a reduction of the polyphosphate reservoir may not be necessary. The question why this group of bacteria increasingly stores phosphate in the aerobic zone needs further investigation.

The variety of the microorganisms partaking in the BIO-P process make modeling especially difficult. Referring to the results presented here it does not seem sensible to concentrate the mathematical models on the metabolism of *Acinetobacter sp.* in order to describe BIO-P at lower temperature conditions.

In the phases of low temperature an extensive appearance of *Microthrix parvicella (M.parvicella)* could be observed.

Operation problems of wastewater treatment plants due to sludge bulking

The composition of biocenosis of activated sludge changed due to the influence of changing substrate and environmental conditions and activated sludge bulking can be observed frequently. Due to the this phenomena the pollution of the receiving water occurred often.

Per definition of the German ATV-working group from 1988 the phenomena of bulking sludge occurs, if the development of filamentous microorganisms leads to the deterioration of

the settleability of the activated sludge and the diluted sludge volume index increases to more than 150 mg/l.

The development of a population of filamentous bacteria in certain treatment plant is dependent of the BOD sludge loading, influent quality and the operation conditions.

Occurrence of bulking sludges in strictly aerobic COD elimination and nutrient eliminating treatment plants should be distinguished in general. In former years the phenomena of bulking sludge in high COD eliminating treatment plants without biological nutrient removal was due to an abundant growth of filaments which grew especially good at low oxygen concentrations respectively on septic waste water (high sulfide concentrations) and/or shock loadings. *Sphaerotilus natans, Halicomenobacter hydrossis,* Typ 1701, *Thiothrix, Beggiatoa* and Typ 021 N belong to this group.

The reason for activated sludge bulking in Bio-P-plants with nitrification and denitrification zone which are operated at low sludge loading and the change of anaerobic, anoxic and aerobic zones is the increase of filamentous bacteria. But besides the activated sludge bulking stable foams on the surfaces of the aeration basins are observed often.

The brown foams are floating sludges with lower suspended solids concentrations which form large viscous bubbles in the aerated zones of the wastewater treatment plant and which collapse in the anaerated zones and then form stable foam like scum layers.

Table 1 clearly indicates that the percentage of wastewater treatment plants with scum problems increased. The main reason is an increase in the number of plants operating advanced waste water treatment including biological nitrogen and phosphorous removal.

	1992/1993	1995
total number of plants	78	46
occurence of scum	31 (= 39 %)	35 (= 76 %)
number of plants with nitri./deni. (partly bio-P)	41	35
occurence of scum	21 (= 51 %)	29 (= 83 %)
number of plants without nitri./deni.	37	11*
occurence of scum	10 (= 27 %)	6 (= 55 %)

Table 1: Results of two inquiries at municipal wastewater treatment plants, * partly there was no information about the BOD_5 sludge loading

Figure 4 shows that 93% of microscopically investigated activated sludges out of foaming nutrient removal wastewater treatment plants showed *M.parvicella* as the dominant filamentous microorganism in activated sludge (Knoop, 1997).

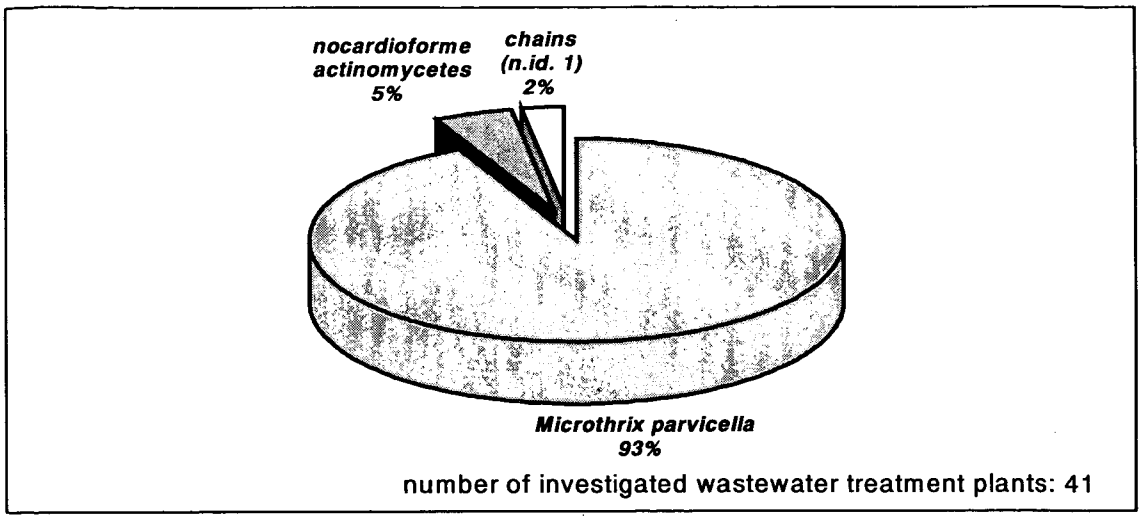


Figure 4: Relative frequency of the appearance of different filamentous bacteria in wastewater treatment plants

M.parvicella is also the most often found filamentous bacteria which causes bulking sludge in international wastewater treatment.

During the last years this filament was more and more connected with scum and foam formation in wastewater treatment plants in different european countries, (Eikelboom and Andreasen, 1995; Rosetti et al., 1994; Pujol and Canler, 1994; Duchene, 1994) South Africa (Blackbeard et al., 1986; Blackbeard et al., 1988; Hart, 1985) and Australia (Seviour et al., 1990; Seviour et al., 1994).

If *M.parvicella* is present in abundant numbers in activated sludge, *M.parvicella* forms due to his long woolen yarn like growth form net structures in activated sludge. In doing so the filaments grow through the compact flocs which afterwards have a loose, diffuse appearance with bad settleability. Gas bubbles attach to the filament net and the activated sludge flotates to the surface. *M.parvicella* filaments accumulate to high abundance in this flotating activated sludges.

Today we know that 3 components are causal for stable foam formation:

Surface active substances (1), which are called biotensides if they are produced by the biomass itself and/or tenside from washing powder lead to an decrease of surface tension of the water. Due to the present of air (2) in the aeration basin foam formation takes place in this basins. Therefor the hydrophobe parts of the tensides turn inside around the gas bubbles and the hydrophilic ends stretch out into the water phase. These foams would be easily destroyable if they would be like soap faoms. But filamentous microorganisms with hydrophobic cell surfaces (3) like *M.parvicella* attach to the tensides on the gas bubbles and stabilise them. These stabilised bubbles in the foams can be seen without magnification instruments and are not mechanically destroyable.

Very often bulking and foam formation caused by *M.parvicella* lead to sludge loss out of the secondary clarifier.

Legitimate limited concentrations of the nutrients nitrogen and phosphorous can not be reached. In extreme cases scum and foam formation which occur at the same time as bulking formation can flow over the walls of the aeration basins. During extremely cold winters these foam formations can freeze and lead to severe operation problems. If surplus sludge is given into the anaerobic digester for sludge stabilisation the anaerobic sludge starts to foam and the anaerobic digestion has to put out of order.

4. *Microthrix parvicella* and Bio-P

Abundant growth of *M.parvicella* occurs in domestic wastewater treatment plants with biological nitrogen and phosphorous elimination. The categories of abundance reach from 0=no filamentous to 7=very high level of filamentous bacteria. Figure 5 shows a part of a microscopical investigation of 41 of such wastewater treatment plants. 7 of these investigated treatment plants were constructed for enhanced biological phosphorous removal, nitrification and denitrification processes. In this plants *M.parvicella* has a growth advantage compared to the non filamentous biomass and is dominant in activated sludge with an abundance of 5. The average sludge volume index in these plants was above 150 ml/g so that operation problems and sludge flow out of the secondary clarifier might occur. *M.parvicella* accumulates in the foam. Its abundance in the foam on the surface of the aeration basins is always one category higher then in activated sludge.

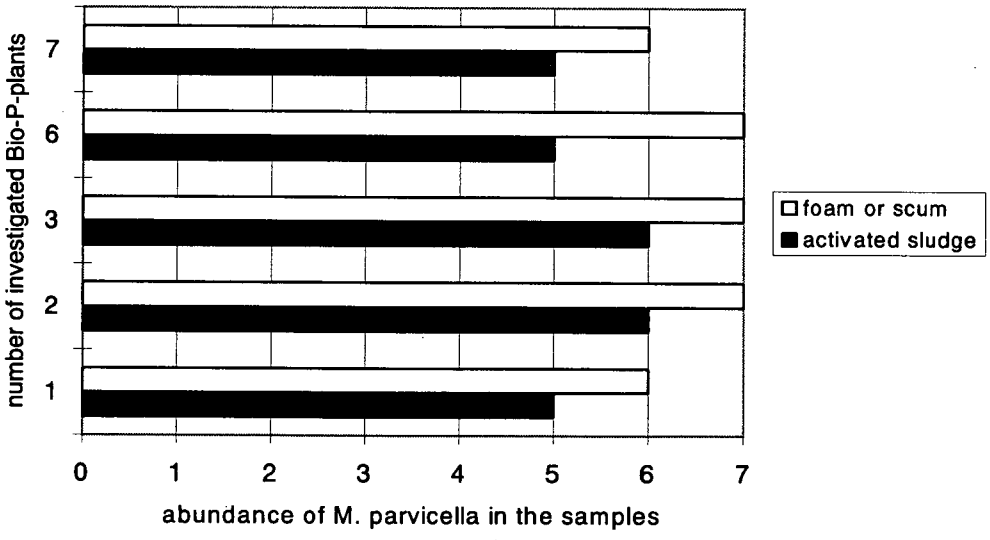


Figure 5: Frequency of *M.parvicella* in activated sludge in wastewater treatment plants operating with enhanced biological phosphorous removal

The change of the population profile of filamentous bacteria in activated sludge under different sludge loading conditions can be seen if a Bio-P-plant is compared with a COD eliminating plant (Figure 6). The former worked at an average sludge loading of 0.5 kg/(kg*d) the latter at 0.1 kg/(kg*d). The activated sludge samples were both taken at 12-15°C which is the optimum growth temperature for *M.parvicella* in activated sludge (Knoop, 1997).

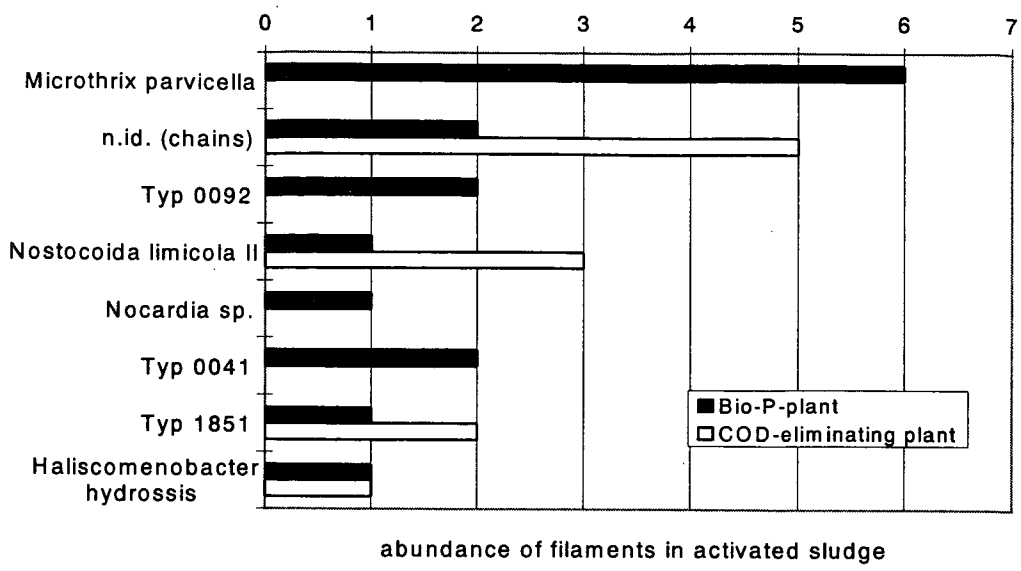


Figure 6: Typical profiles of filamentous bacteria populations in activated sludge of a wastewater plant operating enhanced biological phosphorous removal and a COD eliminating plant

M.parvicella appeared with an abundance of 6 in the activated sludge plant with Bio-P removal whereas this filament could not grow in the high loaded COD eliminating plant. In the activated sludge of the latter plant, a chain like organism which could not clearly be identified was found with an abundance of 5. Although both organisms have strongly hydrophobic cell surface and lead to the formation of scum and foam layers on the water surface bulking activated sludge with a sludge volume index > 250 ml/g could only be observed in the Bio-P plant. Under the conditions of a biological nutrient removal plant *M.parvicella* grows out to a length of 200-500 µm and the abundant growth of this filament and its net like formations caused a loose, diffuse floc structure and to activated sludge bulking. The chain like organisms had a maximum length of 80 µm and did not affect the sludge volume index which was 100 ml/g in average. Besides the influence of the anaerobic zone of biological phosphorus removal plants on the growth of *M.parvicella* there is also a growth dependence of *M.parvicella* on low BOD-sludge loading conditions which is in general usual for nutrient removal activated sludge plants. The ATV in Germany recommends a BOD-sludge loading of ≤ 0,1 kg/(kg·d) which results in an average sludge age ≥ 12 days. Because of the slow growth of *M.parvicella* it is able to multiply very easily at this sludge age. Therefore it can be concluded that because of the fact that the process of biological phosphorus removal is usually connected with nitrification and denitrification processes in biological nutrient removal plants, an abundant growth of *M.parvicella* will always occur in these plants. The abundant growth of *M.parvicella* is therefore not directly dependent on the process of biological phosphorus removal.

Besides the influence of sludge loading on activated sludge bulking the influence of different temperatures on sludge settleablity and the growth of *M.parvicella*in activated sludges of Bio-P plants was investigated using laboratory scale plants. It could be proofed that *M.parvicella* cannot grow at temperatures ≥ 20 °C even at a BOD sludge loading ≤ 0,1 kg/(kg·d). This filament falls apart into 30 to 80 µm pieces. Within 15 days the sludge volume index sinks

below 150 ml/g. Optimum growth of *M.parvicella* takes place at ≤ 12 to 15 °C and BOD sludge loading ≤ 0,1 kg/(kg·d). Under these conditions *M.parvicella* grows out to 200 to 500 µm long filaments and since this filament has strongly hydrophobic cell surfaces it causes bad dewaterability and in consequence sludge indices of 250 ml/g in average with maximum values of 490 ml/g in large scale wastewater treatment plants (Knoop, 1997). The polyphosphate granula of the organisms which participate in the Bio-P-process will be well visible after staining with Toluidine blue (Helmer, 1994). In the past a lot of authors described the ability of *M.parvicella* to store polyphosphate in form of granules inside the filament (van Veen, 1973;). The polyphosphate granula of *M.parvicella* are an important feature for its morphological identification (Eikelboom, 1977;).

As a contribution for clearing the assumption that *M.parvicella* has a selection advantage in Bio-P plants because of its ability to store polyphosphate, Knoop (1997) investigated the appearance of *M.parvicella* under phosphate release and phosphate uptake conditions. Therefor activated sludge was taken from different domestic wastewater plants with Bio-P-process and filled into 5 liter batch reactors. After the first 48 hours anaerobic phase, in which the activated sludge was stirred but not aerated, an 7 hour aerobic phase with constant aeration followed. To show if there are polyphosphate granules in the sample and the quantity of those granules Toluidine blue staining was the best method to use (Figure 7).

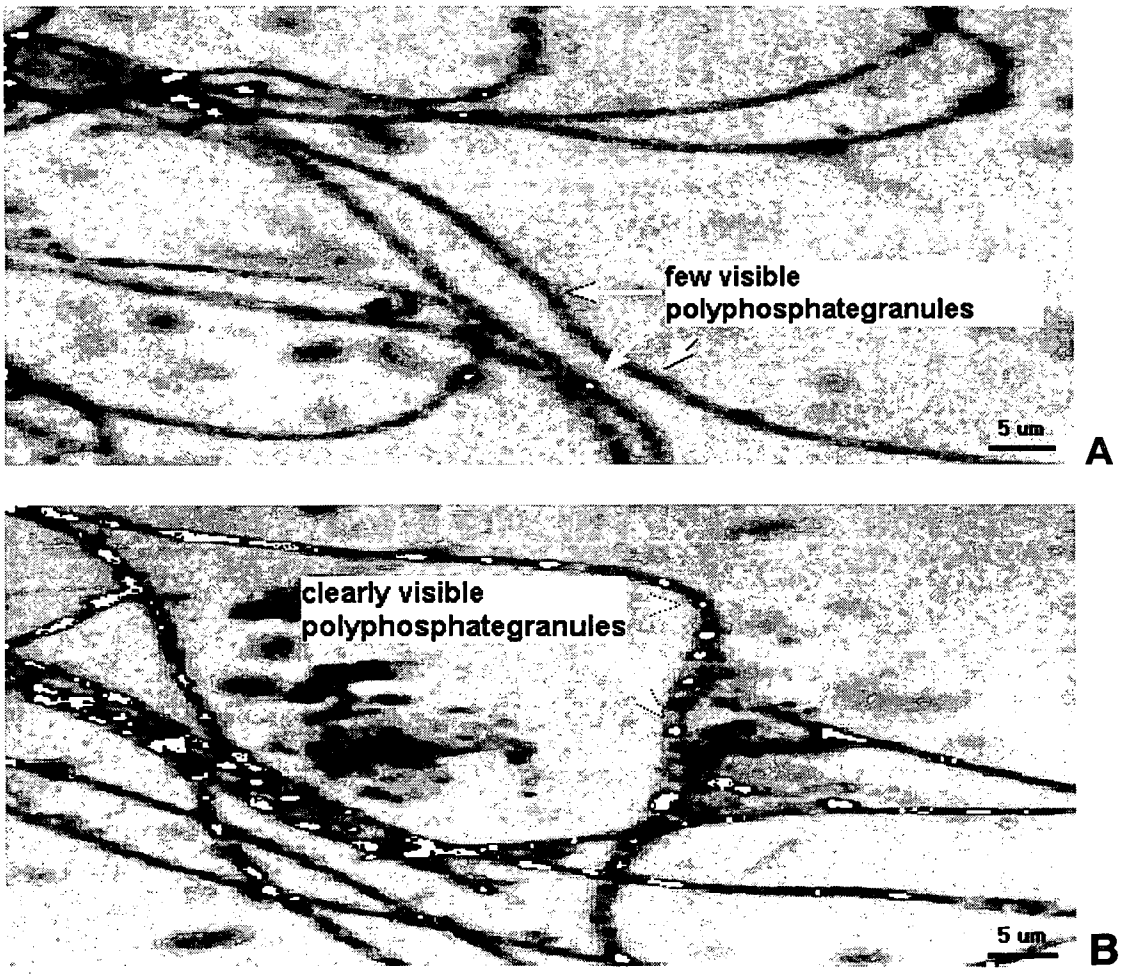


Fig. 7: Polyphosphatgranules visible in *M. parvicella* both at the end of the anaerobic phase (A) and at the end of the aerobic phase (B) using defined experimental conditions

It is clearly visible that at the end of the aerobic phase there are more and bigger polyphosphate granules in the *M.parvicella* filament then at the end of the anaerobic phase after phosphate release.

For these pictures a Toluidine blue stained colored picture in which the phosphate granules stain violett was treated with the Lucia G picture analysing computer program from NIKON. The polyphosphate granules were detected and marked white. Using this method the coloured granules stay clearly visible after black and white reproduction.

Besides the Toluidine blue stain Neisser stain was used to confirm the observations and to show that the appearance of the polyphosphate granula in the *M.parvicella* filament is dependent on the oxygen concentration. After staining the granula appear as characteristic blueblack balls inside the filament. Schön (1996) and Wedi et al. (1995) described that obligate aerobic bacteria can not use the lipid storage as poly-ß-hydroxybutyricacid (PHB) for cell growth under anaerobic conditions.

Like Bio-P-bacteria *M.parvicella* is obligate aerobic (Slijkhuis, 1983) and cannot use its PHB storage under anaerobic conditions for cell growth.

This could be shown by an experiment in which the abundance of *M.parvicella* did not increase even under anaerobic conditions up to 83 days. It seems that *M.parvicella* builds up PHB storage use it as an energy source for cell maintenance and by using this way delay cell death and lysis. Since gram variability of *M.parvicella* was observed under long anaerobic conditions (>25 days) and the filament did not break apart gram variability of *M.parvicella* does not seem to be a matter of cell death and cell lysis but might be explained by the observations of Foot et al. (1992). In this case the gram variability of *M.parvicella* seems to be the result of selective substrate accumulation as PHB and lipids. It might be possible that *M.parvicella* can use these substances for protein synthesis under aerobic conditions (Foot et al., 1992). The accumulation of PHB inside the cell could be a protection mechanism of the cells against lysis and cell death, which was proofed for Bacillus megaterium cells by Dawes and Senior (1973).

Based on our results it can be suspected that *M.parvicella* is able to do the basic processes of biological phosphorous elimination, like Bio-P-bacteria. This means that during the change from anaerobic to aerobic condition *M.parvicella* is able to store polyphosphate, release phosphate and synthesise a PHB storage. The latter enables him to survive extreme oxygen limited conditions. The ability to survive extreme long anaerobic times on one hand and to store polyphosphates under aerobic conditions on the other hand make *M.parvicella* able to compete in large scale wastewater treatment plants with biological phosphorous removal. But the accumulations of the PHB is so slow that anaerobic contact times for enhanced biological phosphorous removal between 0.75 and 2h (Boll, 1989) are not long enough for *M.parvicella* for the synthesis of PHB.

Therefor *M.parvicella* is not able to use PHB as endogenous substrate to compensate low concentration of exogenic substrates (Rensink, 1985) and through that is not able to get a growth advantage.

But there might be another possible explanation for the survival strategy of *M.parvicella* in wastewater treatment plants with biological phosphorous removal. Although *M.parvicella* is a strictly aerobic bacterium, it is able to take up oxygen at low oxygen concentration by an up to five times higher respiration rate then non filamentous floc forming bacteria such as *Acinetobacter* (Slijkhuis, 1983).

Based on this oxygen affility *M.parvicella* will reach a growth advantage in low loaded activated sludge plants with enhanced biological phosphorous removal because this filament is able to use the little substrate by using low oxygen concentration effectively for cell growth. The polyphosphate storage is than used as an additional energy source.

5 Foaming in anaerobic digesters of Bio-P plants

During the last years it had been very frequently reported about foaming of anaerobic digesters in biological nutrient removal plants. After having a closer look at the activated sludge, the foam on the aeration tanks and the foaming anaerobic digesters, we could see that all plants with foam in the aeration tanks had also trouble with foaming anaerobic digesters. The causative connection became clear after the microscopical identification of the filamentous bacteria. Parallel with the increase of *M.parvicella* in the foam fraction of the aeration tank compared to the mixed liquor activated sludge abundance the concentration of extrapolymere substances (EPS) of the foam increased too. Addition of foam and foaming surplus sludge into the digester caused an enrichment of *M.parvicella* in the digested sludge and foaming of the digester. Figure shows that the optical estimated amount of EPS in the foam was always one category higher in the foam than in the mixed liquor activated sludge.

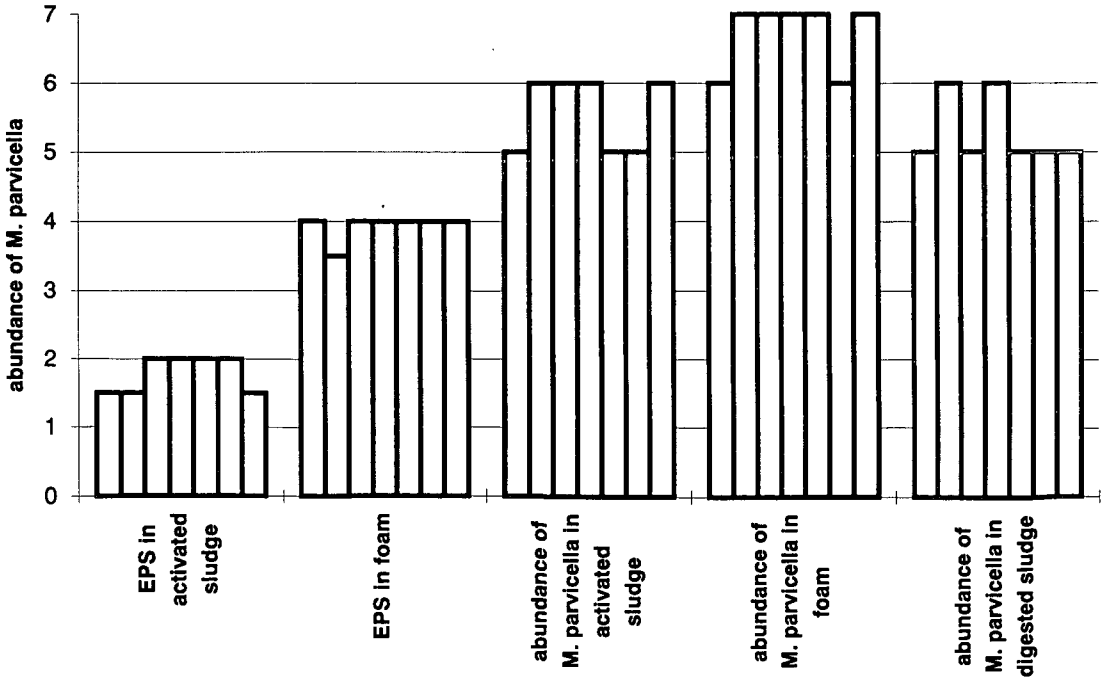


Figure 8: Extensive appearance of *M.parvicella* in activated sludge, in foam and in digested sludge and creation of EPS in seven examined wastewater treatment plants

This is caused by an increase of viscosity of the digested sludge (Figure). The measurement of viscosity was done using a rotational viscometer.

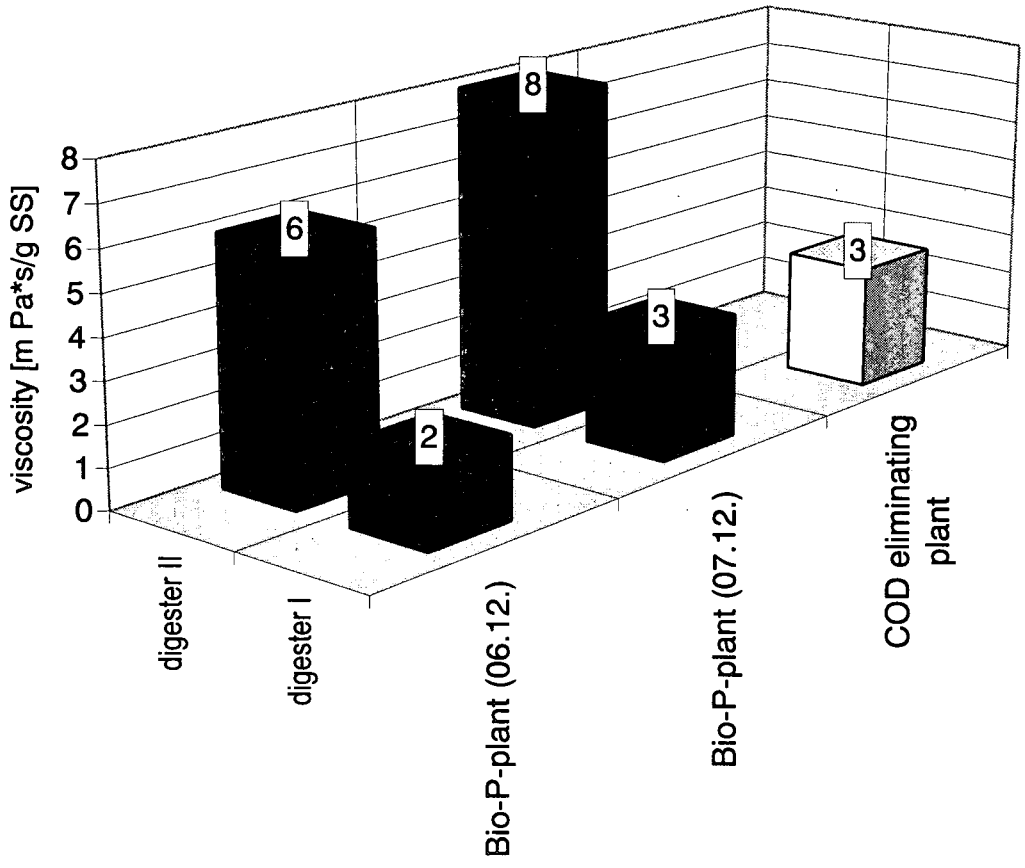


Figure 9: Increase of viscosity of the digested sludge caused by addition of *M.parvicella* dominated foam into the digester II

Of special interest are the results of the Bio-P plant from two following days. During these days digester I did not receive foam from the aeration tank and the digester did not show any foaming. The viscosity of the digested sludge is within the measurement range of the viscosity of the non foaming digested sludge of the COD eliminating plant. The viscosity increases to the doubled value and at the same time the sludge starts foaming if foam is given into the anaerobic digester II.

6. The fight against scum and foam

6.1 Continuous skimming of floating sludge and scum directly from the aeration tank

The research results confirm that at wastewater temperatures below 20 °C the emergence of *Microthrix parvicella* can hardly be avoided in municipal wastewater treatment plants with secondary wastewater clarification. Tests with selectors have shown that anaerobic, anoxic, or aerobic selectors do not have any decisive, reproducible influence on the growth of *M. parvicella* /Ekama et al., 1996; Still et al., 1996/. Thus, we used experiences made at the wastewater treatment plant of Johannesburg/South Africa; there, the operators succeeded in improving the emergence of scum and the sludge volume index by skimming the scum layer from the surface of the activated sludge plant /Wentzel, 1995/.

In the following, we will present the results of a three-month operation period with a new system which continuously skims the scum from the aeration tank. The analyses were run at the wastewater treatment plant at Hildesheim, which was designed for the entirely biological elimination of nutrient salts. In contrast to many other wastewater treatment plants, at Hildesheim there are problems with scum or floating sludge on the aeration tanks almost throughout the whole year. One reason for this phenomenon is that the wastewater temperatures hardly ever rise considerably above 20 °C, not even during the summer. In times of heavy scum emergence, the aerated part of the aeration tank is covered completely with scum bubbles, which deflate in the ensuing denitrification-zones and form into a dense, massive layer of floating sludge. This leads to the following major problems: high sludge volume index; floating sludge, which does not settle in the secondary clarifier; but is conveyed into the receiving water, a frozen layer of floating sludge in winter, bubbling of the digesters during co-digestion of primary sludge and surplus sludge. Since the scum emergence in the digesters was sometimes that high that the scum was pushed into the gas pipelines, primary sludge and surplus sludge were digested separately in the three digestion tanks.

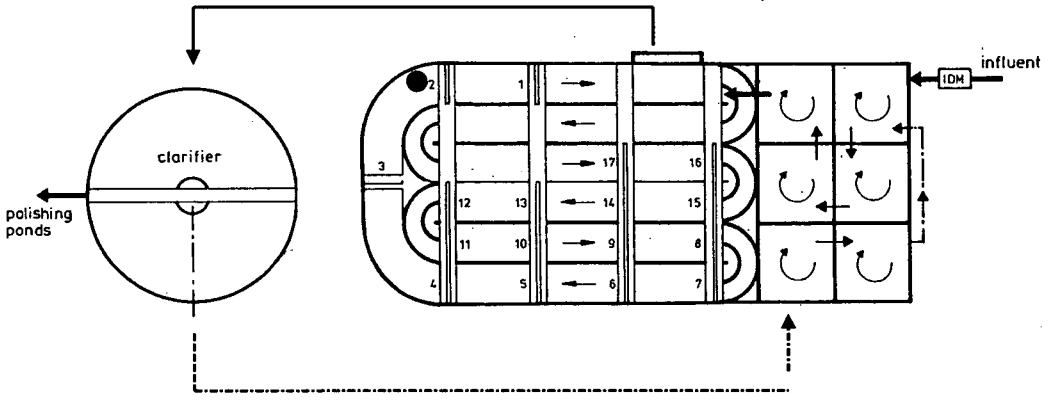
6.2 Wastewater Treatment Plant at Hildesheim

The wastewater treatment plant at Hildesheim was designed 1983 by Prof. Seyfried and extended 1993; nitrification and denitrification occur simultaneously in rotary ditches. For the biological phosphorous removal, the plant employs the ISAH-process, the main asset of which is that the return sludge is denitrified in a separate anoxic tank in order to prevent any possible impairing of the phosphorous removal by return nitrate. Up to December 1996, the biological stage consisted of two lines. As the capacity of this stage was not sufficient, two additional lines were built, the first of which was started in operation in the middle of December 1996. The wastewater treatment plant is now designed for 240.000 population equivalents (Fig. 10).

The two old lines and the new third are fed with wastewater according to their volume. During the test period from April to June 1997, the sludge loading in the entire activated sludge plant amounted to < 0,1 kg BOD/(kg MLSS*d).

Table 2: Dimensioning Data

	line 1 and 2 (1983)	line 3 and 4 (1993)
aeration tank	V = 2 * 7.100 m^3 = 14.200 m^3 V_{anox} = 2 * 625 m^3 = 1.250 m^3 V_{an} = 2 * 875 m^3 = 1.750 m^3	V = 2 * 10.700 m^3 = 21.400 m^3 V_{anox} = 8 * 630 m^3 = 5.040 m^3 V_{an} = 4 * 500 m^3 = 2.000 m^3
secondary clarification	A = 2 * 1018 = 2.036 m^2	A = 2 * 3.135 = 6.270 m^2



RS

- skimming plant

1,2,3.. aerators

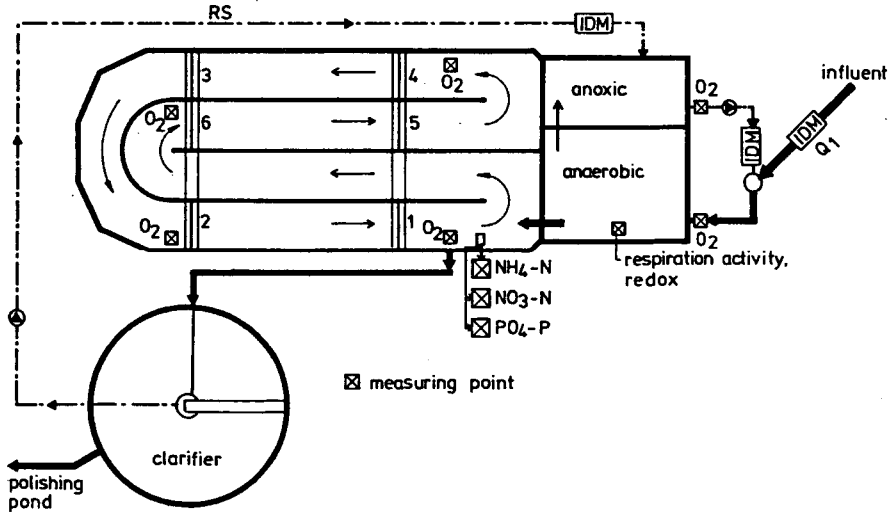


Figure 10: Flow diagram of one of the two identical lines

6.3 Description of the special Foam and Scum (SFS) - Skimmer

The special foam and scum (SFS) -skimmer was engineered by a company at Fallingbostel, Germany. As can be seen in Figure 11, the central element is a strainer belt which continuously lifts the scum from the surface of the water, dewaters it simultaneously and conveys it into a rectangular high-grade steel container. From there, the scum is continuously extracted by a pump which is controlled by a volume measuring device implemented in the container. During the test period, the scum was at first conveyed into a storage tank with a volume of 8 m^3. The scum amounts were registered as weight in mass by manometric capsules which were connected to a chart recorder. The dried residues of the scum were ascertained by grab samples which were taken throughout the day from the influent to the storage tank. From the storage tank, the scum was conveyed into the fourth basin for secondary treatment which at that time had not yet been set in operation, and collected there for the time being.
The black dot in Figure 10 shows the place where the scum skimming device was lowered into the basin. In order to make the system work efficiently, it is necessary to achieve a sufficient streaming velocity of the scum. Furthermore, to skim as much scum as possible in a short time, the scum should already be extensively deflated. Thus, the mammoth rotors were switched on in a way that Rotor 3 was operating continuously and that Rotor 2, implemented behind the skimming plant, stood still as long as possible to function as barrier against the scum. In the first two weeks of the test period, Rotor 2 had to be switched on every three to four hours for a few minutes, because the incoming scum waves threatened to reach the rim of the basin. In the first week, the system was operated only in the daytime; after some technical problems had eventually been solved, it could be run continuously.

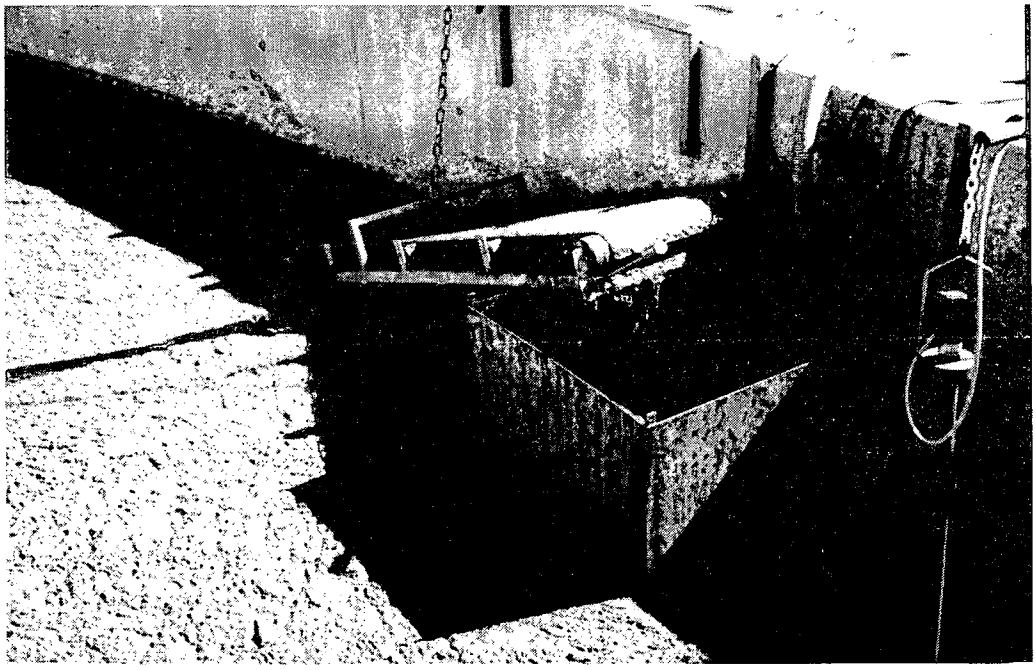


Figure 11: System for scum skimming

Three to four times per week, samples were drawn from the aeration tanks of lines 1 and 3 and analysed in regard to the parameters mixed-liquor suspended solids (MLSS), sludge volume index (SVI), viscosity, and capillary suction time (CST) (German Standard Methods); furthermore, microscopic analyses were run to ascertain the contents of exopolymerous substances (EPS) and the filament abundance. The EPS are dyed using a method developed by /Jenkins et.al., 1986/. It is a reverse dying with Indian ink, which dyes the entire sample black, with only the EPS remaining visible as light areas. In order to ascertain the filament abundance, the sludges were dried by air and then dyed with Crystal Violett /Jenkins et.al., 1993/. The classification of the filament abundance was done according to /Knoop, 1997, see also Chap. 4/.

6.4 Results

The SFS-Skimmer, which because of its simple design could be implemented into the aeration tank without any problems, is able to extensively dewater the extracted scum. The average volume of the dry residues of the extracted scum over the entire test period amounted to 45 g/kg, although the consistency of the scum changed considerably. At the beginning, the scum bubbles on the aeration tank were small and very stable, which led to a compact layer of floating sludge; the more the test advanced, the bigger and less stable did the bubbles become, so that they deflated to a loose layer of floating sludge.

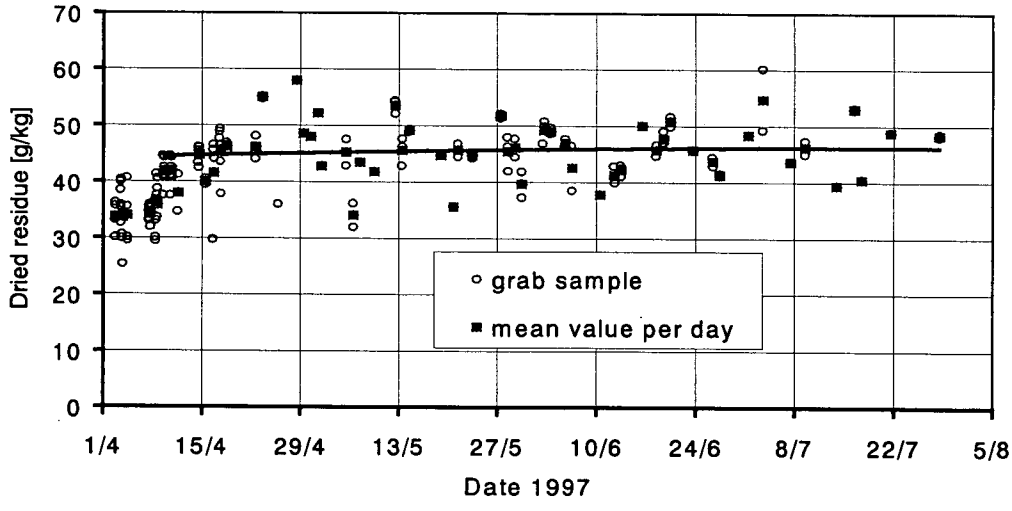


Figure 12: Dried residues of the scum

At the beginning of the tests, the plant was run with a MLSS-contents of about 3 g/l. Approximately 15 m^3 of surplus sludge were extracted per hour (6-8 g MLSS/l). When the plant was switched to continuous operation on April, 9th, the surplus sludge extraction was reduced by one third down to 10 m^3. After the MLSS-contents had successively dropped to < 2,5 g/l, the extraction of surplus sludge was stopped on April, 18th. From the third week of April (April 22nd - 29th), the activation unit of line 3 was almost devoid of floating sludge. During this period, the average scum skimming dropped from approx. 1,9 t/d dried residues to 1,2 t/d dried residues. Further decrease of the scum skimming and thus a reduction of the re-emergence of scum could be observed after approx. one week after the wastewater temperature had risen to degrees of 17 °C - 18 °C (Fig. 13).

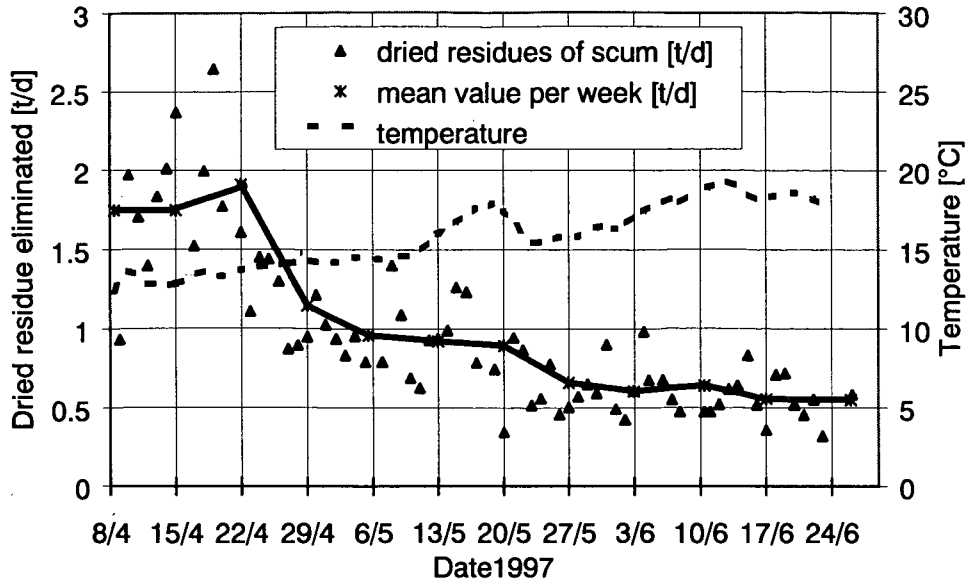


Figure 13: Progress of scum skimming from the start of the skimmer

At the beginning of April high sludge volume indexes of > 200 ml/g were measured for both lines at wastewater temperatures of 12 °C. During the first two weeks after initiating the extraction system, the activated sludge of both lines showed unsatisfactory sedimentation performance.

Figure 14 shows the sludge volume index of activated sludge from line 1 and 3 in relation to temperature after one week of test operation.

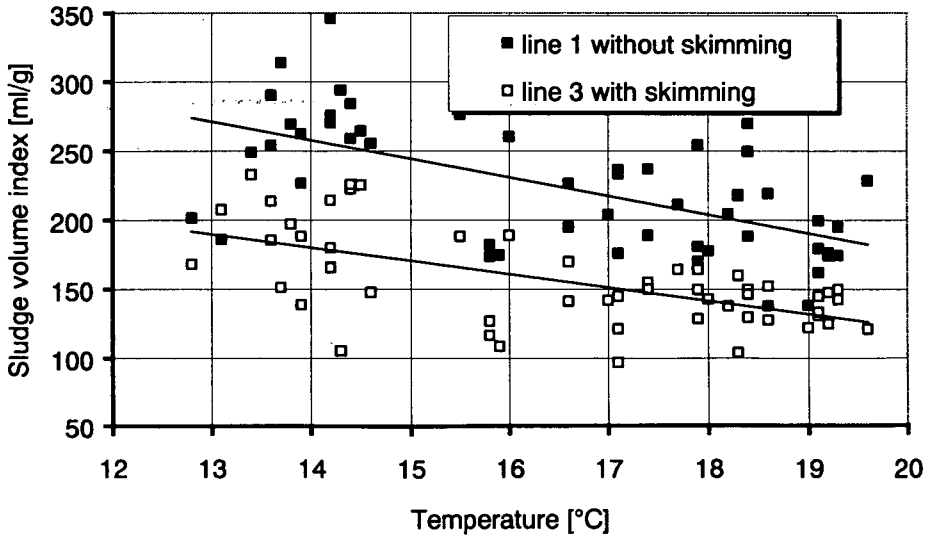


Figure 14 Sludge volume index in relation to sewage temperature

For both plants, the impact of the temperature on the sedimentation performance of the activated sludge is easily discernible. From May, 10th, the wastewater temperature rose above

15 °C, which led to a general improvement of the sludge volume index. Together with the sludge volume index, viscosity and CST as yardstick for the dewaterability of the sludge improved in line 3 (cf. Figure 15).

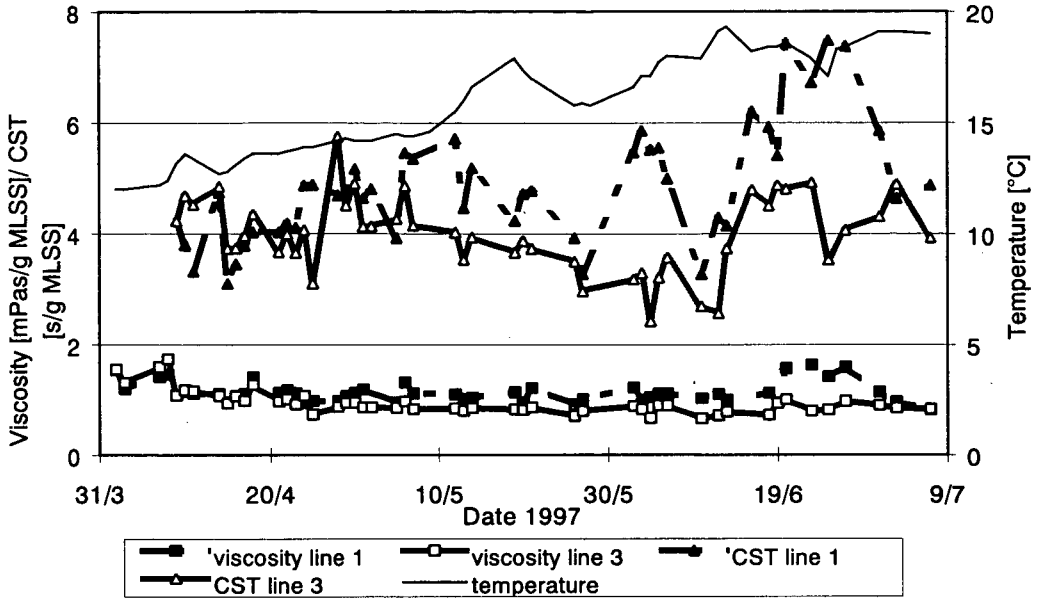


Figure 15: Development of Viscosity and Capillary Suction Time (CST) of the sludge in the aeration tanks in lines 1 (without skimming) and 3 (with skimming) during the test period

Measurements of hydrophobicity of activated sludge taken from line 1 and 3 displayed a wide variation for both sludges (see figure 16). No reduction of hydrophobicity can be observed after scum withdrawal. When averaging the date over a temperature interval of one degree celcius only a temperature depending change of hydrophobicity shows up. The hydrophobicity decreases with increasing sewage temperatures since the microorganism *M. parvicella* decreases in number in the sludge of both lines.

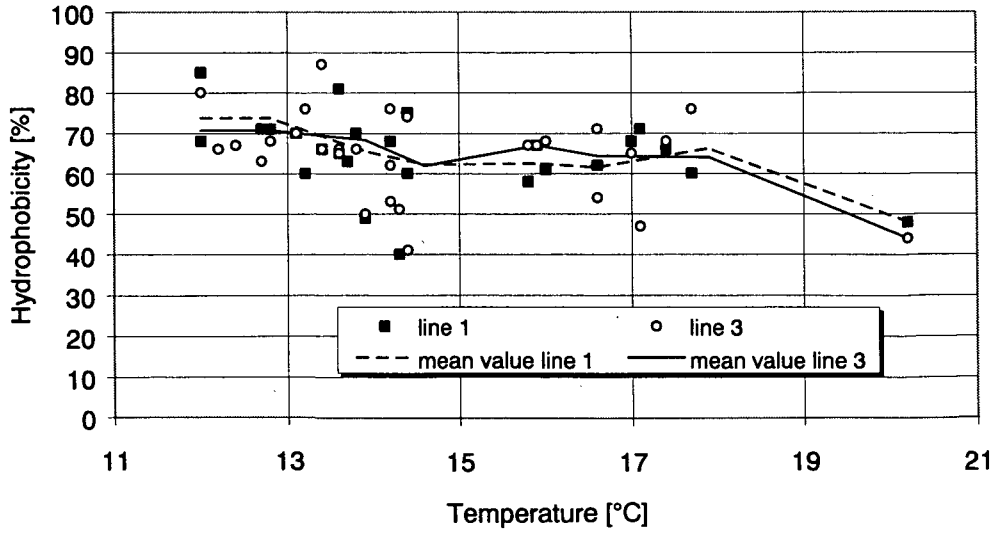


Figure 16: Hydrophobicity of the activated sludge of line 1 and line 3

The microscopic analyses have shown that *M. parvicella* was the dominant filament in both lines throughout the test period. The filament abundance of the activated sludge was the same in both lines. Slight differences did only occur after May, 12th. From April to June, the extracted scum sported a filament abundance of Class 7. The EPS contents neither differ largely. On a scale from 1 - 4, for most of the time the EPS-contents moved in the area of 2 - 3 for both sludges.

Table 3: Filament abundance of the activated sludge (line 1 without skimming, line 3 with skimming)

date	2nd April	16th April	28th April	12th May	21th May	3rd June	31th June
line 1	6	6	5	6	6	5	5
line 3	6	6	5	5-6	5	5	4

At the beginning of the tests, it was assumed that the continuous skimming of scum which was highly charged with *M. parvicella* would lead to a successive elimination of the filaments from the activated sludge (Tab. 2). Although over a period of one month the surplus sludge was removed only via scum skimming, the filament abundance of the activated sludge in line 3 did decrease, but only scarcely so compared to line 1. The favourable impact on the sedimentation performance of the activated sludge however could be proven unequivocally. The microscopic analyses have shown that filament size was reduced in the sludge of line 3.

The skimming of scum had no negative influence on the quality of the effluent of the secondary clarification. The biological phosphorous removal was not impaired, because *M. parvicella* is able to store phosphate. During the test period the contents of phosphate of the scum ranges between 32 - 37 mg P/g dried residue. The average contents of phosphate of the return sludge of line 1 and line 3 was 33 mg P/g dried residue.
First operation results showed that the oxygen transfer capacity in line 3 could be improved thanks to the continous skimming of scum.

6.5 Homogenization

It is not possible to add withdrawn sludge to the digestion tank since this may cause - as mentioned earlier - the digestion tank to overflow. Laboratory experiments were done to find out a way to destroy the filamentous structure of *M.* parvicella to prevent overflows when adding sludge to the digestion tank. A treatment of the sludge with a high pressure homogenizer for laboratory use turned out to be very successful. The homogenizer was able to build up a pressure of 1000 bar maximum.

Homogenisation is the formation of a stable, homogenous liquid phase by mechanical means. The dispersed phase, whether solid or liquid, is subjected to severe mechanical forces both to decrease particle size and to increase the number of particles. Typically, intense shearing forces are used to accomplish this effect. A high pressure pump forces the liquid through a homogenization valve with a very narrow gap. The combination of high pressure and narrow gap results in extremely high velocities which shear any particles and/or globules into much finer units. Immediately after exiting the homogenization gap, there is a massive pressure drop; this causes air bubbles to form and collapse in a cavitation, which also disrupts any

liquid globules. Finally, there is often a major change in flow direction within a homogenizer valve; this results in high impact forces which again disrupt any particles or globules.
The homogenisation of the sludge lead to a clear decrease of viscousness as can be seen in figure 17. Since the maschine is for laboratory use only the sludge had to be thined down to a dried residue content < 20 g/l.

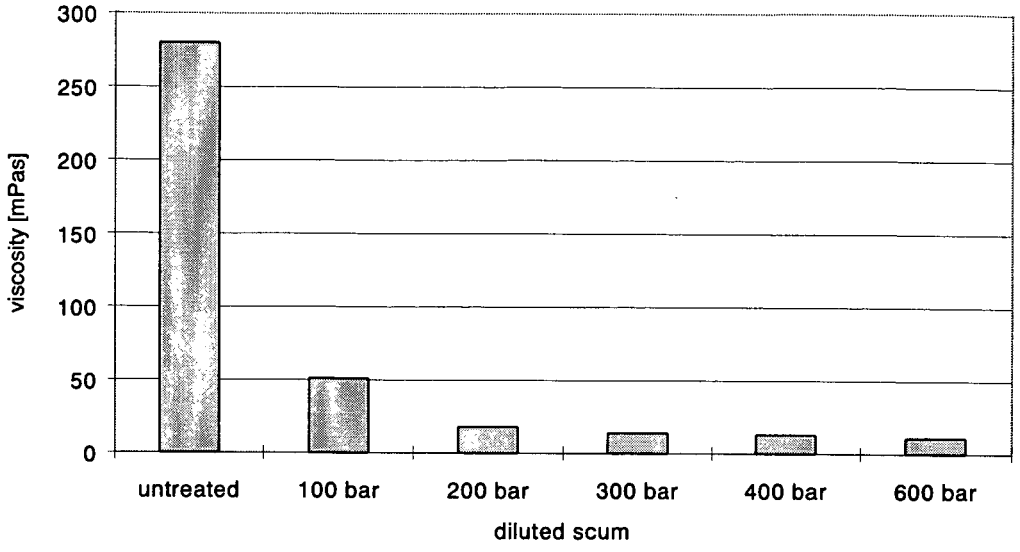


Figure 17: Decrease of the viscosity of the diluted sludge with increasing pressure

Already a pressure of 100 bar reduced the length of *M.* parvicella considerably. When applying 500 bar only very small fragments were left. Sludge treated this way was digested without any problems.
First large scale investigations show that when using a high pressure homogenizer with a flow-through of 3,5 m^3/h a pressure of 300 bar is enough to destroy the filaments completely.

7. Effects of the enhanced biological phosphorus removal on the operation of wastewater treament plants (WWTP)

Based on the technical principles of the biological nitrogen and phosphorous removal as well as on the operating experiences of technical plants the following conclusions could be drawn for the planning of wastewater treatment plants:
sewer system:
- sediments in the sewer system negatively influences BOD:N and the BOD:P ratios
- retention tanks acts the same way as the sediments in the sewer systems considering the BOD:N and BOD:P ratios
- no need of pretreament only for the reduction of COD respectively BOD, but without N-elimination

screening system
- supplemented with sieves→ protection of sensible measurement and control devices,

grit chamber:

- unaerated or at low rate aerated grit chamber prevent the consumption of readily biodegradable substrates

primary settlement tank
- in the case of anaerobic sludge stabilization the retention time in the primary settlement tank should be limited to 20-30 min
- in the case of simultaneous sludge stabilization a sieve should replace the primary settlement tank
- a aeration via the weirs or the outlet-pipes should be avoided
- a bypass to provide a direct substrate supply to the anaerobic tank should be planned
- a possible recirculation of the primary sludge to the inlet should be provided to raise the readily biodegradable COD in the influent

anaerobic tank
- all non intended aeration as fast running agitator should be avoided
- it is positive to plan the anaerobic tank as a cascade to prevent the introduction of O_2 and NO_3-N all over the tank
- to cover the anaerobic tank can limit the O_2 introduction via the surface

denitrification
- the external recirculation sludge should be denitrified (ISAH-process)
- the denitrification zone should be variable to adapt the volume relative to the nitrate concentrations so that a secondary phosphate release can be avoided

nitrification
- a minimum of oxygen supply of 2 mg/l should be installed to secure a good phosphorus uptake
- the volume of the aeration tank should be adapted to the phosphate uptake capacity

clarifier
- short sludge retention times are important to avoid a secondary phosphate release

8. Conclusions

After the documentation of the status of the application of enhanced biological phosphorous removal in the German speaking area based on a stock taking undertaken by Scheer et. al. (1996) some environmental influences on the process were discussed.

The effects of low temperature on the BIO-P process and the consequently changes of the biocenosis were analysed. The results of this research show that the existing models can only correctly describe BIO-P processes when applied on tests at operating temperatures of 20 to 15°C with a dominant amount of aerobic microorganisms. Because of a reduced nitrification at low temperatures, making the anoxic zone additional anaerobic, facultative anaerobic microorganisms accumulated in the microbial population. In batch tests mainly these facultative anaerobic strains were able to store polyphosphate, whereas the „classic" aerobic bio-P-bacteria lost their polyphosphate storing capacities. Furthermore an extensive growth of filamentous under low temperature conditions could be observed.

Wastewater treatment plants operating nitrogen and phosphorous removal have operating problems with filamentous bacteria and bulking sludge. The microscopical analysis of

activated sludge has shown that *M.parvicella* in 93% of the examined samples the dominant filamentous bacteria was.

Wastewater temperatures below 15 °C and BOD_5 sludge loading < 0,1 kg/(kg*d) provide optimal conditions for the growth of the filamentous organism *M.parvicella* if the wastewater treatment operate denitrification and Bio-P. Very often bulking and foam formation caused by *M.parvicella* leads to sludge loss out of the secondary clarifier. By consequence legitimated requirements of the nutrients nitrogen and phosphorous cannot be reached.

In the case that excess sludge containing filamentous bacteria is given into the anaerobic digester in order to obtain sludge stabilization it could be possible that the anaerobic sludge starts to foam cuased by the high EPS contents which leads to an increase of viscosity and the anaerobic treatment has to put out of order.

The continuously skimming of the scum from the aeration tank improves the sedimentation of the activated sludge and minimizes floating sludge.

Skimming of the sludge from the aeration tanks is the first step to minimize the problems with scum and floating sludge in wastewater treatment plants with denitrification and bio-P. The disposal of this scum is a problem which hitherto has not been solved on an industrial scale. Direct dosing into the digesters would lead to over-foaming; it is thus not advisable. On a laboratory scale, tests have been run to destroy the filiform structure of the scum to a degree which allows for non problematic anaerobic digestion. A particularly successful method was the treatment of the scum with a high pressure homogenising device, which at a pressure between 300 and 500 bar extensively disintegrates the filaments. Tests on an full-scale plant are meanwhile started with good results.

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EVALUATION METHOD FOR THE CONSTRUCTION MATERIAL MADE OF SEWAGE SLUDGE - TECHNICAL STANDARD AND THE LEACHING TEST METHOD

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ABSTRACT

It is becoming more important to utilize sewage sludge as construction material in Japan. Blocks are the good examples of solid waste recycling. Two types of leaching tests were conducted to investigate the standardized test for construction material made of sewage sludge. One type is considered as a worst-case test, while the other type is used to estimate the heavy metal release into the ground water. Those methods were investigated by using the sewage sludge and the crushed samples of blocks. At first, the characteristics of leaching tests were investigated by using the sewage sludge. Modified Swiss method was considered a little severer method than Japanese Environmental Agency (JEA) method. Next the relationship between the major metal release and the trace metal release was investigated by using the construction material. And a close relationship between them was observed by Holland and Swiss method. At last modified Swiss method was applied to the blocks. The effect of sample diameter was discussed by the results of major metal release. Consequently modified Swiss method, which sample is medium size, was supposed to be proper as one of the standardized test considering the effect of acid rain.

KEYWORDS

Sewage sludge; construction material; technical standard; leaching test; sample size

INTRODUCTION

The amount of sewage sludge generated from sewage treatment plants is steadily increasing year by year with the expansion of sewage coverage in Japan, so it is becoming more important to treat and utilize sewage sludge. Many cities have begun to consider the reuse of sewage sludge as a

construction materials, and several municipalities and some companies have already started to construct plants in which construction material is produced from sewage sludge, but the quality is controlled according to the standard for usual material.

There are several regulations on waste disposal to preserve soil and ground water quality, and national leaching test methods are used in some countries. However there is no evaluation method for assessing the release of heavy metals from re-products which include sewage sludge as raw material. Now there is a big discussion in Japan about the standardized leaching test for recycling material. There are two prospects for this discussion, which are environmental preservation and recycle promotion. From the first point of view, the severe condition will be required. But the recycling has become more important in these days.

SITUATION OF THE SEWAGE TREATMENT IN JAPAN

More than 90% of wastewater is treated by the conventional activated sludge process including step aeration. Figure 1 shows the annual trends of generated sludge based on the solids taking out from the liquid treatment system to the sludge treatment system. The generated sludge has increased every year at a rate of about 5%. On the other hand, treated wastewater volume did not increase continuously. It is estimated that the wastewater volume is related to the consumption of water which is affected by weather and business activity, and the generated sludge volume is increased in accordance with the spread of sewerage.

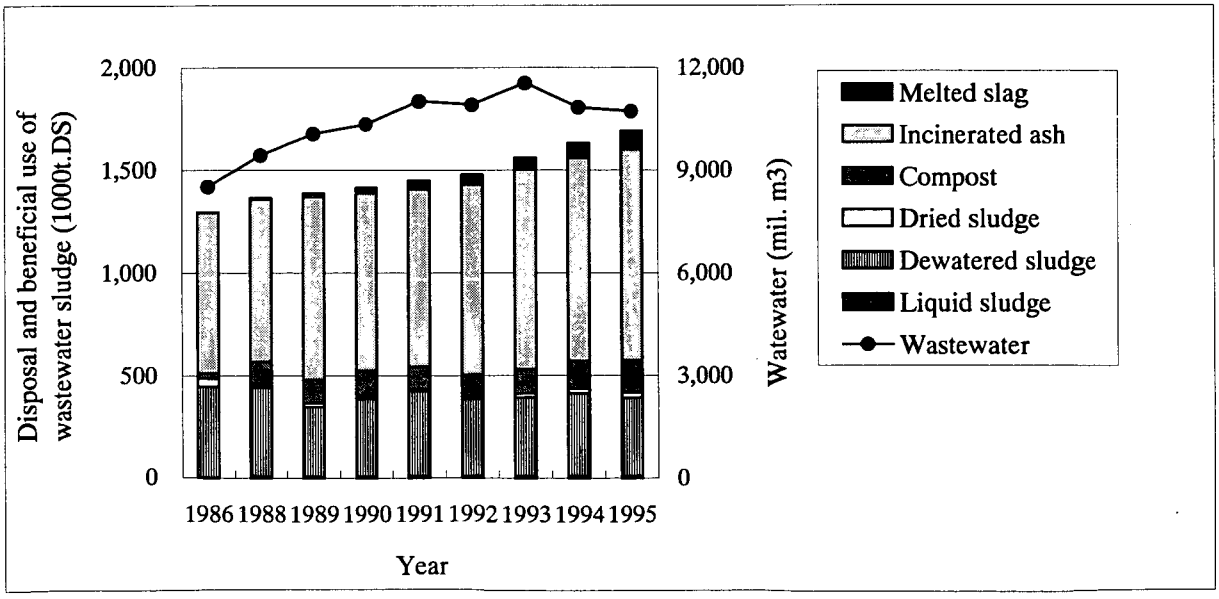


Figure 1 Annual trend of wastewater and generated sludge

Table 1 indicates the generated sludge in FY 1995. Ultimately 61% of the generated sludge was incinerated, 13% was beneficially used for agriculture and landscaping and 17% was utilized as construction material out of 1.69 million. Especially 6% was utilized as a raw material of blocks and 4 % was used as a raw material for Portland cement.

Table 1 Disposal and beneficial use of wastewater sludge in Japan (FY 1995)

(Unit: 1,000ton.DS)

Final stabilized	Form final destination of stabilized wasewater sludge					Total (%)
	Landfill	Agricultural and landscaping	Construction material	Ocean dumping	Others	
Liquid sludge	0	0	0	9	0	9 0.6%
Dewatered sludge	312	51	3	10	8	384 22.7%
Compost	14	142	0	0	0	156 9.2%
Dried sludge	9	14	0	0	1	24 1.4%
Incenerated ash	776	19	226	0	6	1,028 60.8%
Melted slag	23	0	53	0	13	90 5.3%
Tatal (%)	1,136 67.2%	226 13.4%	282 16.7%	20 1.2%	28 1.6%	1,691

CONTENT DATA OF CONSTRUCTION MATERIAL MADE OF SEWAGE SLUDGE

Table 2 shows the six kinds of sewage sludge and the five kinds of blocks which were collected as samples. Each block included sewage sludge as part or whole of the raw material. Re-product "A" includes 25% of incinerated ash "a" and melted slag "e" respectively. Cement consolidation is applied for re-product "A", "D" and "F", and sintering is applied for re-product "B" and "C" for stabilizing.

Table 2 Samples for leaching test

Raw materials			Re-products		
	sludge	furnace type		kind of block	treatment method
a	ash	fluidized bed	A	interlocking block	cementalization
b	ash	fluidized bed	B	permeable block	sintering
c	ash	fluidized bed	C	burned brick	sintering
d	ash	fluidized bed	D	interlocking block	cementalization
e	slag	spiral-flow	A	interlocking block	cementalization
f	slag	surface melt	F	interlocking block	cementalization

* A: 25% of "a" and "e" and 50% other materials
B: 50% of "b" and 50% other materials
C: 100% of "c"
D: 9% of "d" and other materials
F: 23% of "f" and other materials

Table 3 indicates the major metal contents as oxides of incinerated ash and melted slag. The five kinds of oxide were as follows: SiO_2 26 - 42%, P_2O_5 12 - 27%, Fe_2O_3 5 - 25%, Al_2O_3 11 - 21% and CaO 8 - 14%. The sum of the five data was 89 - 94%. These metal content in sewage sludge varied by sewer system, wastewater and sludge treatment method.

Table 3 Content data of sewage sludge

wt%	a	b	c	d	e	f
Al_2O_3	15.6	14.8	15.3	11.1	17.9	20.9
CaO	12.3	7.9	10.9	7.6	10.4	14.3
Fe_2O_3	5.4	11.9	5.5	24.6	8.3	9.2
K_2O	0.5	1.7	1.9	0.8	0.8	2.0
MgO	2.5	2.8	3.8	3.3	3.2	4.2
Na_2O	0.3	0.6	0.4	0.7	0.9	0.5
P_2O_5	14.0	20.7	26.7	22.1	12.1	12.0
SiO_2	41.6	34.6	31.8	25.7	40.2	37.9
Total	92.2	95.1	96.3	95.9	93.8	101.0

Table 4 indicates the major metal contents as oxides of blocks. The four kinds of oxide were as follows: SiO_2 20 - 61%, P_2O_5, 1 - 27%, CaO 6 - 24% and Fe_2O_3 4 - 14%. Except the data of sample "D", the sum of the four data was 71 - 84%. It was estimated that the SiO_2 data of sample "D" was not measured enough. CaO of blocks "A", "D" and "F" were increased by cement consolidation. It is considered that the heavy metal content of blocks was affected by other materials included in it. The data of block "C" was not greatly changed from the incinerated ash, because ash was the only raw material.

Table 4 Content data of construction material

wt%	A	B	C	D	F
Al_2O_3	9.7	11.1	14.3	3.9	8.2
CaO	23.7	6.5	10.9	11.9	20.5
Fe_2O_3	5.1	3.9	5.4	3.1	4.5
K_2O	0.5	1.0	1.7	0.3	0.8
MgO	2.2	0.9	4.0	1.3	1.9
Na_2O	0.5	0.4	0.5	0.1	0.2
P_2O_5	7.1	5.8	26.6	1.3	4.0
SiO_2	30.6	60.7	32.0	20.0	50.6
Total	79.4	90.3	95.2	41.9	90.7

ELUATION BEHAVIOR OF SEWAGE SLUDGE AS RAW MATERIAL

The five kinds of leaching test methods, indicated in Table 5, are conducted to sewage sludge. The Japanese Environment Agency standard (JEA) method is usually applied for waste in Japan, while in other countries, the Swiss method, US-EPA Extraction Procedure Toxicity (EPA) method and Holland Availability Test (Holland) method are used. These methods were arranged and used in this research. Especially in the case of Swiss method, carbon dioxide gas is usually continuously injected, but solvent is initially saturated by carbon dioxide gas for Swiss method ③.

Table 5 Leaching test method

	JEA method ①	US-EPA method ②	Swiss method (initial saturated) ③	Swiss method (continuous injection) ④	Holland availability test method ⑤
Sample preparation	<φ5 mm	<φ9.5 mm or ≧3.1 cm2/g	original structure	original structure	<φ125 μm
Elution agent (initial pH)	de-ionized water (pH=5.8 - 6.3)	de-ionized water adding 0.5 N acetic acid <4 mg/l (pH=5.8 - 6.3)	de-ionized water saturated with CO_2 initially (pH=4)	de-ionized water continuous injection of CO_2 (pH=4)	de-ionized water adding 1 N nitrate acid (pH=5.8 - 6.3)
pH value	no control	pH=5	no control	pH=4 - 4.5	pH=4
Eluate: solid	10:1	20:1	10:1	10:1	100:1
Elution time	6 hrs	24 hrs	24 hrs	24 hrs	6 hrs
Filtration	φ1 μm	φ0.45 μm	φ0.45 μm	φ0.45 μm	φ0.45 μm
Movement	horizontal shake 200 rpm	stirrer 200 rpm	stirrer 200 rpm	stirrer 200 rpm	stirrer 200 rpm

Regarding the major metal release from incinerated ash, the relationships between the content and concentration in leachate are showed in Fig. 2. The concentration in leachate is calculated as units of mg/kg, heavy metal release per sample, to compare with the content. Ca and P, which were relatively high in both data, showed a larger concentration by the Holland method than by other leaching test methods. Al, which was large in the content data but small in concentration, was detected only by the Holland method. These major metals showed a larger concentration in leachate with increase of content data by the Holland method. Na, which was small in the content data but large in concentration, showed a large concentration in leachate with increase of content data by all the leaching test methods.

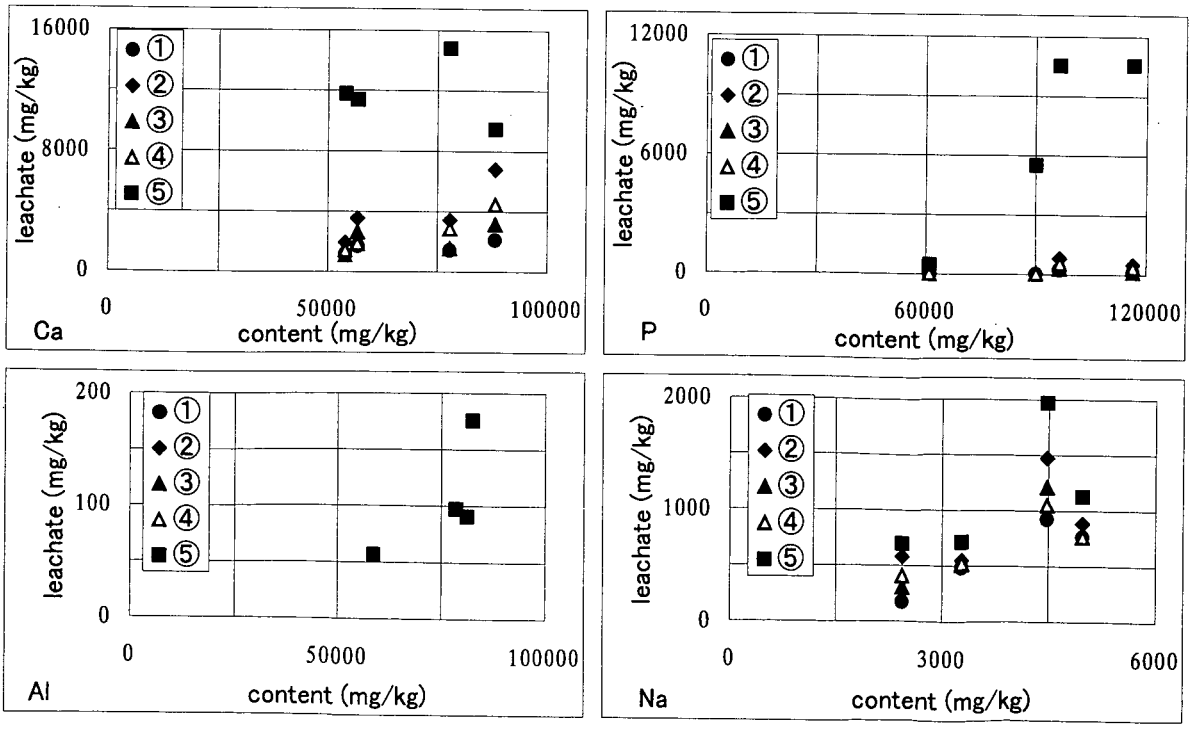


Figure 2 Relationship between the content and concentration in leachate (incinerated ash)

Regarding the trace metal release, Pb, Hg and Cr(VI) were not detected from incinerated ash. The concentration of Cd was high by the Holland method but low by the other methods. On the other hand, the concentrations of As and Se were relatively high by all the leaching test methods. The relationships between the final pH and the concentration in leachate are shown in Fig. 3. The lower the pH value of leachate, the higher the concentration of trace metals observed in leachate. Regarding As, the relation between the final pH and the ratio of concentration to content (L / C) in leachate is shown in Table 6. The data of the Holland method gave the highest value, followed by the EPA method, Swiss method ④, Swiss method ③ and JEA method in that order. Especially, 19.7 - 46.9% of As was extracted into leachate by the Holland method. If the L/C by the Holland method is 1.00, those of other methods were 0.20 - 0.43. The relationships between the leaching test methods are indicated in Fig. 4. The JEA method was found to have a close relationship to the Swiss method ③. The Swiss method ③ was considered one of the standardized leaching test methods, when the Japanese environmental standard for soil was applied.

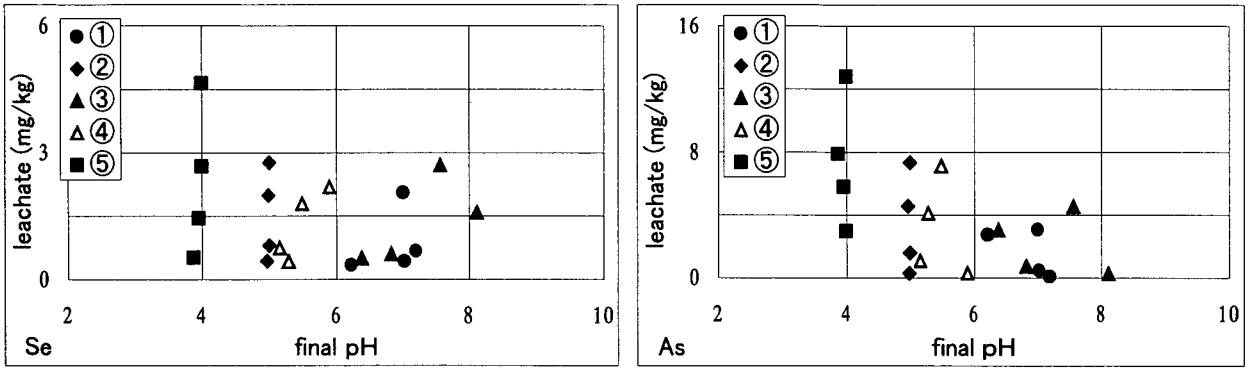


Figure 3 Relationship between the final pH and the concentration in leachate (incinerated ash)

Table 6 L/C of As comparison by leaching test methods

Leaching test methods	L/C of raw materials (%)				L/C (%)	
	a	b	c	d	ave.	<variation>
JEA	0.7	1.7	11.3	9.7	5.9	< 0.20 >
EPA	2.3	5.4	26.9	16.0	12.7	< 0.43 >
Swiss (initial)	2.2	2.6	16.7	10.8	8.1	< 0.27 >
Swiss (contimous)	2.5	3.7	26.1	14.4	11.7	< 0.40 >
Holland	23.4	19.7	46.9	27.7	29.4	< 1.00 >

ELUATION BEHAVIOR OF CONSTRUCTION MATERUIAL

Concerning the re-products, the Swiss method ④ and Holland method were used for the leaching test. Among the leaching test methods which controlled the pH of leachate, trace metal release from sewage sludge is largest by the Holland method. The data of the Swiss method ④ was larger than that of the JEA method among the pH no-controlled method.

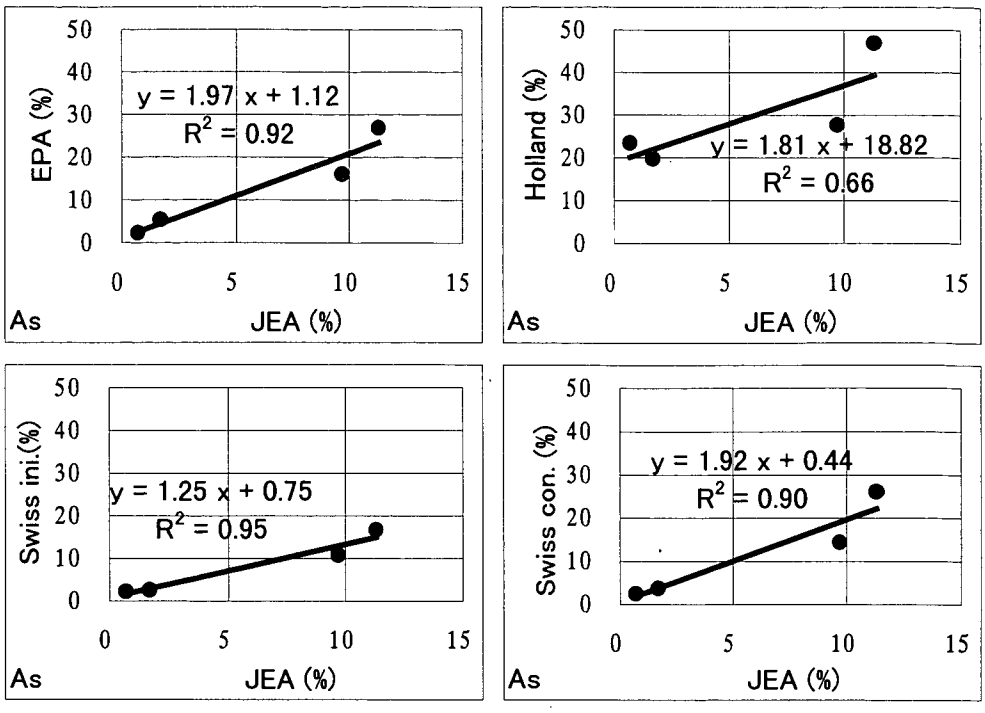


Figure 4 Relationship of L/C between the leaching test methods

Regarding the major metal release from re-products, the relationships between the content and concentration in leachate are shown in Fig. 5. Ca, P and Al, which were relatively high in the content data, showed a larger concentration by the Holland method than by the Swiss method. These major metals did not have a clear tendency like sewage sludge. Na, which was small in the content data but large in concentration, did not have a clear tendency either.

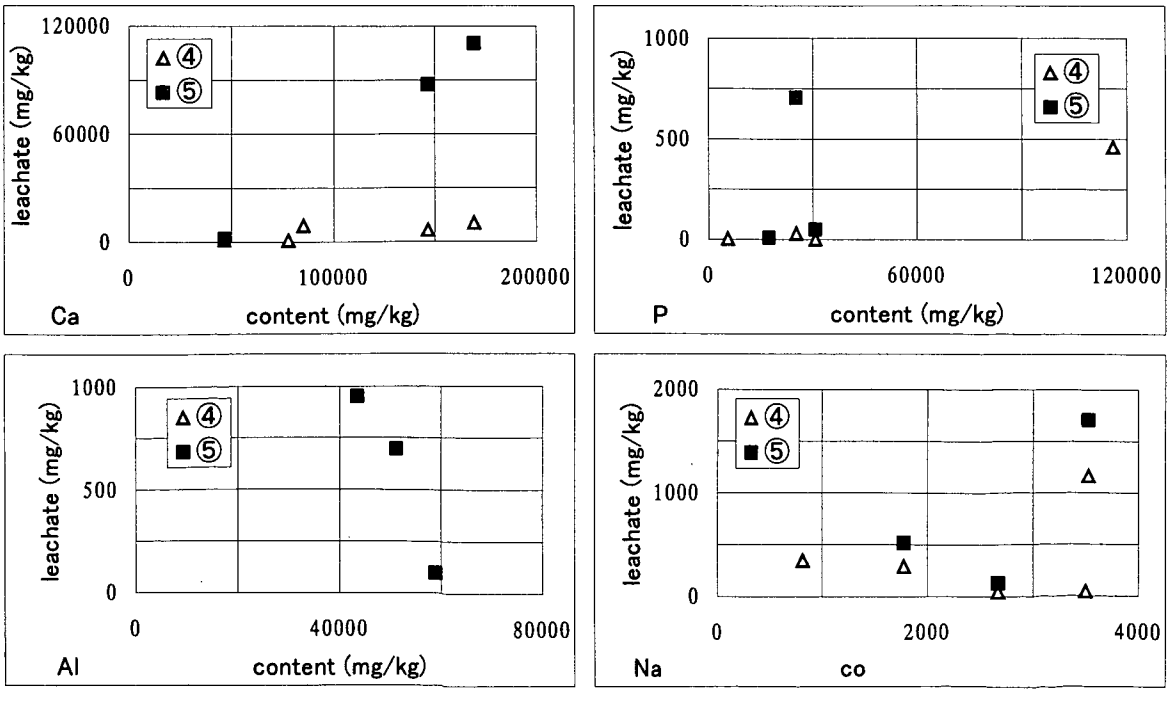
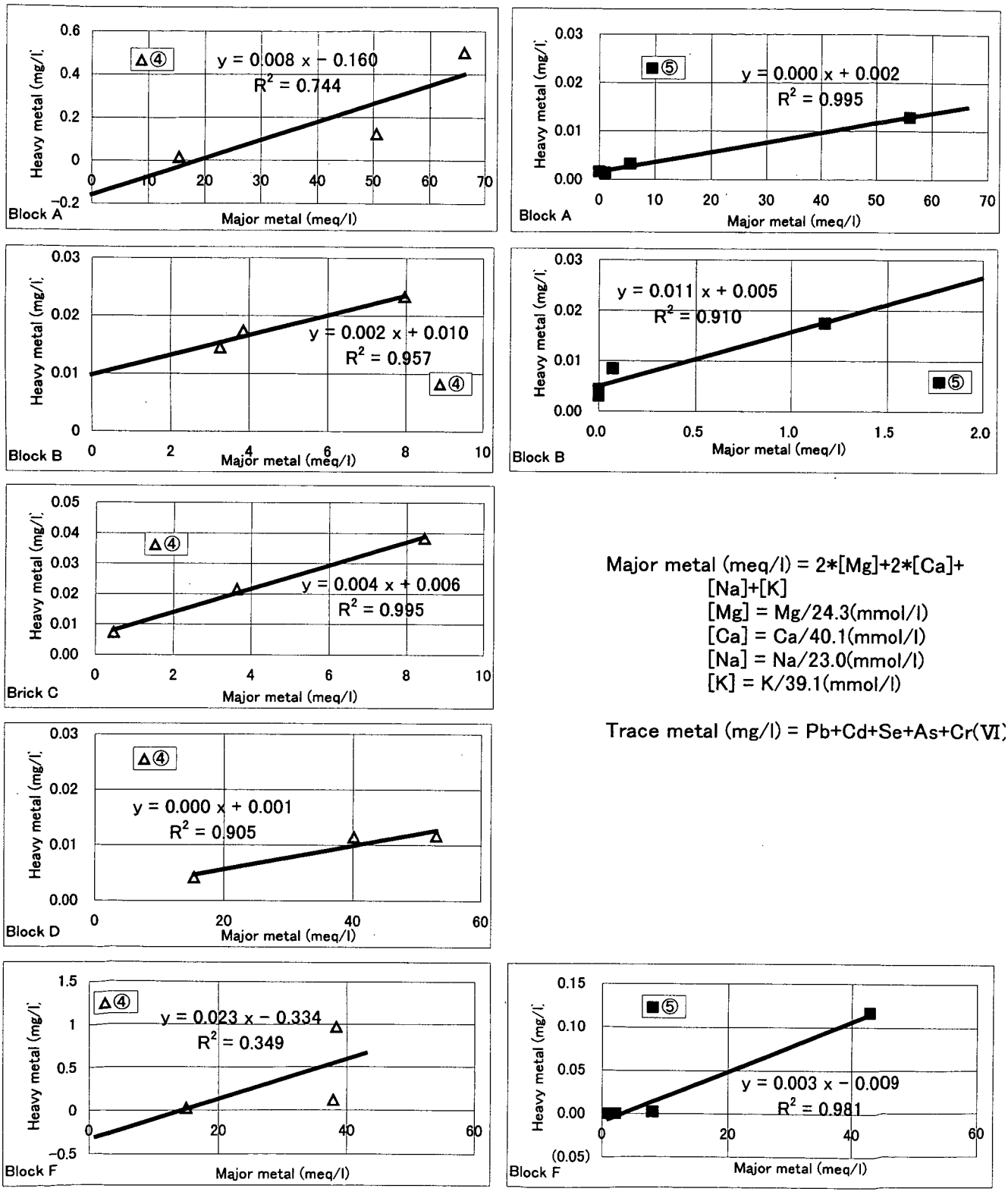


Figure 5 Relationship between the content and concentration in leachate (re-products)

Regarding the trace metal release, a close relationship was observed with the major metal release about the incinerated ash (Watanabe, 1996). Figure 6 shows a similar tendency of construction material made of sewage sludge. So the major metal release from construction material was considered as an index of the trace metal release.



Major metal (meq/l) = 2*[Mg]+2*[Ca]+[Na]+[K]
[Mg] = Mg/24.3(mmol/l)
[Ca] = Ca/40.1(mmol/l)
[Na] = Na/23.0(mmol/l)
[K] = K/39.1(mmol/l)

Trace metal (mg/l) = Pb+Cd+Se+As+Cr(VI)

Figure 6 Relationship of major metal and heavy metal concentration in leachate

STANDARDIZED LEACHING TEST METHOD

Four kinds of blocks, A, B, C and F, were used as samples. Crushed samples, which diameter was 20-50 mm, were prepared to investigate the characteristics of leaching test method. About the results the major metal release from the crushed samples was discussed, because the trace metal release was very low and it has a close relationship with the major metal release.

Regarding the crushed samples of blocks, the concentrations of Mg, Ca, Na and K were relatively high among the major metals. L/C by each method is indicated in Table 7. And Figure 7 shows the characteristics of leaching test when the L/C by Swiss method ③ is 1.00. Except the results of Mg, the JEA method was found to have a close relationship to the Swiss method ③. Though the results of Mg and Ca were different, EPA method, Swiss method ④ and Holland method were severer than the others. Generally speaking the smaller the pH value, the bigger the heavy metal concentration in leachate observed. It was considered that the results were affected mainly by pH value.

Table 7 L/C comparison by leaching test methods

Leaching test methods	L/C (%)				Range of final pH
	Mg	Ca	Na	K	
JEA	0.00	0.56	8.36	4.73	6.85 - 12.11
EPA	1.91	7.13	11.18	5.37	4.24 - 5.07
Swiss(initial)	0.09	0.48	8.24	5.36	7.77 - 11.92
Swiss(continuous)	0.71	2.35	9.32	3.59	4.95 - 6.23
Holland	0.00	1.84	2.37	1.79	3.93 - 3.99

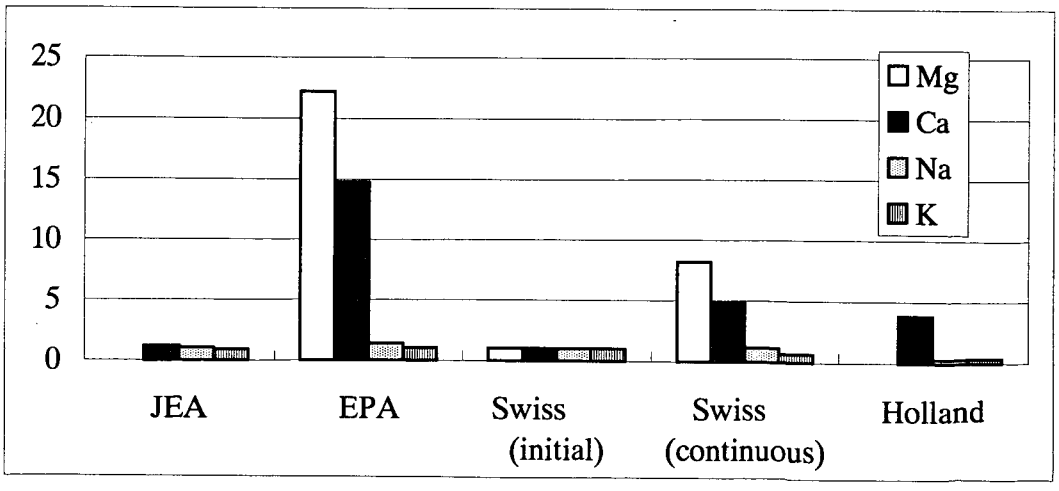


Figure 7 Characteristics of leaching test method

There are two types of leaching tests for solid waste. One type is a worst-case test to estimate the leaching availability, the other type is a standardized test to estimate the heavy metal release into ground water. EPA method, Swiss method ④ and Holland method are a worst-case test rather than a

standardized test. During the leaching test, pH value is controlled by acid or CO_2 gas and kept acid side (pH<7, Table 7). On the other hand, the pH value changes to alkaline during the leaching test by JEA method and Swiss method ③ according to the alkalinity of samples.

Swiss method ③ was investigated as one of the standardized method, considering the effect of sample diameter. Each sample was crushed and the diameter was controlled to be less than 2 mm, 2-20 mm and 20-50 mm, respectively. The L/C by Swiss method③ is indicated in Table 8 with regard to sample diameter. And Figure 8 shows the effects of sample diameter when the L/C of 20–50 mm is 1.00. Crushed sample of diameter less than 2 mm indicates 1.4-3.6 and that of 2-20 mm indicates 0.8-1.5. It was observed that the effect of sample diameter was rather large. As blocks are usually utilized in original shape, small particles are not appropriate to samples. So the medium size should be utilized as samples for leaching tests.

Table 8 L/C comparison of sample diameter

sample diameter (mm)	L/C (%)			
	Mg	Ca	Na	K
<2	0.17	1.75	18.08	7.56
2<20	0.08	0.39	12.39	4.64
20<50	0.09	0.48	8.24	5.36

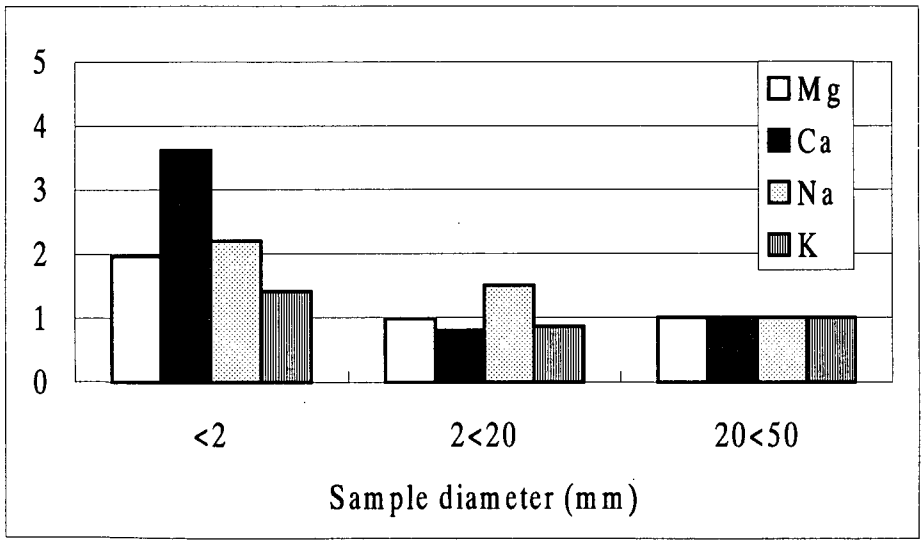


Figure 8 Comparison of sample diameter

ENVIRONMENTAL COMPATIBILITY

In Japan, about 17% of sewage sludge is utilized for construction material as a part or all of the raw material. For example besides the blocks, ash conditioned by lime for dewatering is reused as soil stabilizer, and slag is reused as a subbase course material. In these cases, the diameter of recycling

material are considered to be usually small particles like soil. If the same standardized test was applied to these samples, it is estimated that the condition become severer. The regulation for recycling material should not be severer than usual material. It will become a problem which method, standardized test or JEA method, should be applied to small particles.

Usually the leaching test is applied to waste solids, before the waste is utilized as material of landfill or landscape. There is one opinion that a severer test, like Holland method, is suitable for considering the aging effect about the heavy metal release from the waste. For the environmental compatibility of recycling material, it will become important how the results of worst-case test is considered.

SUMMARY

1. Regarding the trace metal release from the incinerated ash, the JEA method was found to have a close relationship to the modified Swiss method. The method was considered one of the standardized leaching test methods, when the Japanese environmental standard for soil was applied.

2. Regarding the trace metal release from the construction material made of sewage sludge, a close relationship was observed with the major metal release. So the major metal release from construction material was considered as an index of the trace metal release.

3. The major metal release from construction material was investigated by modified Swiss method. Regarding the crushed samples of blocks, the JEA method was found to have a close relationship to the modified Swiss method. The method was considered one of the standardized leaching test methods for construction material made of sewage sludge, when the Japanese environmental standard for soil was applied.

4. The modified Swiss method was investigated as one of the standardized method, considering the effect of sample diameter. And it was observed that the effect of sample diameter was rather large. As blocks are usually utilized in original shape, small particles are not appropriate to samples. So the medium size should be utilized as samples for leaching tests.

ACKNOWLEDGMENT

This research was conducted as a Joint-Research project between Japan and Germany. Japanese side researched about the evaluation method, because many municipalities have already developed the construction material made of sewage sludge and the standardized test method was required for a recycling material. German side also conducted leaching test for the evaluation of their samples. Both data will be utilized and the final results will be presented in 1998.

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Impact of sewage sludge ashes on brick manufacturing Technical aspects and environmental compatibility

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Abstract

Several aspects of using ashes from sewage sludge incineration in the brick and tile industry have been examined. After discussing the issue of ash production in Germany, the impact of different wastewater treatment methods is described; for instance, the use of precipitation agents containing iron will considerably influence the ash quality. Depending on their respective chemical composition, different ashes have different effects on the ceramic qualities of the bricks made of material blended with ashes. These effects are shown in regard to the major ceramic parameters. Similarly, the quality of the ashes also influences the elution behaviour and the mineral fixation of heavy metals.

Kurzfassung

Der Einsatz von Aschen aus der Klärschlammverbrennung in der Ziegelindustrie wird in mehreren Teilbereichen betrachtet. Nach Erläuterung des Ascheanfalls in Deutschland wird auf den Einfluß der Verfahren zur Abwasserreinigung hingewiesen. So kann der Einsatz von eisenhaltigen Fällungsmitteln die Aschequalität erheblich beeinflussen. Verschiedene Aschen wirken sich je nach chemischer Zusammensetzung unterschiedlich auf die keramischen Eigenschaften der mit Asche versetzten Ziegel aus. Dies wird anhand der wichtigsten keramischen Parameter aufgezeigt. Ebenso wird durch die Aschezusammensetzung das Auslaugverhalten und die inerte Einbindung von Schwermetallen beeinflußt.

1 Introduction

The introduction of the latest *Technical Instruction for Disposal of Municipal Solid Waste in* May 1993, which restricts the maximum ratio of organic substances in disposable waste to 5 wt.-%, will necessitate an increase in incineration of municipal wastes. As in Germany sewage sludge is generally classified as waste, this increase of incineration capacity is also expected in regard to sewage sludge incineration. All incinerator ashes are liable to the utilization request according to § 7 of the *Federal Law on Emission* and to the *Closed Substance Cycle and Waste Management Act (Oct. 1996)*. This fact has in recent years led to much activity in the building industry in regard to the utilization of ashes from power plants and slags from municipal solid waste (MSW) incineration plants. However, as ashes from power plants are authentic - that is their origins can be retraced - this does not apply to ashes from sewage sludge incineration. Depending on the infrastructure of the respective residential sewage area, on place, time, season, time of day, etc., the composition of what goes into the waste-water-treatment plants varies, and so, accordingly, does the composition of the sludge. This ever-changing composition makes sewage sludge a material with a low acceptance rate, in particular in regard to agricultural utilization; the same problem is likely to occur with ashes from sewage sludge incineration.

As part of a scientific co-operation project between the Japanese Ministry of Construction (MOC) and the German Ministry for Education, Research, Science and Technology (BMBF), the Institute of Sanitary Engineering and Solid Waste Management (ISAH) and the Public Works Research Institute (PWRI) are running a joint research project on the utilization of sewage-sludge ashes as construction material, focusing on how such ashes can be used in the production of bricks made of sewage-sludge ashes and clay.

7th Japanese-German Workshop on Waste Water and Sludge Treatment, Kyoto, December 10-12, 1997

Within the German part of the project, the following aspects have been examined:

- Survey of the state-of-the-art in sewage sludge incineration.
- Impact of waste water and sludge treatment on ash quality (ascertaining of an annual progressive curve showing the chemical composition of the ashes)
- Utilization of sewage-sludge ashes from fluidized bed furnaces as clay substitute - Tests in the ceramic laboratory.
- Estimation of the environmental compatibility of the bricks made with sewage-sludge ashes - Running of leaching tests; examination of the mineralogical fixation of heavy metals.

2 Situation of sewage sludge incineration in Germany

In Germany, there are currently 12 municipal and 6 industrial plants for mono-incineration of sewage sludge; 5 plants are in the planning or construction stage. The municipal plants incinerate 250000 t dried solids (DS) per year, thereby producing 110000 t of ashes; the amount of the industrial plants is 180000 t DS per year, with 85000 t of ashes. Together with the 5 plants which are still in the planning stage, the entire amount of ashes produce in Germany will be about 300000 t per year. The average specific ash amount at the moment is 0.45 t for every ton of incinerated sludge, which makes for an ignition loss of 55%. Two plants sport a multiple hearth furnace or multiple fluidized hearth furnace, respectively; the other plants use fluidized bed furnaces.

The results of an inquiry on the situation of mono-incineration of sewage sludge - as part of a joint venture between ISAH and the Federal Environmental Agency (UBA), are published in [1]. Four sewage sludge incineration plants were chosen as source of ashes for brick manufacturing.

3 Influence of waste water and sludge treatment on ash quality

Table 1: Average chemical composition and standard deviations of the examined ashes (over a period of one year, 52 samples) and of one of the brick clays

	"Fe-ashes"				"Ca-ashes"				
	Ash A		**Ash B**		**Ash C**		**Ash D**		**Clay IV**
	Av. [wt.-%]	St. dev. [%]	Av. [wt.-%]	St. dev. [%]	Av. [wt.-%]	St. dev. [%]	Av. [wt.-%]	St. dev. [%]	[wt.-%]
SiO_2	36.2	20.9	36.5	13.5	30.3	11.3	35.5	13.4	64.8
Al_2O_3	14.2	46.4	12.3	33.7	16.2	6.7	16.9	14.2	20.7
Fe_2O_3	**17.9**	35.1	**15.1**	33.5	2.8	10.3	5.6	46.7	6.7
CaO	10.0	15.7	13.2	9.2	***20.8***	7.0	***16.9***	14.1	0.5
P_2O_5	*11.5*	21.4	*13.2*	11.0	*18.4*	13.3	*13.8*	18.9	*0.2*

In order to evaluate the suitability of sewage-sludge ashes as raw material for brick production, the influence of waste water and sludge treatment on the ash quality has been examined, ascertaining changes in the chemical composition in dependence on time. In 4 sludge incineration plants, long-term tests of the ash output were carried out, in order to gain annual progressive curves from weekly composite samples. The average ash compositions measured over the period of one year (Oct. 1995 to Sept. 1996) are shown in Table 1, concentrating on five main components.

The differences in chemical composition are apparent. The main component of the clays - about two thirds - is silicium oxide (SiO_2), which in the ashes makes up for one third. The Al_2O_3-amounts are similar, whereas the Fe_2O_3-amounts are different with the different ashes; thus, from an amount of 15-20% onwards of the respective component, one differentiates between *iron containing ashes* (Fe-ashes) and *calcium containing ashes* (Ca-ashes). One crucial difference between both clays and ashes is the amount of phosphorus pentoxides (P_2O_5). For ashes, this amount can range from 10-20 wt.-%, whereas clay normally does not contain any phosphorus. Table 1 also indicates high standard deviatons, especially for the Fe- and the Al-contents. This effect depends on the use of precipitation agents - Fe- and Al-salts - to eliminate the dissolved phosphorus during waste-water treatment.

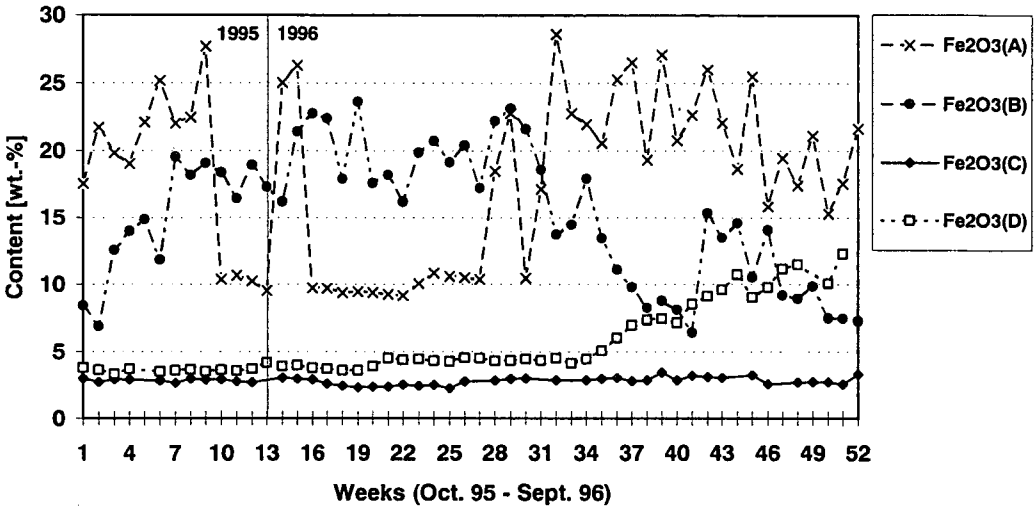


Fig. 1: Progressive curves of the Fe_2O_3-contents of 4 different kinds of sewage-sludge ashes over one year (Oct. 1995 - Sept. 1996)

Figure 1 shows the iron oxide contents of the 4 examined ashes (A to D) in the course of one year. It becomes apparent that ash A shows strong short-term variations, which are likely to be due to the operation of the waste-water-treatment plant, for instance to the impact of the chemical precipitation of dissolved phosphorus. Ash B also shows strong but probably seasonal variations. Ash C does not vary. Waste-water treatment plant D changed the precipitation agent in June 96 from a Al-salt to a Fe-salt.
These variations are important for the evaluation of ashes as raw material for brick production; for instance, variations of the iron oxide contents between 10-20 wt.-% considerably influence the colour of the bricks but also the compressive strength (cf. Chapter 4).

Not only the precipitation agent used during waste-water treatment, but also the kind of sewerage system - combined or separate- has a big impact on ash quality. The cities A, B and D use mainly the combined system. Therefore, a strong dependency between the SiO_2- and the P_2O_5-content occurs, which is described in Figure 2. The higher the silicate content in the ashes is, the lower is the content of phosphorus. The coefficients of correlation "r" between the SiO_2- and the P_2O_5-content of the 52 weekly composite samples are for the ashes A, B and D higher than 0.90.

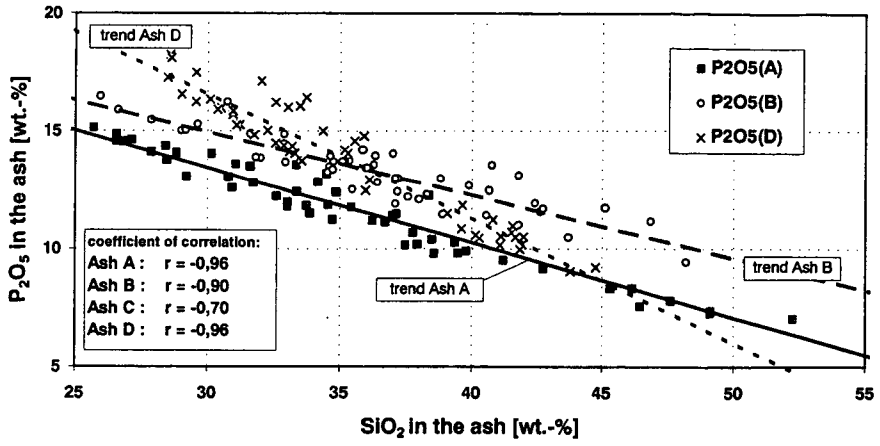


Fig. 2: Relation between the SiO_2- and the P_2O_5-content in sewage sludge ashes from cities with combined sewerage system

4 Utilization of sewage-sludge ashes as construction material - Bricks made of clay and ashes

The general technical feasibility of using sludge ash as additive or opening agent for clay has been shown in tests from Japan [2], USA ([3], [4], [5]), Great Britain [6], Germany [7] and other countries. However, more detailed information about the influence of sewage-sludge ashes on the shaping, drying and firing behaviour, nor on the properties of the finished products are necessary.

In regard to **shaping properties**, none of the four examined sewage-sludge ashes had any negative effect, given amounts of 20 wt.-% of ashes added. The addition of ashes, however, cannot be increased at will, because from a certain amount onwards the ashes will impair the fundamental workability of the clay-ash-mixture. The addition of sewage-sludge ashes led to a considerable increase of the necessary amount of gauging water or mixing water.

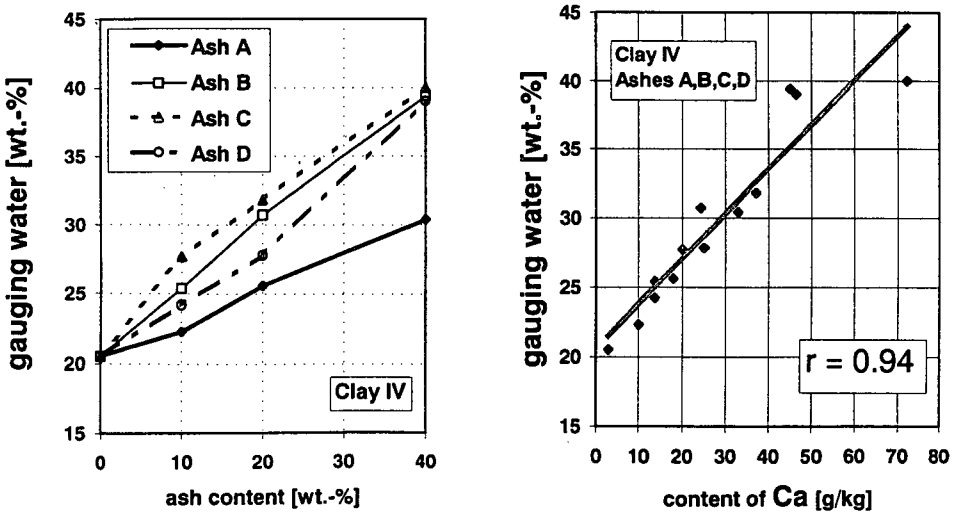


Fig. 3a/b: Influence of the ash contents and/or the Ca-content of the raw mixture on the demand of gauging water (mixing water) of one clinker clay with ash addition (Clay IV, Ash A)

Figure 3a indicates the increase of gauging water with higher ash contents using Clay IV. Generally, the high porosity of the ashes is responsible for the higher demand of gauging water. However, differences between Fe-ashes (e.g. ash A) and Ca-ashes (e.g. Ash C) are also obvious. Figure 3b shows that the higher the Ca-content of the raw mixture of the ash bricks is, the higher is the demand of gauging water.

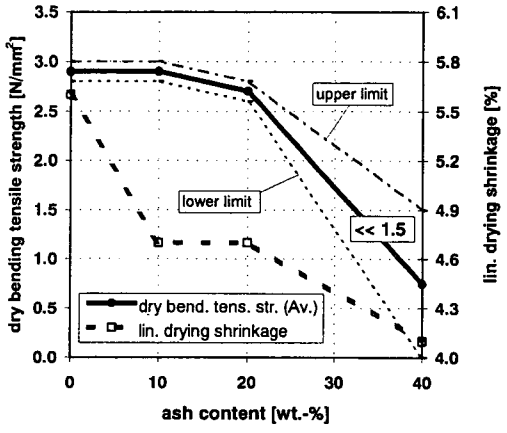


Fig. 4:
Influence of the ash content on the drying behaviour of one clinker clay with ash addition (Clay IV, Ash A)

Figure 4 describes the **drying behaviour** of raw brick material with clinker properties at increasing ash contents with the parameter dry bending tensile strength and linear drying shrinkage. Despite the considerable increase of gauging water necessary (Figure 2a), there was no increase of the linear drying shrinkage. In fact, the drying shrinkage decreases. This effect, which is known as opening, is connected with the decrease of the dry bending tensile strength, which at the ash content of 40 wt.-% is far below the 1.5 N/mm^2 barrier.

Furthermore, the ashes cause **porosity**, which is characterised in a decrease of the **bulk density**. In Figure 5, this aeration of the body is indicated for the clay bodies burnt at 1000 °C. The feasible reasons for this phenomenon are on the one hand the intrinsic porosity of the ash, which leads to a low apparent density; on the other hand, the Ca-content of the ash brick, which has a strong impact on the bulk density, as it is shown in Figure 5b. The coefficient of correlation amounts to r = 0.97. The higher the Ca-content of a sewage-sludge ash is, the stronger is the pore-forming behaviour of the ash.

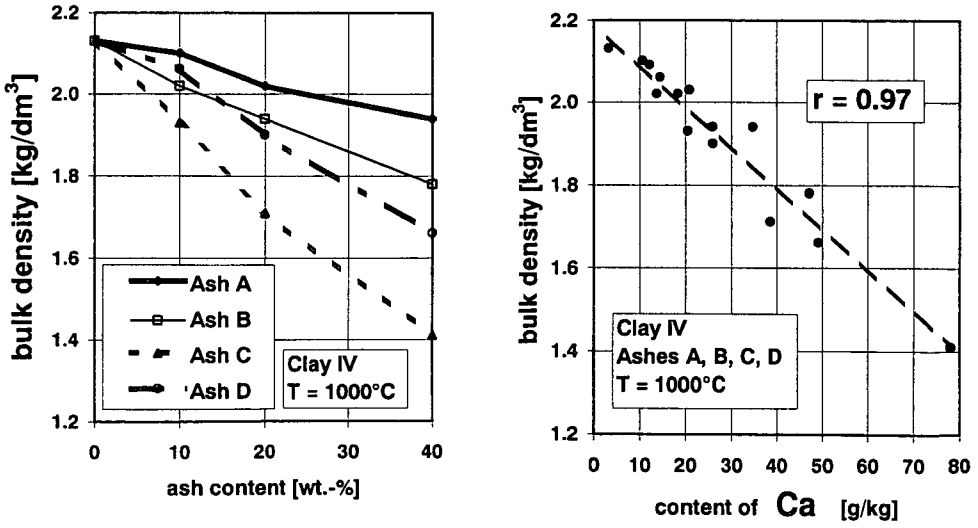


Fig. 5a/b: Influence of the ash content and/or the Ca-content of the raw mixture on the bulk density of the ceramic body of one clinker clay with ash addition (Clay IV, Ashes A, B, C, D)

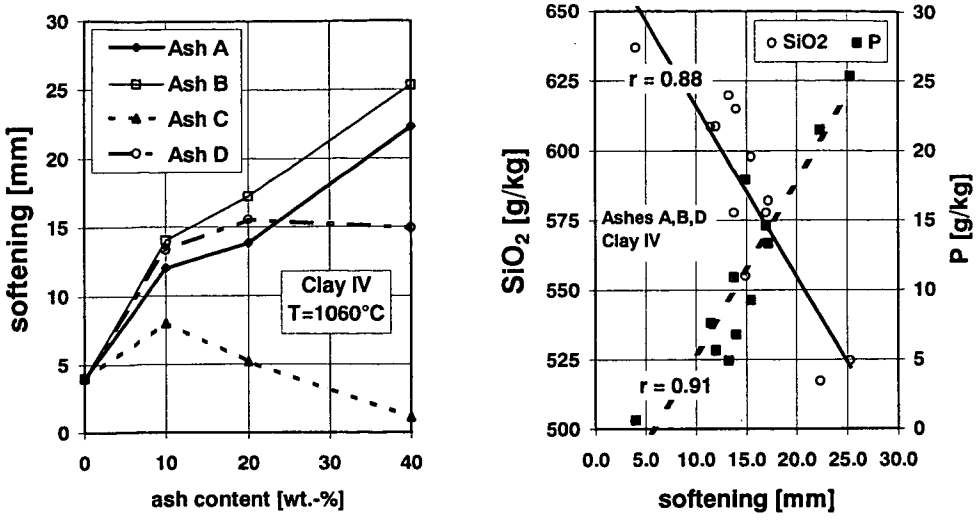
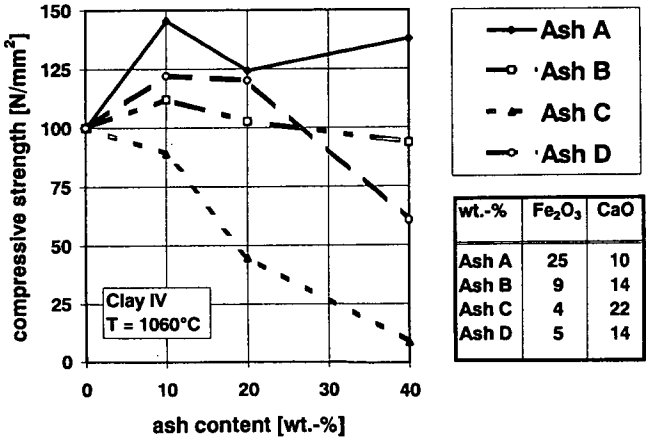


Fig. 6a/b: Influence of the ash content and/or the SiO_2- and P-content of the raw mixture on the softening of the ceramic body of one clinker clay with ash addition (Clay IV, Ashes A, B, [C], D)

With an increase of the firing temperature, the impact of the ashes as fluxing agents prevails. Thus, in Figure 6a the bodies burnt at 1060°C illustrate that the softening increases with higher ash contents of the ashes A, B and D. The softening, developed at the Brick and Tile Research Institute in Essen, correlates strongly with the firing shrinkage. Ash C shows a different behaviour, probably relating to the high Ca-content of Ash C. Considering the ashes A, B and D, which are influenced by a combined sewerage system, the SiO_2 and the P-content have a strong impact on the softening of the ceramic body (Figure 6b). The lower the content of silicate and the higher the content of phosphorus is, the higher is the melting temperature of sewage-sludge ashes, and the higher is the softening of the ceramic body of ash bricks. Due to the high phosphorus content of sewage-sludge ashes, they work as fluxing agent in brick manufacturing process.



wt.-%	Fe_2O_3	CaO
Ash A	25	10
Ash B	9	14
Ash C	4	22
Ash D	5	14

Fig. 7:
Impact of ash contents on the compressive strength [N/mm²] (Clay IV; Ash A, B, C, D; 1060°C)

Figure 7 shows the inter-dependence between the compressive strength and the ash content for different ashes and the Clay IV. Regardless of the ash addition, the compressive strength of the body increases with increasing firing temperatures. Therefore, Figure 6 is made for 1060°C, the highest firing temperature of Clay IV. At this temperature the ceramic body is mostly sintered. Additionally the Fe_2O_3- and the CaO-contents of the 4 ashes are shown. And it is obvious that ashes with a high Fe_2O_3- (> 15 wt.-%) and a low CaO-content (< 15 wt.-%) - e.g. Ash A - increase the compressive strength. Reverse, ashes with a low Fe_2O_3- (< 10 wt.-%) and

a high CaO-content (> 15 wt.-%) - e.g. Ash C - decrease the compressive strength. Additionally to phosphorus also the Fe_2O_3 seem to be a fluxing agent. Hematite develops during the sintering process. That is why Fe_2O_3 makes the ceramic body harder. Ca works as pore-forming agent and makes the ceramic body softer. Therefore, Ash C strongly reduces the compressive strength.

However, the eventual decision on the marketability of bricks made with sewage-sludge ashes, will depend on their environmental compatibility.

5 Environmental compatibility of bricks with addition of sewage-sludge ashes

Basing on the results of elution tests which are used for municipal waste, the elution behaviour of the ash-containing bricks will be examined. Elution tests (also called leaching tests) of construction materials containing mineral waste are problematic due to the fact that there are contradictory demands on the purpose of such tests: On the one hand, these tests are to show the natural environmental influences including all kinds of long-term effects, on the other hand these tests must be simple and reproducible by everybody.

5.1 Methods of describing the elution behaviour

Table 2 gives a survey over the elution methods, which are used to evaluate the environmental compatibility. The German standard leaching test (DEV-S4) is the only one which is standardized in Germany. The "pH-stat-Test" is developed by [8] and is accepted as a worst-case elution test. It is not regulated by official standards.

In Table 2, the main influencing parameters on the leaching behaviour of solid matter are mentioned. Variegating these variables, the results of e.g. heavy metal release could change considerably. Using non-regulated leaching tests, the results could not be compared with legal limits. On the other hand some parameters have to be variegated, because the leaching tests have not been developed for recycling material. In Germany recommended limits for the leaching behaviour of mineral recycling material are existing for soils (LAGA [9]) - not for bricks produced with waste material.

Table 2: Comparison of two leaching tests used for the ash bricks

Influencing parameters	elution agent	pH-value	elution time	sample preparation	eluate/solid ratio	movement
1. Germ. Standard Leaching Test (DEVS4-Test)	de-ionised water (pH = 5.7-6.5)	no pH-control (final pH = 8.8-9.9)	24 hrs, 1 elution	< 10 mm or particle-size distribution curve	10:1	overhead circulation ≈ 10 rpm
2. pH-stat-Test (modified)	de-ionised water adding nitrate acid	pH = 4	24 hrs; 1 elution	< 10 mm or particle-size distribution curve	10:1	column test (pumped water)

The advantage of the pH-stat-Test is that leaching conditions could be well reproduced. During the DEVS4-Test the pH-value changes up to 9.9 after the leaching test according to the alkalinity of the samples (here bricks made of sludge ash and clay). Having used ash bricks, the conditions *movement* and *particle size* were changed.
Movement: During the DEVS4-Test the samples were circulated overhead. In the modified pH-stat-Test the samples were filled into glass columns and de-ionised water was pumped through the column [10].

Sample Preparation: Concerning a sustainable consideration, it is necessary to leach out crushed bricks, since after having been used as bricks, the material will be crushed in future and will be utilized as stone chips again. Two kinds of crushed bricks were distinguished:

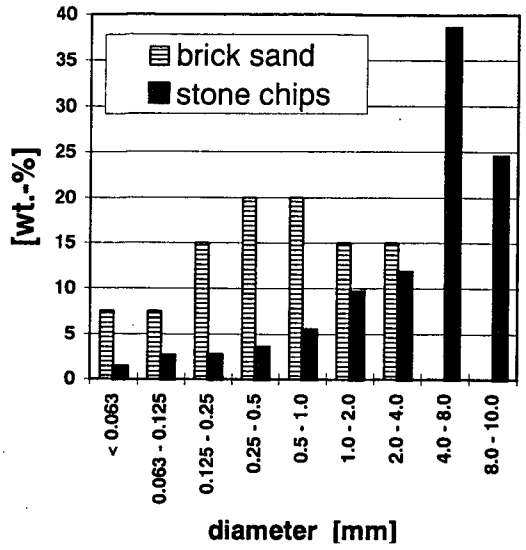


Fig. 8:
Particle-size distribution of the stone chips made of crushed ash bricks (<Ø10 mm) in comparison with the determined particle-size distribution of the brick sand

"Stone chips": The DEVS4-Test for solid waste requires a particle size < 10 mm. Therefore the brick samples were only crushed in particles < 10mm. The particle-size-distribution curve of these stone chips resulted by chance. Therefore, 60% of the particles are bigger than Ø4 mm. Average values for the different ash bricks are shown in Figure 8. The theoretical surface of the stone chips is 0.12 m^2/100 g and the standard deviation of the particle-size-distribution between bricks containing different ashes (Fe- or Ca-ashes) amounts to 15 %.

"Brick sand": This particle-size distribution was fixed before crushing the brick samples and is related to usual particle-size-distribution curves of brick powder, which is recommended for the construction of sports grounds or tennis courts in the German industrial norm (DIN) 18035. On the one hand, it would be a sustainable estimation of the environmental compatibility to use such fixed and well reproducible particle-size distributions. On the other hand, it is hard work to crush the brick samples without metal tools and to prepare the fixed particle-size distribution, which is shown in Figure 8. The theoretical surface of the brick sand is 0.62 m^2/100 g, 5.3 times larger than that of the stone chips.

5.2 Description of the elution behaviour of ceramic products with ash addition

At first the leaching behaviour of the ash bricks should be discussed for the alkaline and earth alkaline metals Na, K, Mg and Ca. These metals are main components of the ashes and their behaviour indicates the leachability of the ash bricks. Furthermore, the alkalinity of the ash bricks affect the pH-value of the eluate during the tests without pH-control (DEVS4-Test) or affect the demand of nitrate acid during the pH-stat-Test to regulate the pH-value to about 4. The results of metal release were calculated as specific elution rate - the L/C-ratio: [g X_L in the leachate / kg X_C solid-content] = [‰] or [10 g X_L/kg X_C] = [%]. The specific elution rate describes the eluted load out of the solid content of each element.

Sample preparation: Figure 9a indicates that in spite of the 5.3 times larger surface of the brick sand, the specific elution rate (L/C) for the metals Na, K, Mg and Ca is only 11% higher than that of the stone chips. For some heavy metals, the value could be around 50%. However, the smaller the particles are, the higher is the specific elution, but there is no linear interdependence between the specific elution rate (L/C) - caused by the surface of the sample - and the particle size of the stone chips (<10mm) and of the brick sand (<4mm). Therefore, it can be recommended to evaluate the environmental compatibility of the ash bricks without preparing a well-reproducible particle-size distribution.

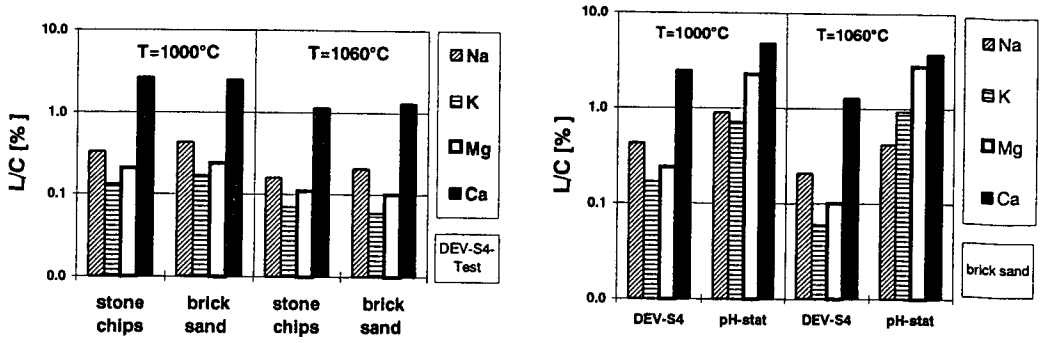


Fig. 9a/b: Leachability of Na, K, Mg and Ca from ash bricks in dependence of the sample preparation (stone chips / brick sand), the firing temperature (1000°C / 1060°C) and the leaching test (DEV-S4 / pH-stat-Test) - Average values Clay IV + 10/20 and 40 % Ash A, B, C and D.

Table 3: brick sand, Na, K, Mg, Ca	relation L/C(DEV-S4) : L/C (pH-stat-Test)
T=1000°C	**0.39**
T=1060°C	**0.21**

Leaching tests: Generally, the lower the pH-value is, the higher is the specific elution (L/C). Figure 9b compares the pH-stat-Test (pH=4) with the DEVS4-Test (pH≈9). Depending on the firing temperature, the specific elution in the alkaline medium of DEVS4-Test amounts to between 20% and 40 % of the specific elution in the acid medium of the pH-stat-Test (Table 3).

Table 4: [Na, K, Mg, Ca]	relation L/C (1060°C) : L/C (1000°C)
DEVS4-Test	
stone chips	**0.45**
brick sand	**0.50**
pH-stat-Test	
brick sand	**0.92**

Firing Temperature: Generally speaking, the higher the firing temperature, the lower is the leachability of the ash bricks. In the alkaline medium of the DEVS4-Test, the brick samples fired at 1060°C have a specific elution of 50% of the samples fired at 1000°C. However, for the strong acid medium of the pH-stat-Test the temperature of 1060°C is not high enough to prevent leaching. Therefore, the specific elution decreases only by 8% (see Figure 9).

The content of the alkaline (Na+K) and earth alkaline (Ca+Mg) metals in the ceramic body of the ash bricks affect the solubility of heavy metals or trace elements. This dependency are indicated in Figure 10. The higher the content of Na, K, Ca and Mg, the higher is the leachability of the ash bricks. As Ca is the largest main component, one can say, Ca increases the leachability of ash-bricks.

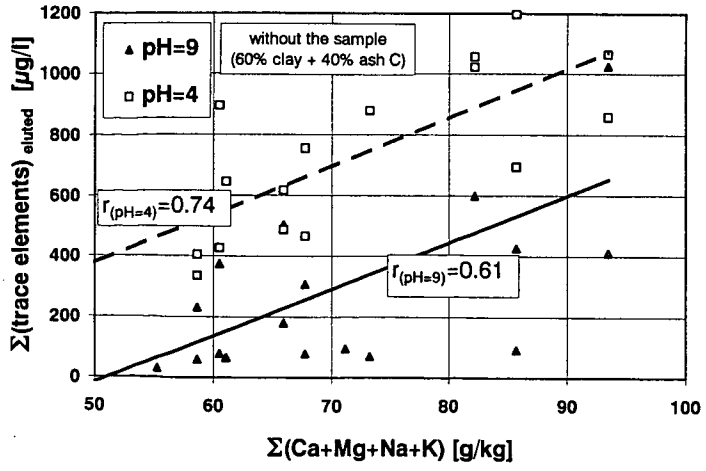


Figure 10:
Influence of the content of Σ(Ca+Mg+Na+K) of the ash bricks on the release of the trace elements Σ(V+Cr+Co+Ni+Cu+Zn+ As+Se+Cd+Pb)

[DEVS4-Test : pH ≈ 9;
pH-stat-Test : pH=4
T = 1000°C and 1060°C]

The relation of heavy metal release in both leaching tests - the pH-stat-Test as worst-case-test (pH=4) and the standardized DEVS4-Test (pH≈9) - is indicated in Figure 11.

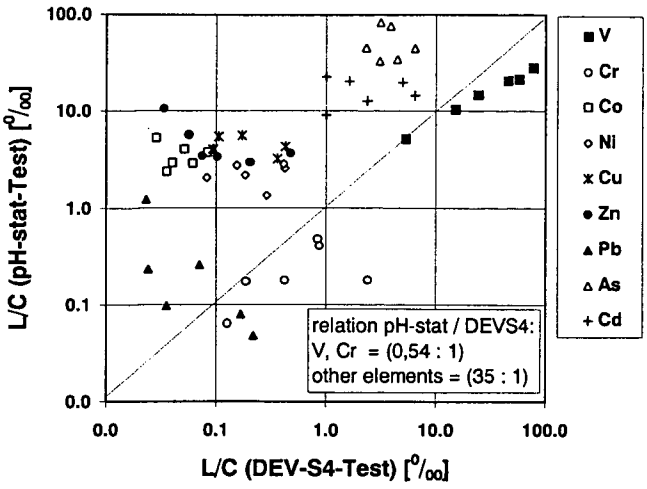


Figure 11:
Relationship of the L/C-ratio between different leaching test methods tested with bricks made of sludge ash and clay (T = 1000° and 1060°C)

Except of chromium (Cr) and vanadium (V), all trace elements have a higher solubility during pH-stat-Test. At the DEVS4-Test, only 3 % of the available load, which is determined by the pH-stat-Test, leaches out. Cr (o) and V ( ) show a higher solubility in the alkaline medium. Also arsenic (As) has a high solubility in both tests. The release of other heavy metals is very low: At pH 4 less than 1 % and at pH 9 less than 1 ‰

5.3 Environmental compatibility of bricks with sewage-sludge ash addition

No public discussion about environmental standards for re-products made with sewage sludge has been held up to now. However, comparing these ash bricks with the recommended value for the unlimited reuse of soils (Z0-values of LAGA [9]) could be reasonable. In LAGA [9] limits for the content of harmful substances in the solid and also for the leachate concentrations according to the DEVS4-Test are recommended.

Usually sewage-sludge ashes have a higher content of heavy metals than the Z0-values for the unlimited reuse. However, [11] investigated more than 1000 clays from North Germany. In many cases the content of some heavy metals (e.g. chromium) in the clays exceeds the Z0-values of [9]. Also most ash bricks will exceed these recommended values. Unlike soils, ash bricks are sintered. Therefore, in the authors opinion, the content values of the ash bricks are not comparable with soils. However, leaching concentrations are comparable. That is why only the recommended values of eluate concentrations for the unlimited reuse of soils ([9]) should be taken to evaluate the environmental compatibility. These concentrations are indicated in Table 5.

Table 5: Recommended limits for an unlimited reuse of soils (Z0-values of LAGA, 1994)

eluates of soils (unlimited reuse) - DEVS4-Test													
selected parameter	pH-value	conduc-tivity	chloride	sulphate	As	Pb	Cd	Cr (total)	Cu	Ni	Hg	Tl	Zn
unit	-	µS/cm	mg/l	mg/l	µg/l								
Z0-value	6.5 - 9	500	10	50	10	20	2	15	50	40	0.2	<1	100

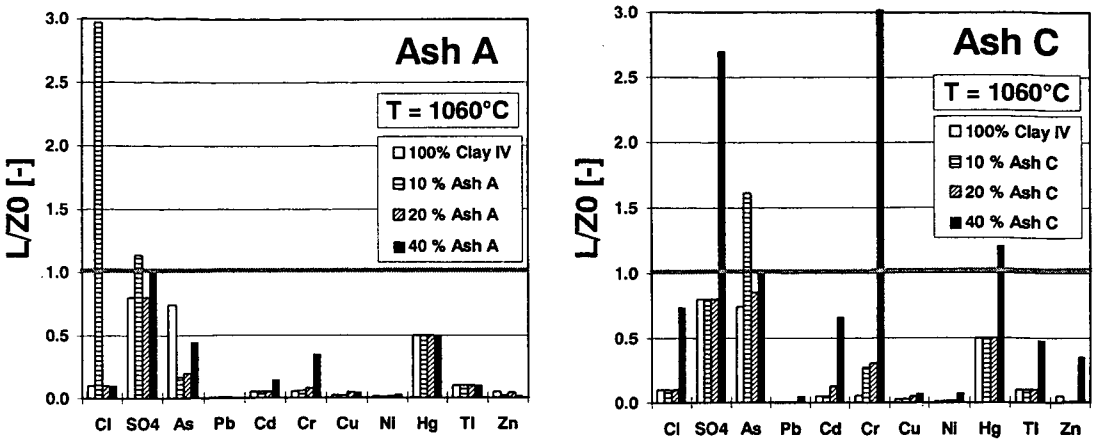


Fig. 12a/b: Leaching behaviour during DEVS4-Test of the two kinds of ash bricks (Clay IV with 10/ 20 and 40 % Ash A and C) in comparison to recommended values for the unlimited reuse of soils (Z0-values of LAGA, 1994)

In Figure 12 the leachability of four kinds of ash bricks - Clay IV with 10%, 20% and 40 % Ash A and C - is compared with national-wide recommended values of LAGA [9]. The relation L/Z0 [-] is calculated from the measured leaching concentration L [μg/l] and the Z0-value [μg/l]. If L/Z0<1, the leaching concentrations remain under the Z0-values.

Generally speaking, the higher the ash content in the brick, the higher is the leaching concentration. The efflorescencable salts chloride (Cl) and sulphate (SO_4) sometimes exceed the limits. But the detection limit for SO_4 was 40 μg/l. Therefore, L/Z0 has to be >0.8. The Cl-elution from the ash brick with addition of 10% Ash A seemed to be a runaway. To avoid a higher solubility of the efflorescencable salts, higher firing temperature can be used. Additionally [1] used chemical coating to avoid the whitening of the surface.

Most trace elements or heavy metals remain under the Z0-values. The elution from the ash brick with addition of 40% Ash C shows a stronger solubility. With regard to this effect, it has to be considered that this brick - with a compressive strength of 8.8 N/mm^2, is not a real brick. The elution of arsenic shows a noticeable leaching behaviour. At first, it is conspicuous that also bricks made of 100% clay reach 86% of the Z0-value of 10 μg/l. Using a ferriferous ash (Ash A, B) the leaching of As decreases strongly. Only the ashes containing Ca (C and D) show a higher solubility of As. Mercury usually reaches 50% of the Z0-value of 0.2 μg/l. The reason is the detection limit of 0.1 μg/l. Therefore, usually the concentration of Hg in the eluate is <0.1 μg/l.

Figure 11 confirms the result of Figure 9: The higher the Ca-content of the ash brick, the higher is the solubility of harmful elements. On the other hand, a high Fe-content in the ash seem to reduce the leachability of some elements like Arsenic (As) or Chromium (Cr). The elution load of iron thus decreases with increasing ash contents [10].

6 Estimation of exhaust gas emissions with a substance balance

Emissions of heavy metals via the exhaust gas of the brickwork could be estimated by substance balances. The heavy metal contents of the fired ceramic body must be compared with the dried body. The loss of ignition during firing of the body, which averages up to 5 %, must be considered.

Comparing the heavy metal contents of the dried and the fired ceramic body, it is obvious that both bodies have the same contents of heavy metals (see Figure 13a). Near the detection limit of 1 ppm the contents start spreading around the"1:1"-line. Sometimes the content in the fired body is higher than in the dried one, sometimes reverse (see Figure 13b). These variations are caused by the usual dispersion of the detection method (here ICP-MS).

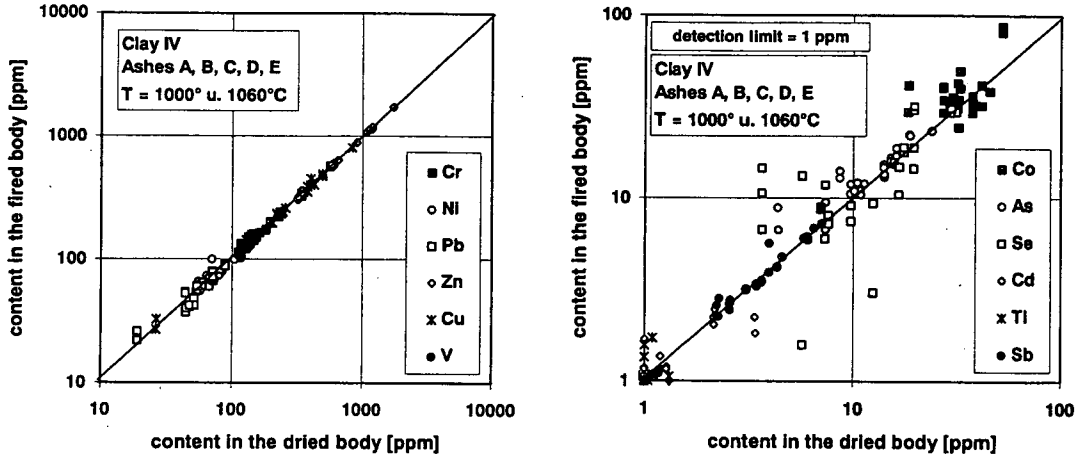


Fig. 13a/b: Comparison of the heavy metal contents in the dried and in the fired ceramic bodies (Clay IV, Ashes A, B, C, D, E; T= 1000° and 1060°C)

Figure 13 shows that it is not possible to indicate any loss of heavy metals during brick firing for temperatures lower than 1060°C. Variations of heavy metals are caused by the detection method.

7 Summary

First results of a broad-range BMBF-Project on the utilization of sewage-sludge ash as clay substitute in brick manufacturing are presented. Thereby, results of the following topics are presented: state of the art of mono-incineration of sewage sludge in Germany, impact of waste-water treatment on ash quality, impact of sewage-sludge ash on brick manufacturing, environmental compatibility and mineralogical aspects of these ash bricks are presented.

In the near future, 300000 t sludge ash per year from 23 mono-incineration plants, mostly with fluidized bed system, will arise. Comparing the chemical composition of sewage-sludge ash with clay, some differences can be noticed. Four sludge ashes - investigated over a period of one year - have usually a lower SiO_2-content (≈35%) than clays (> 60 wt.-%). Unlike clays, sewage-sludge ashes contain much phosphorus (10-20% P_2O_5). It can be distinguished between "Fe-containing ashes" and "Ca-containing ashes".

The impact of the chemical phosphate elimination with iron or aluminium salts (phosphorus precipitation) during waste-water treatment is indicated. Another main influencing parameter is the kind of sewerage system - combined or separate system. At sewage-sludge ashes from cities with a combined sewerage system, a strong interdependence of the SiO_2- and the P-content could be indicated. Rainfall affects the SiO_2-content in the ashes. That is why the higher the silicate content is, the lower is the phosphorus content in the ashes.

Sewage-sludge ashes have the following effects on the **ceramic properties** of the ash bricks:

1. Ashes work as opening agents, because of their higher particle sizes.
2. The high water-absorption potential and the higher Ca-contents of the ashes lead to an increased demand for gauging water during the production of the raw mixture.
3. Ash works as pore-forming agent. This effect can be measured by examining the decreasing bulk density of the bodies and an increase of water absorption. The Ca-content of the ashes seems to have the main influence, but also the intrinsic porosity of the ashes affects the porosity of the ceramic body.
4. Ash works as fluxing agent, that is ashes decrease the sintering temperature of the mixture. The higher the phosphorus content (P_2O_5) and the lower the silicate content (SiO_2) of the sewage-sludge ashes, the stronger is their softening behaviour. However, also Fe_2O_3 seems to work as fluxing agent.
5. In dependence of the Fe- and the Ca-content of the ashes, ash addition could increase or decrease the compressive strength . Fe-containing ashes make the ceramic body harder, Ca-containing ashes make it softer.

The leaching behaviour was investigated by means of two tests - the standardised DEVS4-Test and the pH-stat-Test as worst-case-test. With the pH-stat-Test the leaching availability was determined. After increasing the firing temperature from 1000° to 1060°C, the specific elution rate (L/C) of the standardized test (DEVS4-Test) - that means the leachability of the ash bricks, decreased from 40% to 20%. To decrease leaching under strong conditions (pH 4) higher firing temperatures of about 1100 °C should be used. In the range of 1000° to 1060°C, 3% of the under pH 4 available heavy metals leach out under standardized conditions (DEVS4-Test, 1 clay, 4 ashes). However, some elements like V and Cr show in the alkaline medium of the DEVS4-Test (pH≈9) a higher solubility than in the acid medium of the pH-stat-Test (pH=4). Generally, As shows a high solubility, also out of the 100% clay brick.

Concerning the sample preparation, crushing the bricks <∅10mm is sufficient for a sustainable estimation of the environmental compatibility. Depending on the strength of the ash bricks, for the presented clay 60% of the particles were >∅4mm. The particle-size distribution of bricks made with different ashes varies about 15 % (= standard deviation).

To determine the environmental compatibility, the recommended limits for the eluate concentrations of soils of LAGA should be used. Most ash bricks remain under the recommended values. Mineralogical tests have indicated that there is only a low mixing of the ash particles with the clay. However, during sintering of the bricks, hematite develops from the iron inside the ashes. This hematite has a low solubility. Therefore, ashes containing much Fe decrease the leachablity of some heavy metals. Reverse, ashes containing Ca and the other alkaline and alkaline earth metals (Na, K, Mg) increase the solubility of trace elements out of the ash bricks.

The final results of this Joint-Research project between Germany and Japan will be presented in 1998.

8 Acknowledgment

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Session 2

Monitoring

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CONTINUOUS MONITORING TECHNIQUE FOR VOLATILE CHLOROORGANICS FROM FACTORIES

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ABSTRACT

Environmental pollution with the volatile chloroorganics such as trichloroethylene (TCE) and tetrachloroethylene (PCE) etc. progressed still. The detector tube is used generally to measure these materials and when a high sensitivity and more highly accurate measurement is necessary, gas chromatography (GC, GC-ECD) is used now. The analysis in the laboratory by the expert is a center also for GC to analyze *in-situ* recently is developed. Then, the investigation concerning the continuous monitoring device which used the Quartz Crystal Microbalance (QCM) sensing system was done. To detect the sample selectively, the surface of QCM was covered with a thin film of the lipid. This lipid film shows a different adsorption character by the sample. Then, it has been understood that the identification of the sample is also possible at the same time as measuring the concentration by comparing the measurement results by two or more QCM covered with a different lipid within the range of 60-1000 ppm.

KEYWORD

Quartz crystal microbalance, QCM, Lipid, Continuous monitoring, Trichloroethylene

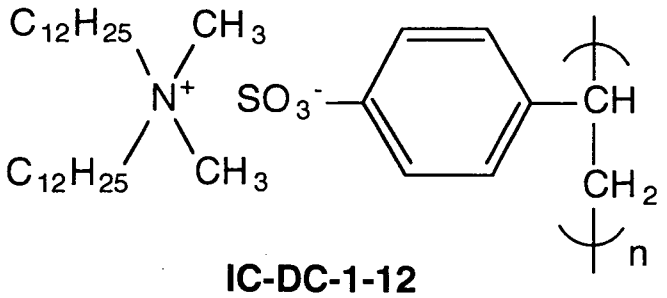
INTRODUCTION

As we reported in the work shop last time, In Japan, it has been found that groundwater is widely polluted by volatile chloroorganics such as trichloroethylene (TCE) and tetrachloroethylene (PCE), which are used in semiconductor factory and laundry(dry cleaning). Heavy pollution of groundwater with high concentration near the factory is decreasing, but the pollution with low concentration is rather increasing in wide area and these compounds are detected even in surface water and drinking water. Under such circumstances, rapid and simple monitoring method for volatile chloroorganics is needed.
Ordinary, these low concentration compounds are determined by gas chromatography with an electron capture detector (GC-ECD), but its operation needs skillful technique and long time per one measurement. On the other hand, detector tube method is simple and easy so widely used but the sensitivity is not enough. With either method, a portion of sample solution must be taken from a monitoring point, and therefore, an on-line continuous monitoring is impossible.
We have been investigate the continuous monitoring method using the Quartz Crystal Microbalance (QCM) sensing system.
The QCM has been used as an *in-situ* high sensitive weighing device. It consists of a thin disk of single-crystal quartz, with a deposited metal (gold) electrode on each side. The principle of operation as an *in-situ* microbalance is that mass adsorbed on or desorbed from the surface of electrode(s) induces a frequency shift, Δf, related to the mass change, Δm [1~3].
In our search, specific adsorption of volatile chloroorganics on a synthetic lipid film were detected by observing frequency changes of a lipid coated QCM.

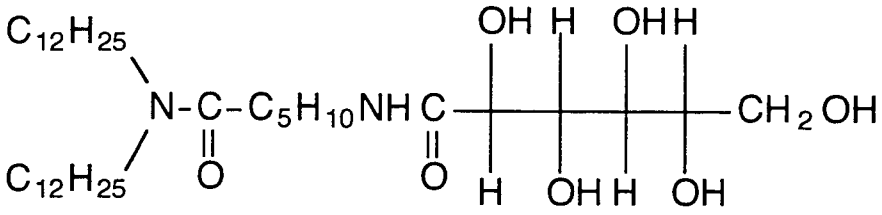
EXPERIMENTAL

Reagents

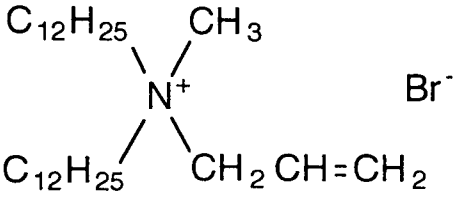
All of synthetic lipid (Fig. 1) were purchased from Sogo Pharmaceutical Co., Ltd., Tokyo, Japan and used without further purification. A standard gas and a liquid sample of volatile chloroorganics were commercially available and used without further purification.



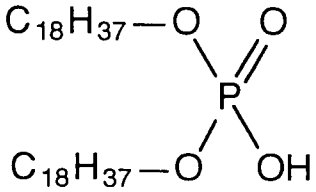
IC-DC-1-12



DN-1-12



DC-7-12



DA-2-18

Fig. 1 Structures of the lipid

Apparatus

Fig. 2 shows a schematic diagram of the experiment device. Frequency measurements were carried out at 25.0±0.3°C with FRAGRANCE SENSOR MSF-450ID (Sogo Pharmaceutical Co., Ltd., Tokyo) attached to the microcomputer system. The flow cell which provided with four detectors connected with the gas control unit which was able to mix a standard gas and the nitrogen gas at an arbitrary rate. Nitrogen was used as a blank.

Preparation for detector

The QCM was coated with the film of thin lipid according to the following procedure. A dichloromethane solution of lipid was cast on electrode of the QCM, dried in air, and then, the vibration frequency decreased ca. 5,000 Hz in air.

Principle

The quartz oscillator has been widely used up to now as a oscillator. Recent years, use as the high sensitivity balance which can in real time measure the mass change with the material which adsorbs the surface is reported [1~3], and the application in the chemistry and the measurement field has come to be paid to attention now [4]~[8]. Mass change Δm takes place by the material's adsorbing the surface of the quartz oscillator and the oscillation frequency changes(ΔF) in proportion to this. Change ΔF in this oscillation frequency is generally shown by the next expression [1, 3].

$$-\Delta F = \Delta m \cdot F^2 / (N \cdot A \cdot \rho)$$

F: Fundamental frequency
N: Frequency constant (It is AT cutting and is 167 kHz cm)
A: Surface area
ρ: Density of crystal (2.65 g cm^{-3})
Δ m: Mass change

Calibration of the QCM used in this system showed that a frequency change of -1 Hz corresponds to a mass increase of about 1 ng (9 MHz, AT-cut).

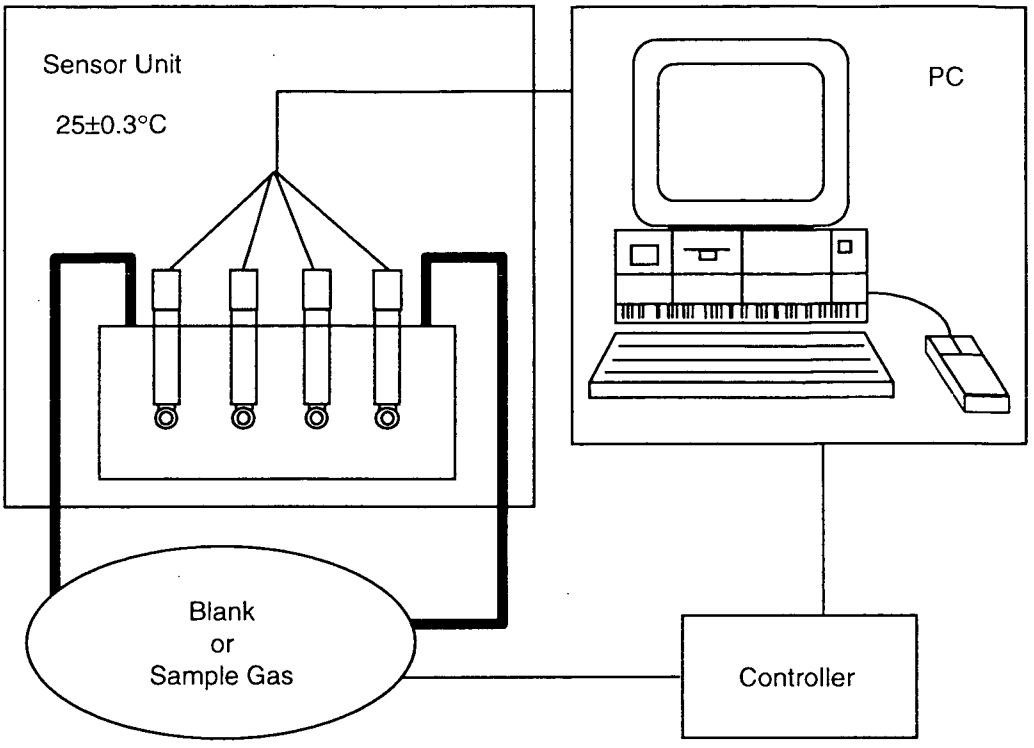


Fig. 2 Schematic diagram of the experiment device.

RESULTS AND DISCUSSION

Selective Adsorption of volatile chloroorganics

Fig. 3 shows the frequency change of the different type of synthetic lipid film coated QCMs responding to 1,2-dichloroethane (DCE) (Fig. 3-1), trichloroethylene (TCE) (Fig. 3-2) and tetrachloroethylene (PCE) (Fig. 3-3).

the change in the frequency was observed to the sample gas even when coating with which lipid. For instance, to saturated TCE in nitrogen the frequency were shift down in the case of IC-DC-1-12 (5212 Hz), DN-1-12 (2500 Hz) and DC-7-12 (2052 Hz). On the other hand, the shift down of DA-2-18 was less than 300 Hz (Fig. 3-2).

However, the response pattern of four kinds of lipid has understood a thing different by the sample gas.

Fig. 3-1

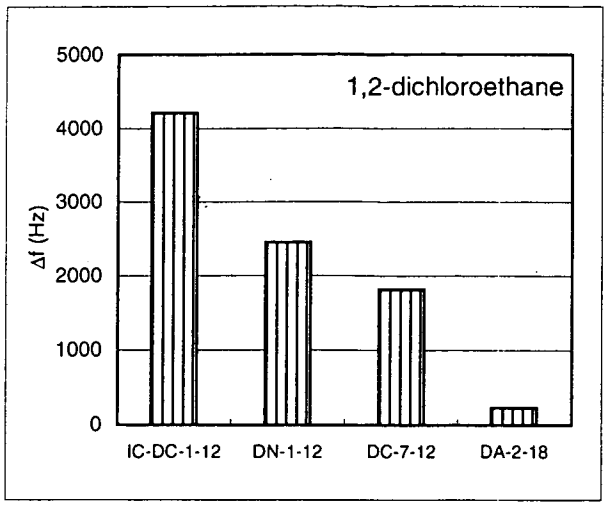


Fig. 3-2

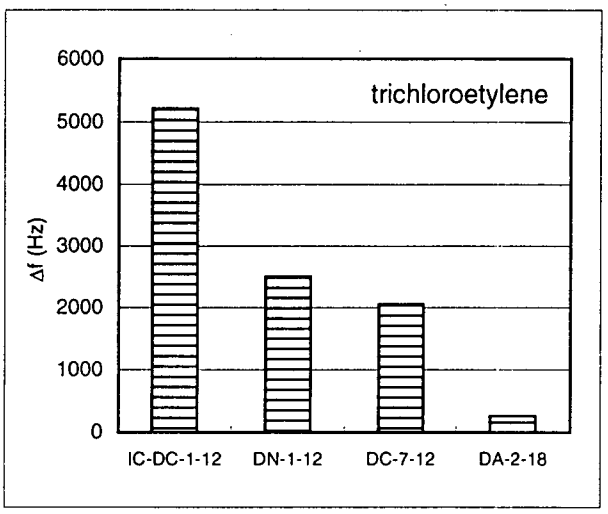


Fig. 3-3

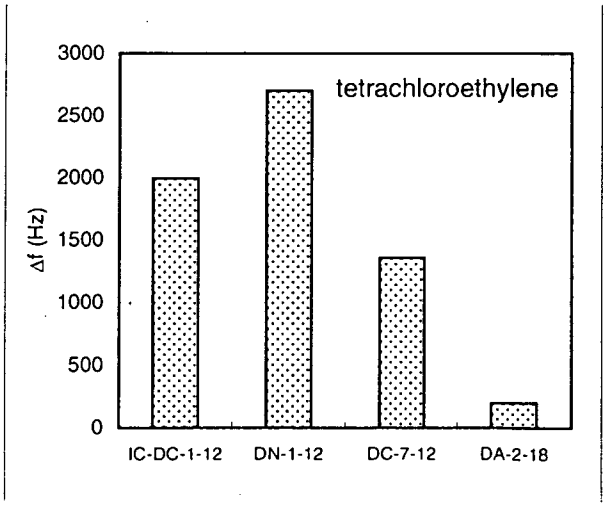


Fig. 3 Comparison of frequency changing with each lipid to the volatile chloroorganics compound.
To saturated DCE: 3-1, TCE: 3-2 and PCE: 3-3 in nitrogen at 25.0±0.3°C

TCE IC-DC-1-12 >> DN-1-12 >= DC-7-12 > DA-2-18
PCE IC-DC-1-12 < DN-1-12 >> DC-7-12 >> DA-2-18

Therefore, the identification of TCE and PCE according to the intensity ratio of the response is possible.

Response characteristics of detector

As shown in Fig. 4, DC-7-12, IC-DC-1-12 and DN-1-12 film coated QCMs responded reproducible to the other volatile chloroorganics, within a few minutes. This detector has the lifetime of several months extremely stabilizing.

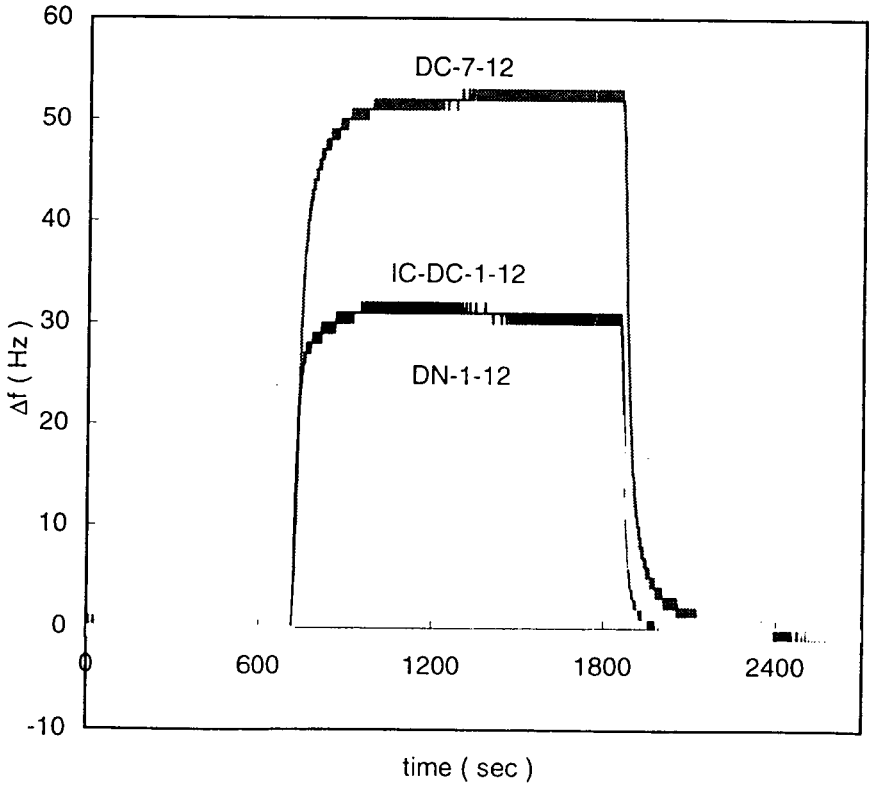


Fig. 4 Response characteristics of detector
TCE (1000 ppm) was ON and OFF each 10 min.

Calibration curves and Sensitivity

Fig. 5 shows the calibration curve of the frequency change in the different lipid film coated QCMs to TCE.

For DC-7-12 film coated QCM, the maximum frequency change was observed for TCE. The slope of the calibration curve of DC-7-12 is 20 ppm/Hz, and good linearity within the range of 60-1000 was shown. The difference of the selectivity was seems to be based on the molecular recognition between the chloroorganics and lipid. The surface of the QCM was modified by the lipid, having a different function groups, and it would be formed characteristic recognition field for chloroorganics.

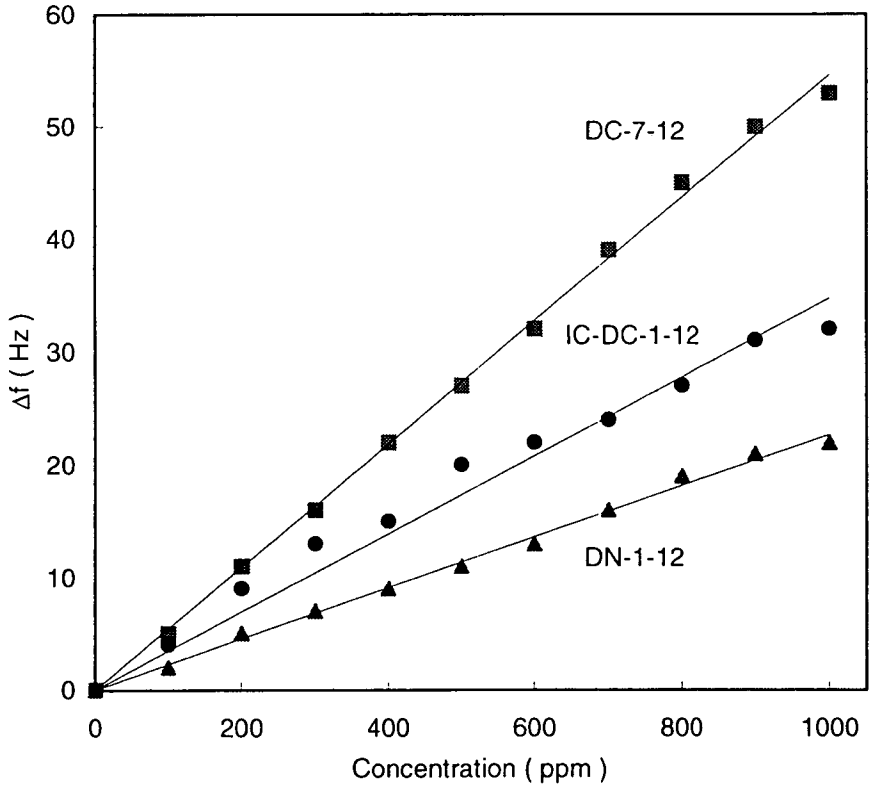


Fig. 5 The calibration curves of the frequency change in the different lipid film coated QCMs to TCE.

CONCLUSION

The new continuous monitoring method of a volatile chloroorganics by QCM coated with the lipid was developed. And it has the sensitivity of several ppm order now. Use to the warning sensor of the early stage such as the leakage accidents in the factory etc. can be expected.

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Highly parallel affinity sensor system for the determination of water contaminants

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1 Introduction

Water analysis for trace contaminants always has been a complex and expensive task. One problem is the low frequency and throughput of analyses, which can be performed. Therefore short-time contamination peaks (typical for accidents) are often missed by conventional analytical methods. Furthermore, it is very important for modern trace analysis to have an idea, which kind of pollutants are likely to be found in a sample. Biosensors and especially immunosensors are a very promising way to solve these problems. Although biosensors have been developed for many years, some significant drawbacks of essentially all biosensors have remained. Biosensors can be very sensitive, but most of them show a characteristic lack in selectivity and therefore only sum parameters can be measured or a kind of screening can be performed. In most cases it is not possible to identify and quantify unambiguously a single compound by a biosensor, hence a conventional analysis is often required additionally. Second, many biosensors have problems with stability, therefore they often are designed only for single use, and have to be replaced frequently. This is suitable for field-testing, but not for a quasi-continuous control of water quality. For this reason, an effective regeneration step is an important prerequisite for the practical use of a biosensor. In real samples, like surface water, a wide variety of chemical compounds can occur, with a large range of molecular weights, strictly hydrophilic to mainly hydrophobic character, different charged compounds, of natural or anthropogenic origin. An ideal sensor should deal with many compounds in parallel, and give as much information as possible in a short time at low cost. Biosensors are good candidates, if some of their main disadvantages can be eliminated or reduced considerably.

There have been many efforts to realize biosensors on the base of antibodies and similar binding molecules [1]. In some sensor systems the antibodies have been immobilized on an exchangeable membrane, which avoided a regeneration problem. Later, sensors with antibodies immobilized on small columns have been constructed [2]. This setup seems to improve the regeneration considerably. Nevertheless, the proof that real regeneration has been achieved is still lacking. As only column-designs work this way, it might be possible that the large amount of antibodies simulates a regeneration, but in reality, antibodies are used up. This hypothesis is backed by the fact that these systems show a sudden break-down of the activity after some cycles of no significant activity decrease. Another system was developed at Ciba-Geigy some years ago, which is based on the evanescent wave technology and fluoresceine-labelled compounds [3]. As the labelled compounds are small, the nonspecific binding (especially critical for regeneration) is low. Some hundred cycles, in the case of oligonucleotides [4] even the potential for several thousand cycles could be shown. Despite of this breakthrough, these sensors are not widely used. One reason might be that only one compound per sensor could be measured (single-analyte approach). Other techniques, e.g. interferometry [5], SPR (surface plasmon resonance) proved to be not sensitive enough to be used in trace or ultratrace analysis. In addition, the scale-up to a multi-analyte system needs considerable efforts and costs and is therefore limited to about 10 sensors in maximum.

Another critical point of immunosensors is the limited selectivity, the cross-reactivity. Although many groups would like to have antibodies with a single specifity, it seems clear that this cannot be reached in general. This is caused by the binding mechanism, which can be described by the well-known lock and key model. It seems convincing that a molecule, which ressembles the original analyte very much, should have a significant affinity and therefore cross-reactivity with a given antibody. Although there are some possibilities to change selectivity (new antibody [6], pH variation, addition of surfactants [7], addition of solvents etc.) a 100% selectivity will never be obtained. To overcome this limitation, several antibodies of different selectivity are needed. In combination with chemometric analysis an identification, as well as a quantification is possible. Some years ago, it could be shown that a 2 analytes/2 antibodies system gives very useful data in pesticide analysis of soils [8]. Information theory demands that at least n antibodies have to be used, if n compounds are (potentially) present in the sample. Therefore this approach is much more powerful if a large number of antibodies is available. To our knowledge, no system has ever been realized, which

can be regarded as a real multi-analyte immunosensor. The work published up to now is, in most cases, based on standard microtitration plate technology, which has to be performed manually. The prediction quality is quite poor at the moment, which may be caused by a low number of antibodies and perhaps inadequate chemometrics.

2 The parallel affinity sensor array (PASA)

2.1 Setup

To realize a system with true multianalyte detection and the possibility to use cross-reactivity data for the identification and quantitation of analytes the following setup was used:

A air-cooled back-illuminated CCD-camera with ca. 360,000 pixels is the core of the detector. The CCD has a quantum efficiency of about 70% at 425 nm and is optimized for low background at relatively long exposure times. The advantage in relation to an intensified system is the ruggedness, excellent linearity and under special conditions even superior sensitivity. Similar systems are used e.g. for astronomical applications. In contrast to these astronomical cameras, we have avoided liquid nitrogen or other liquid cooling, as the exposure times are not long enough to justify the additional complexity of the system. The setup is shown in **Fig. 1**. The system consists of the CCD-camera (with air-cooled head), which is fitted to a dark box to enable flexible use of different optical systems and flow-cells. The optics consists of two standard objectives (50 mm, 1.4, NIKON). We tried other objectives and arrangements, but most of them showed severe optical faults, for instance: high light losses, vignetting, non-uniform intensity, low resolution. The flow-cell is a modified standard flow-cell made of glass, which is placed on an optical rail to obtain optimal reproduction of the flow-cell to the CCD-chip. The CCD-camera needs a special controller, which is plugged to a personal computer (only for camera control). The raw data are converted to ASCII and transferred to an other, more powerful PC. This computer is used for the control of the whole system and the data evaluation. The liquid handling system is based on several syringe pumps. This approach has the advantage that the overpressure in the system significantly reduces problems with air bubbles. Furthermore, a 6-port and a 3-port valve are integrated, and finally a commercial liquid-autosampler was fitted to the system to facilitate

facilitate the use of calibration solutions. The system can be operated 24 hours a day without any intervention.

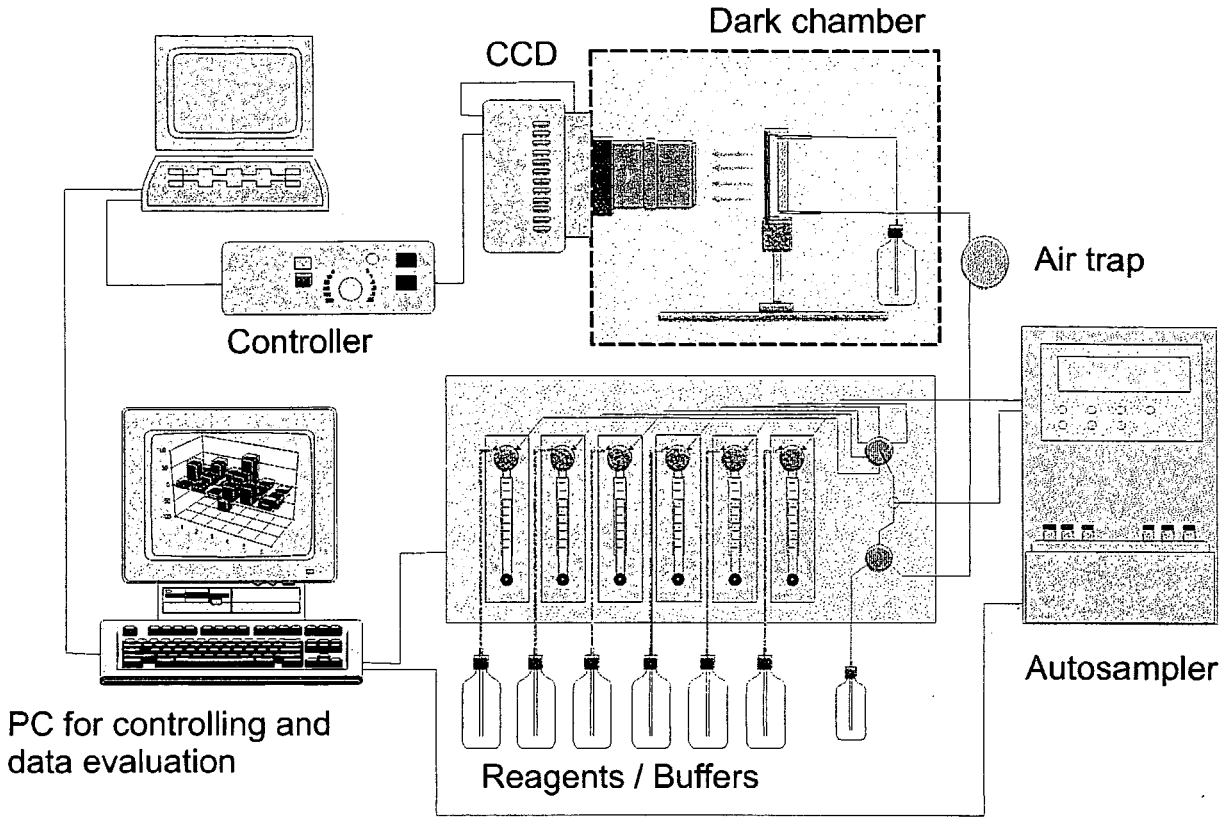


Fig. 1: *Setup of the parallel affinity sensor array (PASA) based on enzyme-enhanced chemiluminescence.*

At the moment the reagent spots on the sensor chip, which is based on cheap microscopic slides, are prepared manually. In the next step we will automate the chip-production, too. In addition, this will lead to a significant miniaturization of the reagent spots. The reagent spots in conjunction with the regeneration of the sensor will lead to the situation that the cost per sample will be very low (estimated to 1 US$/sample) and even much lower, if calculated per analyte. The whole system is clearly of bench-top size and not miniaturized yet. The advantage of this system is high flexibility, as many different options have to be checked to find out the optimum configuration. Later on the system has obviously a very high potential for miniaturization, which would lead to a remarkable reduction in the cost per system. In **Fig. 2** the construction of the flow-cell with the affinity chip (left) is shown.

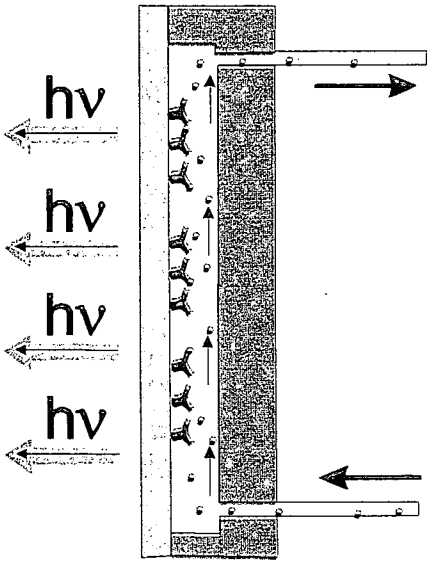


Fig. 2: *Flow-cell made of glass with a removable affinity chip (left wall). Immobilized antibodies and other reagents are not to scale. The thickness of the fluid chamber is about 500 µm . The dead volume is about 100 µL. The affinity chip is not glued to the cell and therefore can be exchanged very easily.*

2.2 Biochemistry

In this system we use several different immunoassay formats, which all have their special merits. Therefore it is not possible to select a "best" format for all purposes. In **Fig. 3** a measuring cycle in a direct assay format is shown. The critical point of the regeneration is the complete removal of the enzyme tracer, which often binds irreversibly to the surface.

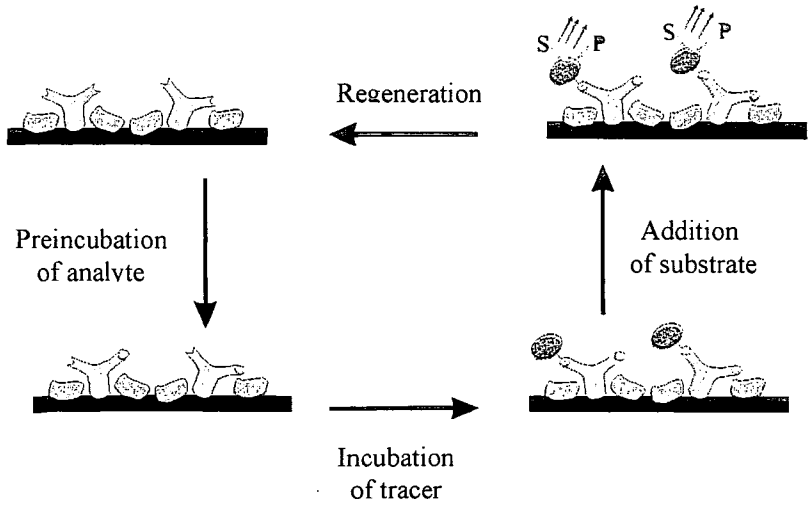


Fig. 3: *Direct assay format (surface blocked with protein).*

Horseradish peroxidase, an extremely sensitive label, was used for detection throughout. The enzyme substrate consists of a mixture of luminol, hydrogen peroxide and special enhancer additives. The reaction mechanism is shown in **Fig. 4.** One obstacle was the development of a suitable stabilization procedure [9] for peroxidase-based reagents, which is crucial for long-term stability of the sensor signal.

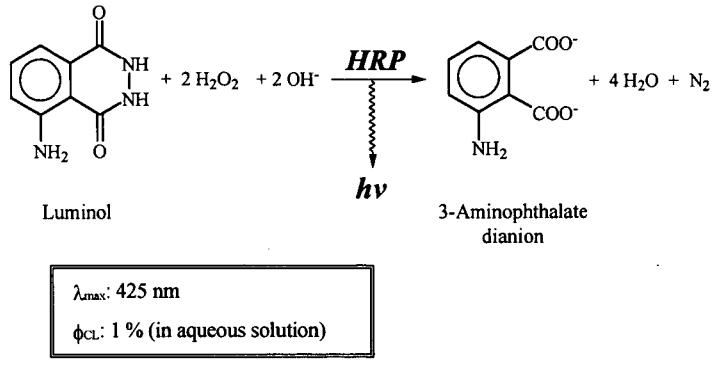


Fig. 4: *Mechanism of luminol chemiluminescence.*

For the indirect assay format the immobilization of haptens (small analyte derivatives) is necessary. This can be achieved on base of an aminosilane chemistry, which is illustrated in **Fig. 5** (exemplified with TNT). Most steps are performed with the complete chip, the coupling of the hapten is only done locally on the suitable spot area.

First, the cleaned glass surface is treated with a special aminosilane (diluted in a toluene/water mixture). After a washing step, the aminosilanized surface is coupled with the hapten, e.g. a trinitrophenyl-derivative (and dicyclohexyl carbodiimide, N-hydroxysuccinimide, dimethyl sulfoxide). The remaining amino groups are chemically blocked with succinimidyl anhydride. It is very important to realize a low coupling density, as high densities are not really useful for immunoassays (sterical reasons). Furthermore, spots with high coupling densities show much higher non-specific binding (NSB). On the other hand, remaining amino groups are detrimental to assay performance, too, as the positive charges lead to excessive NSB. The negative charges introduced by the succinimidyl anhydride in general lower the NSB, which is probably caused by ionic repulsion (most proteins are negatively charged at neutral pH).

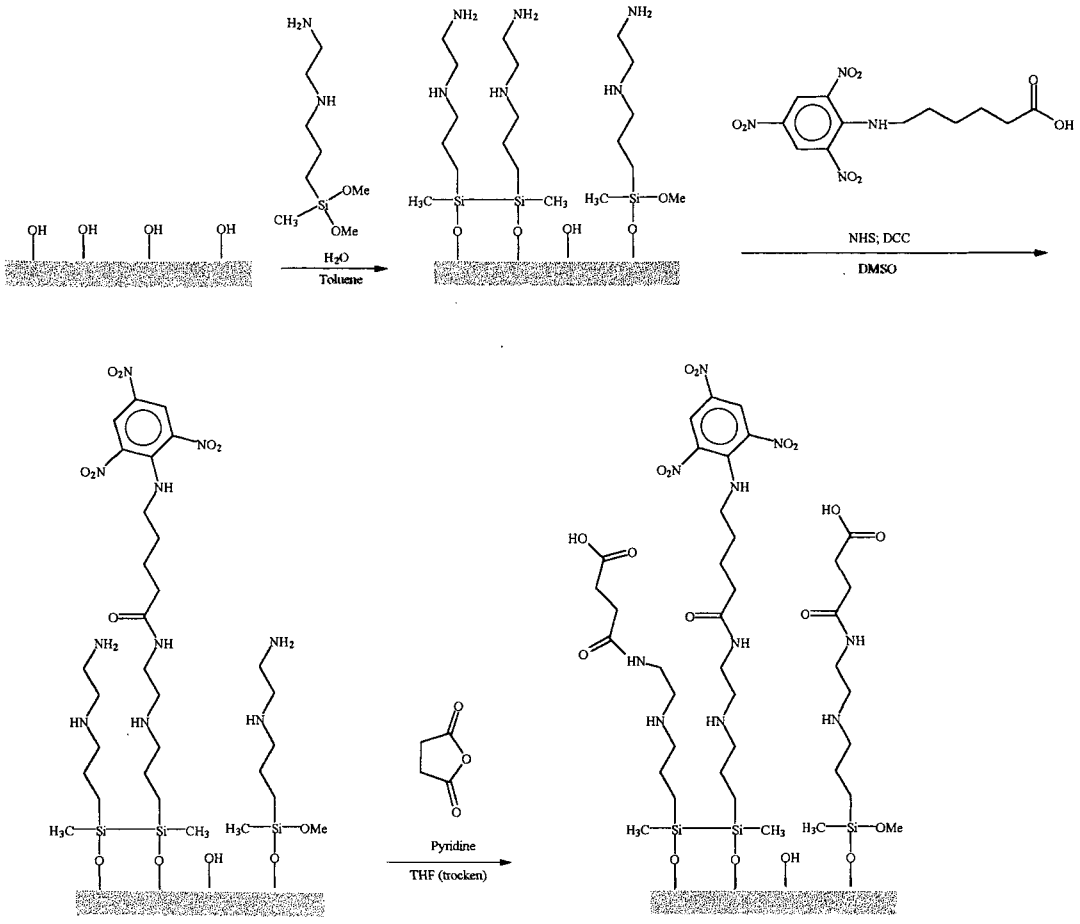


Fig. 5: *Silanization of glass surface, coupling of nitroaromatic hapten and chemical blocking (surface suitable for TNT sensing).*

3 Results

The parallel measurement of many compounds has not been realized yet. Nevertheless, it could be shown that two completely different compounds can be detected without difficulty in one step and in one flow-cell (**Fig. 6**).

The spots are relatively large at the moment (ca. 1 mm in diameter), as they are made manually. But the photon flux is the same, whether a pixel of a large or a small spot is examined. Therefore the production of smaller spots should not lead to intensity problems (as long as the reproduction of the spots does not reach the dimensions of the pixels).

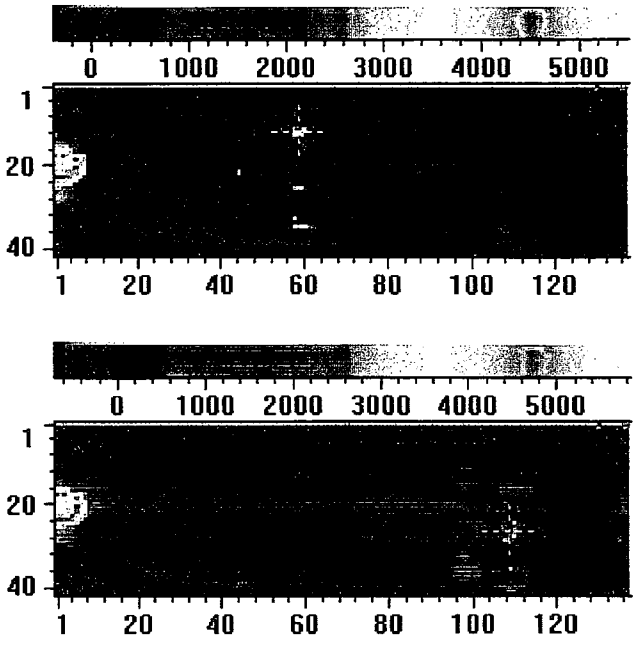


Fig. 6: *Pictures show the possibility of independent measurement of two analytes on one chip, the triazine herbicide terbuthylazine and the nitroaromatic compound TNT. The TNT antibody spots are located at the right, the terbuthylazine antibody at the left. A high concentration of the corresponding analyte leads to an inhibition of the signal. (The intense spot at the left is the inlet of the flow-cell. Upper scales: relative intensity, lower scales:8*8 superpixel No.)*

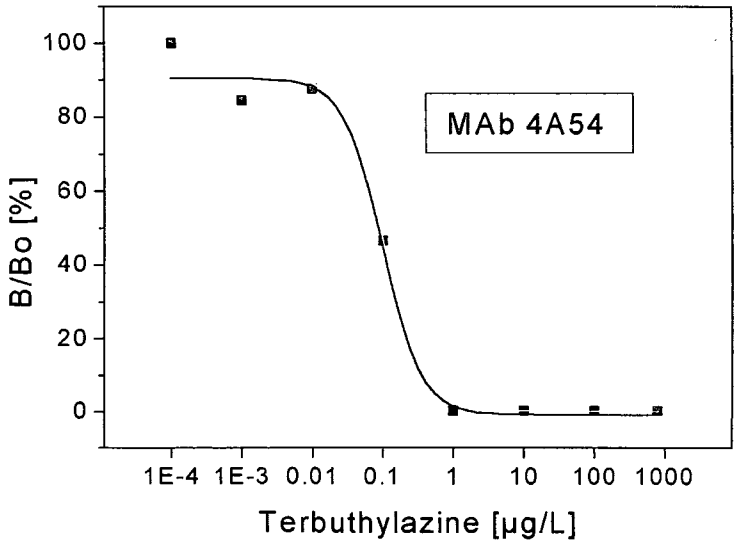


Fig. 7: *Calibration curve of the triazine herbicide terbuthylazine on the base of the sensitive monoclonal antibody MAb 4A54 ([6], direct assay format). It can be seen that concentrations well below the limit of the EU drinking water regulation of 0.1 µg/L can be detected.*

If different concentrations of an analyte are used to obtain a calibration curve (**Fig. 7**), it can be shown that the sensitivity is nearly as good as on a microtitration plate. The EU pesticide limit could be reached without problems (presupposed a good antibody is available).

4 Conclusions

A novel parallel affinity sensor array (PASA) was developed, which is suitable for multianalyte detection and the use of cross-reactivities to identify and quantify substances in water. All important parts of the system are fully operative and automated measurements are already possible. All results are very promising and therefore it is very likely that significantly more than the current project aims will be attained. It should be considered to begin a second part of the project, which will deal with the miniaturization of the PASA. This should facilitate the widespread use of this sensor for many applications, not only for pesticide analysis, but also for algal toxins, hormone-like substances and even for heavy metal ions.

5 Acknowledgements

The financial support of the BMBF (project 02-WU9573/3) is greatfully acknowledged.

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MONITORING OF THE TOXICITY IN WATER USING NITRIFYING BACTERIA

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ABSTRACT

A significant number of chemicals used in our daily lives as well as manufacturing processes have the potential to migrate into wastewater and finally reach receiving waters which are used for drinking water and ecological habitat. Thus, in controlling such chemicals in water, enforcement of discharge to sewerage and public waters is essential, but one of the most critical problems in the enforcement is monitoring of individual hazardous substances. Spill accidents occurring in river basins are also menace to water supply. Monitoring of total toxicity is more effective in order to prevent the crisis resulting from spilled toxic substances. Bioassay is prospective ways for integrated water quality monitoring of hazardous substances. This paper describes a new biosensor monitoring system using nitrifying bacteria that can sensitively detect the toxicity in water. First, the effectiveness of nitrifying bacteria for monitoring the toxicity is described. The toxicity sensor developed in this study can detect many toxic substances listed in the Effluent Water Quality Standards at relatively lower concentrations than the method of monitoring fish that was recently applied in some water purification plants. However, more improvement is necessary if the detection limits of the toxicity sensor need to be raised to the Effluent Water Quality Standards. The toxicity sensor can have functioned properly as a monitoring system under the field test conducted at a river water quality monitoring station up to this present.

KEYWORD

toxicity, biosensor, bioassay, water quality monitoring, nitrifying bacteria, *Nitrosomonas eauropaea*, river water, sewerage, spill accident.

INTRODUCTION

A significant number of chemicals used in our daily lives as well as manufacturing processes have the potential to migrate into wastewater and finally reach receiving waters which are used for drinking water and as ecological habitat. Thus, the control of hazardous substances in sewerage systems is important. Specific hazardous substances discharged by specific dischargers into sewerage systems have been regulated as low as direct discharges to public waters in Japan. However, one of the most critical problems in enforcement of regulations is monitoring of individual hazardous substances. Monitoring of total toxicity in water would be a more appropriate method to determine its total adverse effects upon human and ecological health than chemical-based monitoring of a huge number of individual toxic substances in water.

Increasing demand of nutrient removal in wastewater treatment plants requires nitrifying process to be controlled stable, but nitrifying bacteria have been known as one of the most sensitive microorganisms in wastewater treatment. More than 70% of the wastewater treatment plants receive wastewater from industrial dischargers dealing with designated hazardous substances in Japan (Tanaka and Minamiyama, 1996). Therefore, inspection and monitoring of such discharges are quite important in order to enforce their observance of the discharge regulation. Thus, development of reliable and inexpensive methods for watching such hazardous substances in sewers or outlets from specific dischargers is useful and desirable.

Big concerns on the safety of surface water sources for water supply are also emerging in recent years because toxic substances accidentally spilled from river basins occasionally enter into rivers. According to the Ministry of Construction (1997), the number of accidental spill accidents occurred in 1995 was 256 in major Japanese rivers. Among them, 21 accidental spills stopped intakes of water supply, which caused large confusion in urban activities in the related municipalities. Continuous monitoring of the safety of drinking water sources, particularly surface water, has been desired.

From the above background, effective and timesaving monitoring tools that can detect toxic substances in wastewater as well as river water are strongly wished for in Japan. This paper describes a new biosensor monitoring system developed by Public Works Research Institute in cooperation with Fuji Electric Corporation Ltd. This biosensor applies nitrifying bacteria that are quite sensitive to many toxic substances. In this paper, first, the effectiveness of nitrifying bacteria assay for monitoring toxicity will be described. Then, the concept of this biosensor and the development of the toxicity monitor using the biosensor will be explained. Finally, the results on a field test of the toxicity monitoring system at a river water quality monitoring station will be reported.

DETECTION OF TOXIC SUBSTANCES BY NITRIFYING BACTERIA ASSAY

Methods of Nitrifying Bacteria Assay

Nitrifying bacteria have been reported to be sensitive to many toxic substances (Grady et al., 1980). Because the nitrifying bacteria assay gives the information on the effects of toxic substances upon nitrification process, it is useful to water quality management in sewerage system. The nitrifying bacteria used in this assay were derived from activated sludge in a domestic wastewater treatment plant. After added in Pramer's culture medium (Lewis & Pramer, 1958) including ammonia, the nitrifying bacteria start metabolizing ammonia to produce nitrite and nitrate. The nitrification rate in terms of the increase in nitrite- and nitrate-nitrogens (NOx-N) was observed in each sample after one day incubation period at 25℃. The nitrification rate defined as the increase in NOx-N concentration of the incubated sample was compared to that in the control (Tanaka and Minamiyama, 1995). The effective concentration of a test sample that causes 50% inhibition of the nitrification rate to the control is here defined as EC_{50}.

Nitrifying Bacteria Assay for Specific Toxic Substances

Toxicities of specific substances were tested using the nitrifying bacteria assay. The EC_{50}s resulting from specific toxic substances of the nitrifying bacteria as well as activated sludge are illustrated in Table 1. Most of the test substances have been regulated as hazardous substances in effluent discharges to public waters and public sewers as well as items in the Environmental Quality Standards as shown in Table 1. Compared to the sensitivity of the nitrifying bacteria, the EC_{50}s of *Vibrio fischeri* that is used for a rapid bioassay kit called MICROTOX™, and the LC_{50}s of *Daphnia magna*, a small crustacean, are also tabulated in Table 1. The EC_{50}s resulting from some toxic substances are low enough to detect the level of the Effluent Quality Standards regulated by the Water Pollution Control Law. The EC_{50}s on the others are not low enough to detect the Effluent Quality Standards. However, the nitrifying bacteria are adversely affected by many toxic substances relatively lower than other bacteria such as heterotrophs in activated sludge and *Vibrio fischeri*. Although endpoints and exposure time differ, the nitrifying bacteria are more sensitive to the test toxic substances than *Daphnia magna*.

Meaning of Nitrifying Bacteria Assay in Wastewater Treatment

Dichlorophenols (DCPs) were used as test substances in order to understand the meaning of the nitrifying bacteria assay in wastewater treatment. As shown in Table 1, the EC_{50} of 2,4-DCP was 0.037mg/L, while that of 2,6-DCP was 1.3mg/L. Therefore, the toxicity of 2,4-DCP is two-order magnitude higher than that of 2,6-DCP. Minamiyama et al. (1994) reported the effects of these substances on the activate sludge process using a bench-scale model receiving actual sewage at Kohoku Pilot Plant in Public Works Research Institute. The experiments when DCPs were constantly dosed to untreated sewage resulted in that 2,4-DCP gives more adverse effects on

nitrification process than 2,6-DCP at the same dosage level. The tendency of the nitrifying bacteria bioassay coincided with the results of the bench-scale experiments of the activated sludge process. Therefore, the level of the EC_{50} based on the nitrifying bacteria assay implies the level of adverse effect on nitrification process in wastewater treatment.

Table 1 Sensitivity of Nitrifying Bacteria to Specific Toxic Substances

	Environ. Quality Standards mg/L	Effluent Quality Standards mg/L	EC_{50} mg/L			*Daphnia magna* LC_{50} mg/L
			Nitrifying Bacteria	Activated Sludge	*Vibrio fischeri*	
1,1-Dichloroethylene	0.02	0.2	0.0016			
cis-1,2-Dichloroethylene	0.04	0.4	0.073		905	
Trichloroethylene	0.03	0.3	0.41		117～1068	94(48hr exposure)
Tetrachloroethylene	0.01	0.1	41		19.5～117	4(16day exposure)
Dichloromethane	0.02	0.2	0.48		998～2878	
Carbon tetrachloride	0.002	0.02	14		5.58～33.7	35(48hr exposure)
1,2-Dichloeoethane	0.004	0.04	20		157～2068	220(48hr exposure)
1,1,1-Trichloroethane	1	3	17		8.04～106	
1,1,2-Trichloroethane	0.006	0.06	0.017		106～176	43(exposure hr?)
Phenol		1*	2.8		46	
2-Chlorophenol		1*	0.068	1000	45	
3-Chlorophenol		1*	0.090	270		
4-Chlorophenol		1*	0.23	1300		
2,3-dichlorophenol		1*	0.088	68		
2,4-dichlorophenol		1*	0.037	40	3.5	
2,5-dichlorophenol		1*	0.58			
2,6-Dichlorophenol		1*	1.3		26	
Isobenphose	0.008**		58			

*Regulated as Phenols.
** Guideline.

TOXICITY SENSOR APPLYING THE AMMONIA BIOSENSOR

Principle of the Toxicity Sensor

The ammonia biosensor applies *Nitrosomonas eauropaea* (ATCC 25978), nitrifying bacteria, immobilized by acetylcellulose membranes to its receptor for ammonia and a dissolved oxygen (DO) probe to its transducer (Tanaka et al., 1993). The ammonia biosensor has been already developed as the automatic analysis system for laboratory use and monitoring use for rivers. The concept of the ammonia biosensor is shown in Fig. 1. The nitrifying bacteria sandwiched with the membranes increase their respiration rate and consume DO in water when a test sample includes ammonia as shown in Fig. 2. The respiration rate is proportional to an ammonia concentration up to a relatively lower level. The DO probe is used for measurement of change in DO resulting from change of their respiration.

The idea of the toxicity sensor discussed here is application of inhibition of toxic substances on the ammonia biosensor (Tanaka et al., 1993). The inhibition of the nitrification rate is measurable by improving the ammonia biosensor. The output of the microbial electrode of the ammonia biosensor has been reported to be unchanged if the ammonia in the sample exceeds a saturation level (Tanaka et al., 1993). An ammonia solution exceeding the saturation level is fed to a sample so as to avoid the change of the microbial electrode output due to the change in the ammonia concentration in a sample.

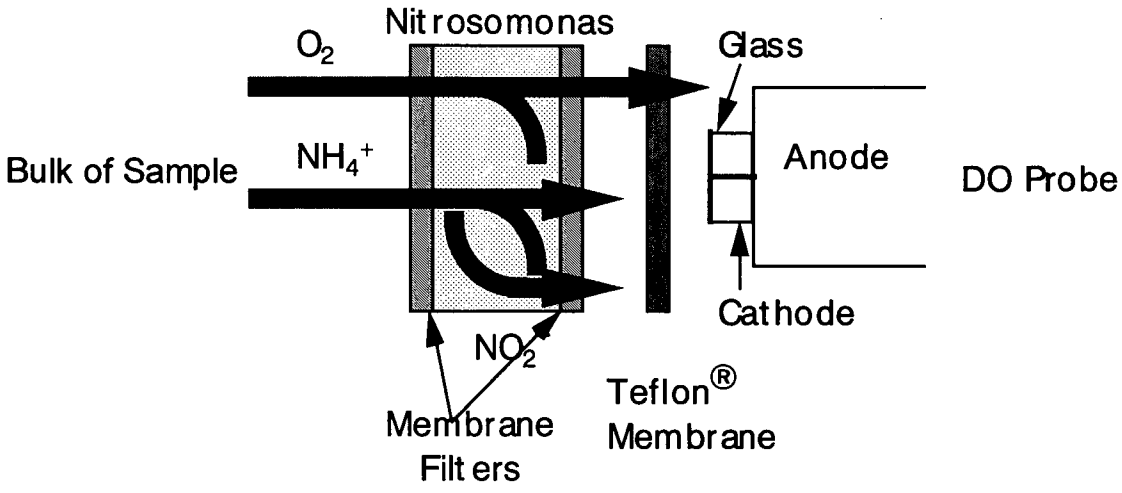


Fig. 1 Principle and Structure of the Microbial Probe

Measurement of Specific Toxic Substances Using the Toxicity Sensor

The toxicity sensor was tested to toxic substances listed in the Effluent Quality Standards as well as the Environmental Quality Standards. An example of the toxicity sensor response is shown in Fig. 2, where a potassium cyanide solution was used as a test substance. A sensor output means here a current/voltage that the microbial electrode outputs. First, the buffer solution without any ammonia was measured; the sensor output was recorded as a base level where endogenous respiration of the microbial membranes occurs. Then, the buffer solution including excessive ammonia was measured, the sensor output shifted to a peak level, where the maximum respiration rate of the nitrifying bacteria metabolizing ammonia occurs under this environment, which results in DO decrease. The difference between the sensor output and the base level is defined here as a span range in general. Among span ranges, the difference between the peak level and the base level is particularly defined as a reference output. The vertical axis shows a relative sensor output that is a span range normalized with the reference output. The sensor output in Fig. 2 is depicted in reverse order, that is, the increase in the relative sensor output means the decrease in DO in the membranes of the nitrifying bacteria, and vice versa. Therefore, the relative sensor output becomes 100% for the peak level and 0% for the base level.

Next, the mixture of the buffer solution, ammonia and 0.02 mg/L of KCN solution is measured for 20 minutes. Then, the sensor output shifts down to a lower level resulting from the toxicity of KCN to the nitrifying bacteria. When the previous mixture consisting of the buffer solution and the excessive ammonia solution was measured again, the sensor output promptly recovered to the peak level. However, if the sensor were exposed to a more toxic solution or were exposed during a prolonged time, the recovery of the sensor output to the peak level would need more time, or would never be observed due to the damage of the nitrifying bacteria. When the mixture including the buffer solution, ammonia and 0.12 mg/L of KCN was measure for 20 minutes, the depression of the respiration rate of the nitrifying bacteria brought about a larger decrease in the sensor output resulting from the larger toxicity of KCN. Therefore, the extent of the decrease in the span range can indicate the toxicity level of the test sample, which can be easily quantified from the reference output that was recorded previously.

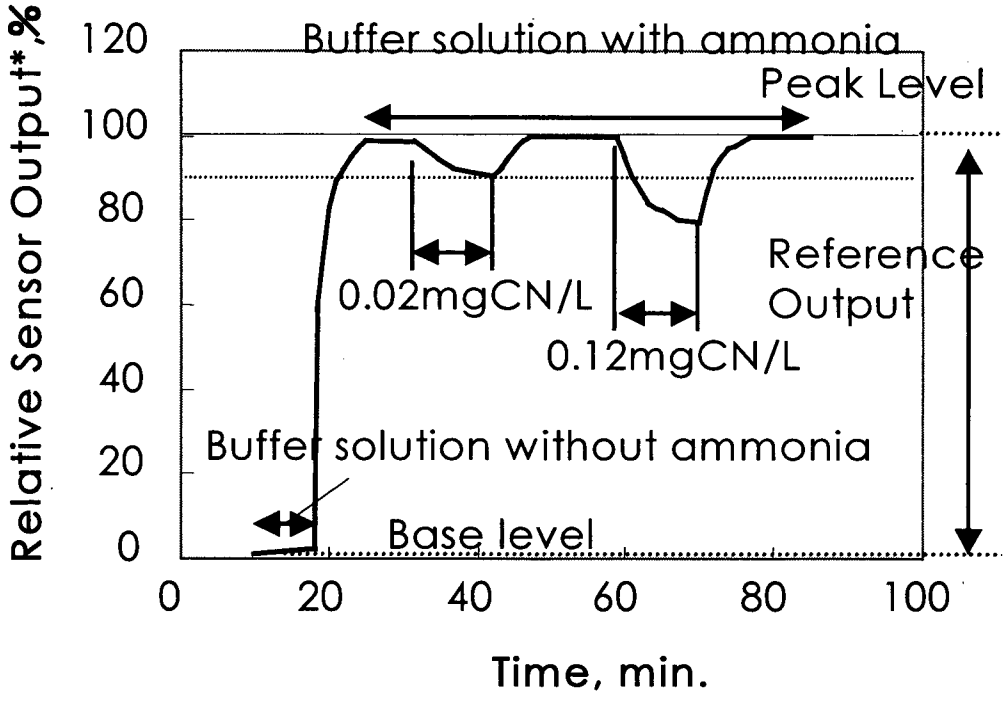


Fig. 2 Output of the Toxicity Sensor when KCN Solution Is Dosed
*: Relative sensor output is expressed in reverse, i.e.,
larger value stands for decrease in DO, and vice versa.

Table 2 demonstrates the items of the Environmental Quality Standards and the Effluent Quality Standards as well as detection limits of the toxicity sensor. A detection limit is defined here as the concentration of a toxic substance that causes the span range to decrease by 10% from the reference output. The detection limits are still much smaller than the Effluent Quality Standards as well as the Environmental Quality Standards. Thus, the toxic sensor has still hurdle to improve the sensitivity if it is aimed to detect the toxic substances as low as the Effluent Quality Standards or the Environmental Quality Standards. However, the lethal concentration on 50% (LC_{50}) of the tested fish population listed in Table 2 is larger than the EC_{10} of the toxicity sensor. Therefore, it

can be concluded that the ability of detecting the toxic substances by the toxic sensor is more sensitive than that of fish based on the lethal endpoint so far as the species listed in Table 2 are concerned. Recently, Sekine et al. (1997) reported that the detection limit of the toxicity sensor is superior to the level of avoidance concentration by fish such as shiners, carp and rainbow trout using the following test substances: cyanide, tetrachloroethylene, chloroform, thiram and simazine. Moreover, the sensor can detect the toxic substances in only 10 to 20 minutes, so the detection time is quite shorter than the monitoring system based on the endpoint that fish is killed. Moreover, the quantification and repeatability of the toxicity sensor are also superior to the monitoring system based on fish.

Table 2 Sensitivity of the Toxicity Sensor to Specific Toxic Substances

	Environmental Quality Standards /Guideline mg/L	Effluent Quality Standards mg/L	Toxicity Sensor Detection limits [a] mg/L	Lethal Concentration for Fishes[f] mg/L
Cyanide			0.05	0.48~0.78[c]
Trichloroethylene	0.03	0.3	9	45 [b]
Tetrachloroethylene	0.01	0.1	6	13 [b]
Carbon tetrachloride	0.002	0.02	20	
1,1,2-Trichloroethane	0.006	0.06	10	
1,2-Dichloeoethane	0.004	0.04	60	430 [b]
1,1-Dichloroethylene	0.02	0.2	30	74 [b]
cis-1,2-Dichloroethylene	0.04	0.4	15	140 [b]
Dichloromethane	0.02	0.2	30	
Benzene	0.01	0.1	60	46 [d]
Thiram	0.006	0.06	0.5	10 [c]
Simazine	0.003	0.03	0.6	
Thiobencarb	0.02	0.2	80	1.6 [c]
1,3-Dichloropropane	0.002	0.02	4	
Phenol		1 [e]	0.7	24.7 [c]
1,1,1-Trichloroethane	1	3	16	72 [b]

a: Detection limits defined here is a concentration of toxic substances that gives 10% decrease of the reference output of the toxicity sensor exposed to a toxic solution for 20 min.
b: Bluegill (96hr exposure)
c: Carp (48hr exposure)
d: Gold fish (24hr)
e: Regulated as phenols
f: Adapted from JWWA (1993)

Monitoring System Using the Toxicity Sensor

The toxicity sensor was developed for a monitor applicable to river water as well as wastewater. An automatic control system is essential for the monitor besides the above sensor unit. The major frame of this monitoring system is illustrated in Fig. 3. The buffer solution consisting of modified Pramer's medium using boric acid instead phosphoric acid and the ammonia solution (feed solution) for food for the nitrifying bacteria are stored in each tank as shown in Fig. 3. Water and the rinse solution for cleaning the transfer tubes and the flow cell, are also stored in each tank. Either a sample, water, or the rinse solution is sent by a pump, while either the buffer solution or both the buffer solution and the feed solution are sent by another pump. Both the solutions coming from the two lines are merged into a line and are aerated by air babbles in order to raise a

DO concentration of the test sample to a saturated level. The mixture of a test sample, the buffer solution, the feed solution and water/sample is heated by an isothermal bath controlled at 30℃, and is sent to a flow cell where the microbial probe consisting of the DO probe and the microbial membrane can detect the toxicity in the sample, and is finally drained out of the system.

When a base level is measured, the buffer solution and water are mixed and monitored. When a peak level is measured, the mixture of the buffer solution, the feed solution and water is measured. The difference between the base level and the peak level is recorded as a reference output. Then, when a sample is monitored, the sample instead of water is mixed with the buffer solution, and the feed solution, and the mixture is monitored. The difference between the base level and the sensor output of the sample, i.e. defined as a span range, is compared with the reference output. If the monitor is used as a continuous system, both the buffer solution and the sample are continuously sent and mixed. The sensor output is continuously measured, and the span range or the difference between the output of the mixed sample and the previously recorded reference output, is continuously monitored. If the span range of the sample indicates 10% smaller value than the reference output, the toxicity monitoring system judges that the sample must have some toxicity and sends alarm and signal, and orders the pump to take a sample for water quality analysis. The rinse solution is used for automatic cleaning of the transfer tubes and the flow cell in order to prevent scaling and bacterial growth in them.

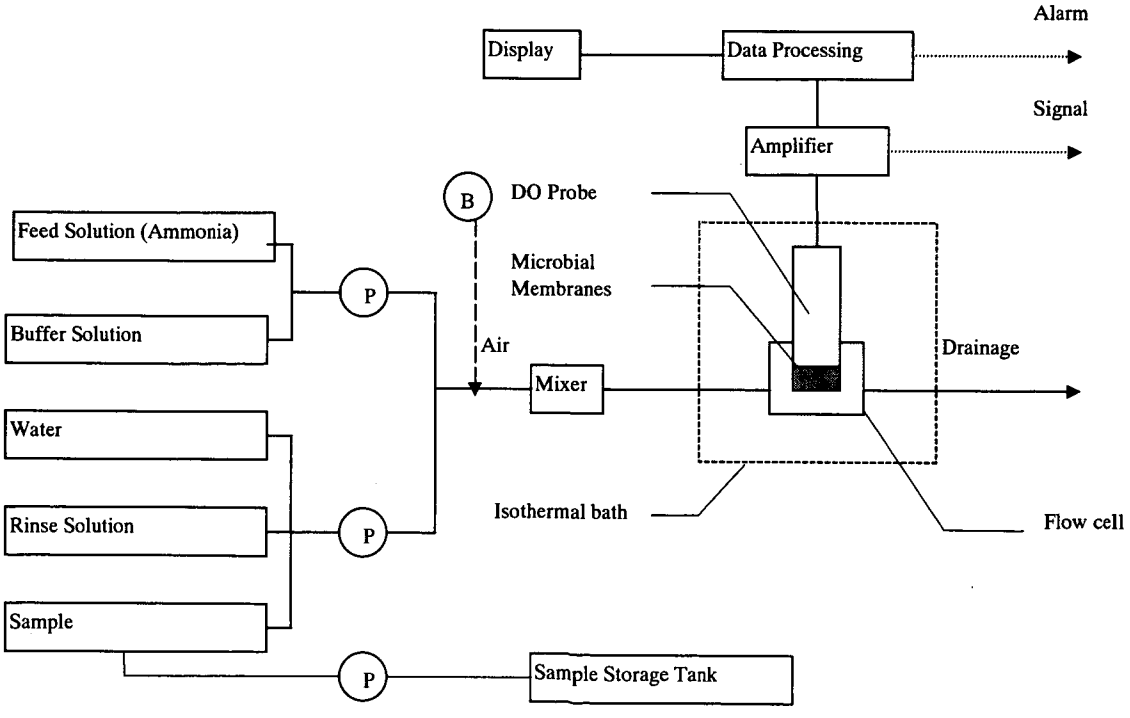


Fig. 3 Outline of the Toxicity Monitoring System

Pretreatment of River Water

A field test of detecting the toxicity in river water has been conducted at Saikachido Water Quality Monitoring Station along the Ayase River that is an urban polluted river flowing through Saitama Prefecture and Tokyo Metropolitan Area. The monitoring station is operated by Edo River Construction Office in the Ministry of Construction. River water is pumped from the Ayase River and is originally used for another monitoring system that measures water temperature, DO, turbidity and electric conductivity using physiochemical sensors called K-82S. The sample water fed to the toxicity sensor was supplied from a sampling storage tank for K-82S and was designed to be filtered through a small sand filtration system. Although the filtration system could remove suspended matters at low concentrations, clogging was occasionally observed due to their insufficient removability of suspended matters. Installation of hollow fiber membranes having 0.1 μm of the typical pore size could bring about improvement of the removability.

Field Test at a River Water Quality Monitoring Station

The developed monitoring system has been operated during more than a year. Except for several troubles of clogging of the transfer tubes that were caused by inefficacy of the sand filtration system, the monitoring system has been working properly. Fig. 4 depicts an example of the sensor outputs during September to November, 1997. The vertical axis stands for the sensor output in terms of voltage of the microbial electrode, which takes reverse order, that is, the larger the DO of the microbial membranes is, the higher the sensor output line is located in Fig. 4. The upper line represents the sensor output while the mixture of the buffer solution, the ammonia solution and the sample was continuously measured as the feed solution. The lower dot marks of ■ are the sensor output when the buffer solution without ammonia was measured for observing the base level once in a day. The sensor output had been quite stable although the base level had varied slightly. The span range in Fig. 5 that is expressed in relative value based on the reference output that was measured just after attachment of the new membrane to the microbial electrode. The span range had also varied due to the variation of the base level. In order to make assurance of the ability of detecting toxic substances, acetone was dosed to the toxicity sensor as simulation of a toxic spill accident every month. The decrease in the span range was depicted in Fig. 6, when 0.3, 0.5 and 0.8%V/V of three different acetone solutions had been dosed to the toxicity sensor for 20 minutes in turn. Although the decrease in the span range varied to some extents, the decrease resulting from acetone and the dependency of the decrease in the span range to acetone had been clearly observed for more than a month.

From early April to early May in 1997, abnormality had been observed from the responses of the toxicity monitor. The decrease of the span range had been observed as low as 5 to 25% of the reference output. The urgent surveys were conducted in April 17, 1997. River water was sampled at three upstream and downstream points of the monitoring station. All the samples were tested again using the toxicity sensor and MICROTOX™ in our laboratories for assurance.

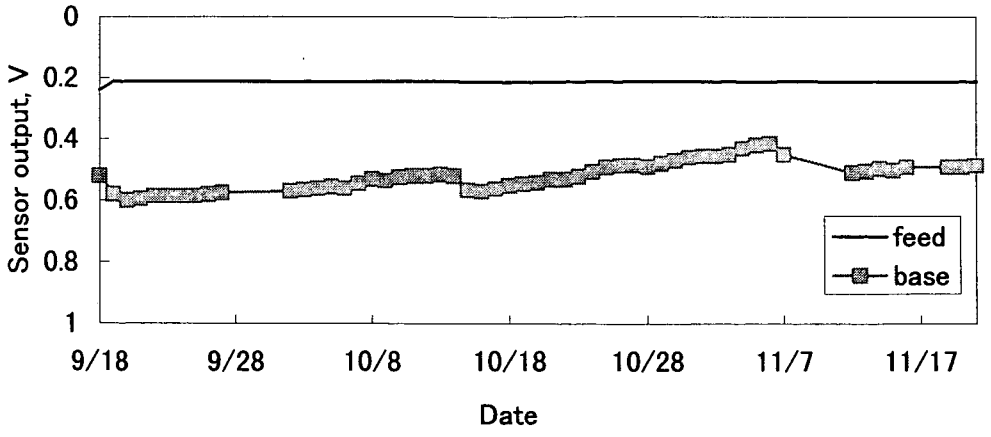


Fig. 4 Change in Sensor Output at Saikachido Monitoring Station along the Ayase River

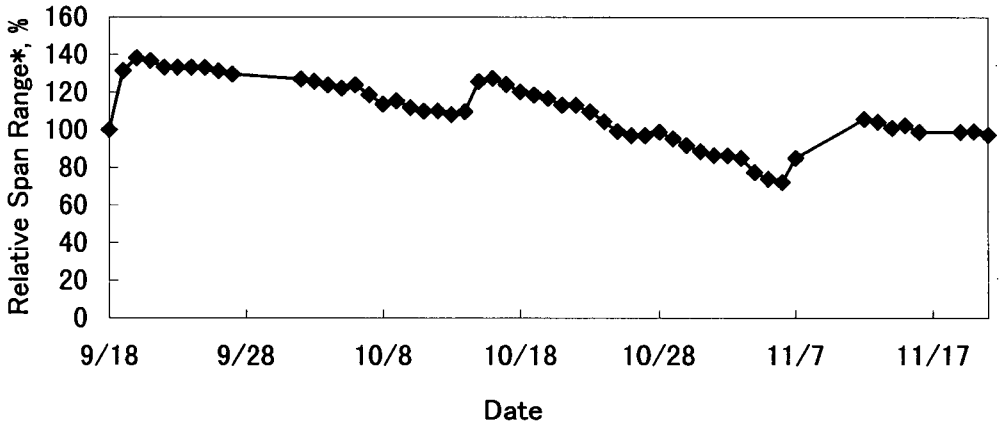


Fig. 5 Chang in Span of Outputs at Saikachido Monitoring Station along the Ayase River

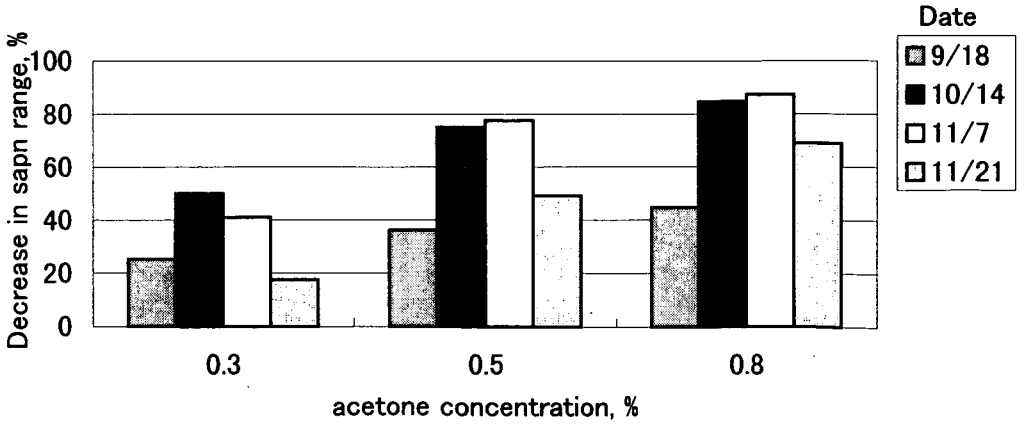


Fig. 6 Decrease in Span Range Resulting from Artificial Dosage of Acetone

The results of the toxicity tests also suggested the samples include toxic some substances because the sensor outputs decreased by 7 to 10%, while the toxicity test using MICROTOX™ indicated no toxicity. Farther investigation to pursue the cause of the toxicity has been conducted at present.

CONCLUSIONS

Bioassay is one of the most prospective ways for integrated water quality monitoring of toxic substances. From the above results, it is clear that the nitrifying bacteria assay is useful not only for evaluation on the adverse effects of toxic substances on nitrification process in wastewater treatment but also detection of the toxicity in river water. The toxicity sensor applying nitrifying bacteria can detect relatively lower concentrations of many toxic substances listed in the Effluent Water Quality Standards than the fish-based monitoring methods when the EC_{10}s of the toxic sensor are compared to the LC_{50}s of selected fishes. However, more improvement will be necessary if the detection limits of the toxicity sensor need to be raised to the Effluent Quality Standards. As the monitoring system, the toxicity sensor has showed proper function under the field test conducted in the river water quality monitoring station. This toxicity sensor and this toxicity monitoring system have already been installed in more than ten water purification plants by public water suppliers in order to watch the safety of their river source water. Active installation of the toxicity monitor to rivers and public sewerage systems is also expected in the near future.

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Session 3

Sludge Management

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PREPARATION OF ACTIVATED CARBON FROM ORGANIC WASTE SLUDGE AND ITS APPLICATION TO WASTEWATER TREATMENT

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ABSTRACT

Preparation of activated carbon (AC) from organic waste sludge and its application to wastewater treatment were examined. For resource recycling and energy conservation, preparation process was conducted using only waste sludge and surplus energy from wastewater treatment plant. AC from organic waste sludge (AC-S) could be used for upgrading the quality of effluent such as color and COD. And it could improve sludge dewatering characteristics and be used also for odor control. The adsorption performance of AC-S was not so high mainly by its high ash content. Adsorption capacity was about 1/5-1/10 as large as that of commercial AC.

KEYWORD

Activated carbon from organic waste sludge, Recycling of sludge, Carbon fixation of sludge color and odor removal, Improvement of activated sludge process.

INTRODUCTION

Generally in Osaka City Japan, waste sludge from municipal sewage treatment plant is landfilled after incineration. But now it has been a big problem to save the land to dispose. Recycling of the waste sludge has been an imperative subject.

On upgrading of the quality of wastewater effluent, color is one of the most refractory

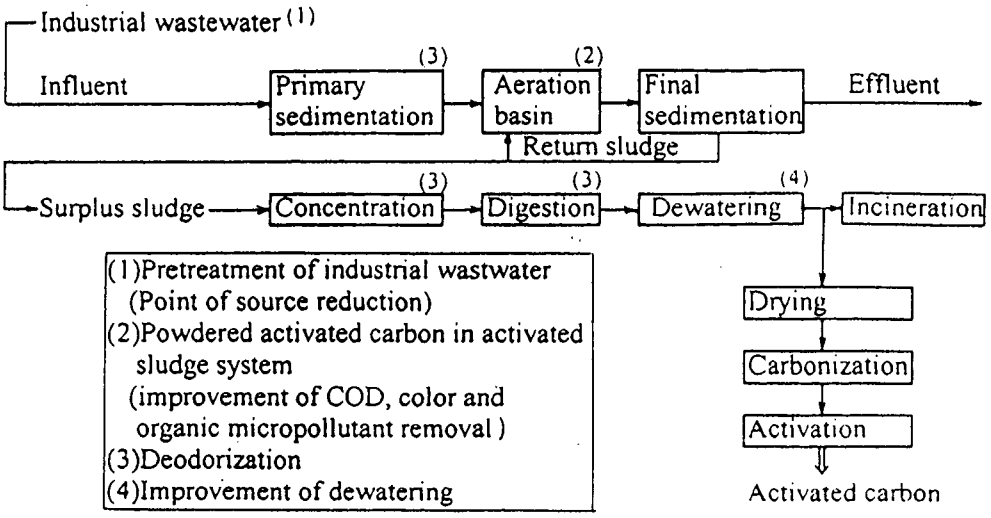


FIGURE 1 Systematic utilization of activated carbon from sewage sludge in sewage treatment system

TABLE 1 Composition and properties of organic waste sludge

Sample No.	C (%)	H (%)	N (%)	Ash content (%)	Volatile content (%)	Fixed carbon (%)	Pretreatment of dewatered sludge*		
1	26.7	4.5	3.6	44.0	49.5	6.5	C	P	D
2	22.2	3.9	3.4	52.3	45.9	1.8	V	I	D
3	22.2	4.0	3.1	52.0	47.8	0.2	V	I	D
4	18.0	3.3	2.0	62.4	45.8	(-8.2)	V	I	D
5	30.1	4.0	4.3	44.8	46.6	8.6	C	P	R
6	30.7	4.8	5.3	37.5	58.1	4.4	C	P	R
7	32.0	5.0	5.0	36.7	57.6	5.7	C	P	R
8	30.6	4.9	4.4	37.8	57.8	4.4	C	P	R
9	32.2	5.3	5.2	33.5	62.5	4.0	C	N	R
10	30.7	5.0	5.3	34.7	59.7	5.6	C	N	R

(*) Dewatering method:centrifugal(C) or vacummed(V)
Coagulant: polymer(P), lime or ferrous sulfate(I), or not added(N)
Sludge treatment: digestion(D) or raw(R)

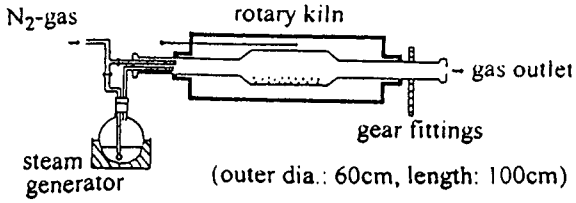


FIGURE 2 Outline of activation apparatus of activated carbon

TABLE 2 Operation condition of activation kiln

sample weight	: 25 g (dry)
activation temp.	: 550 - 950 °C
activation time	: 60 min
rate of heating	: c. a. 10°C/min
flow rate of N_2	: 500 ml/min
steam applied	: 25 g
rotation of kiln	: 2 rpm

substances to remove conventional biological treatment. Upgrading the effluent level of COD is also a problem for maintaining river and riverside environment. Revised activated sludge process such as powdered activated carbon in activated sludge process has been considered effective. Activated carbon (AC) has been considered effective for color and COD removal, but because of its high cost AC has not been popular to apply now. The main object of this study is to prepare AC from organic waste sludge and to try its application to wastewater treatment. AC is also considered effective for odor control in wastewater plant and can be used for improvement of sludge characteristics such as sedimentation and dewatering. AC has various and high potential for upgrading the wastewater treatment system. In this study, the preparation of AC was conducted only using waste sludge and surplus energy from wastewater treatment plant itself. This process could be evaluated as carbon fixation process, compared with the combustion-mineralization process.

The application of AC prepared from waste sludge (AC-S) to wastewater treatment system is shown in FIGURE 1. The raw materials are only dewatered sludge and steam, and the energy for activation is supplied from sludge incineration furnace. AC-S is applied to wastewater treatment system and also to pretreatment of industrial wastewater containing color.

MATERIALS AND METHODS

Preparation of Activated Carbon from Organic Waste Sludge

Organic waste sludge was dried, carbonized and activated by steam. The composition of waste sludge depends on the characteristics of influent wastewater and dewatering process. Especially whether dewatering process uses inorganic coagulant or not is related to the ash content which affects the activation process and the quality of AC-S. The composition of waste sludge as raw material of AC was examined by elemental analysis (C, H, N) and industrial analysis of coal (JIS M 8802). TABLE 1 showed 10 kinds of sludge samples from Osaka municipal sewage treatment plants. Composition and properties depended mainly on pretreatment process. Thermogravimetric analysis of the sample was also conducted.

Batch-type rotary kiln shown in FIGURE 2 was used for activation. After drying 4 hours at 110℃, dried sludge sample was pulverized to 1-3 cm particles and put into the kiln. According to the conditions shown in TABLE 2, AC was prepared. Steam was applied with N_2 gas when the temperature of the kiln attained to that for activation.

Examination of Activated Carbon from Waste Sludge

Various adsorption tests were performed on AC-S. Test items were iodine number in

accordance with JIS K 1474 and methylene blue decoloring ratio. Specific surface area and pore distribution were measured by N_2 gas adsorption method. On the application to wastewater treatment, mainly AC prepared from sludge sample 1 (AC-S-1) in TABLE 1 was used. Except odor control test, commercial grade powdered activated carbon A (AC-A, Futamura Chemicals Co.) was used as a control. In odor control test, commercial coconut-based and impregnated AC were used.

Application of Activated Carbon from Waste Sludge to the Wastewater Treatment System

Adsorption test on dyestuffs was performed to examine the adsorption capacity on color from industrial wastewater. Adsorption isotherms were obtained on 6 dyestuffs including acid-, direct-, reactive- and basic-type ones at 25℃. Freundlich's adsorption constants were compared with those of AC-A.

On the improvement of effluent quality on color, tinted effluent by industrial wastewater from sewage treatment plant was submitted to decolorization test by AC. Adsorption spectra in visual region of the effluent sample was measured before and after adsorption.

Improvement of COD removal in the aeration basin was also evaluated. It is known effective to add powdered AC (PAC) into the last part of the aeration basin to remove color in the sewage treatment system without installing new adsorption facilities[1]. The effects of addition of PAC (pulverized to particles $<74\,\mu$ m) to the aeration basin were examined using a batch-type reactor. The removal rate of COD were measured for 24 hours.

Vacuum filtration test of concentrated activated sludge was performed to check the improvement of dewatering characteristics of activated sludge. The effect of addition of AC-S was compared with AC-A.

On adsorption test of odorous substances, concentration change of each substance in adsorption chamber (10L volume) was measured at room temperature. Typical 12 kinds of odorous substances that were suggested to be discharged from sewage treatment plant were used for test.

RESULTS AND DISCUSSIONS

Properties of Activated Carbon from Organic Waste Sludge

Sewage sludge sample used in this study had high volatile content and low fixed carbon content as shown in TABLE 1. Carbon and ash content varied with the method of sludge conditioning (digested or not, centrifuged or vacuummed, kind of coagulant).

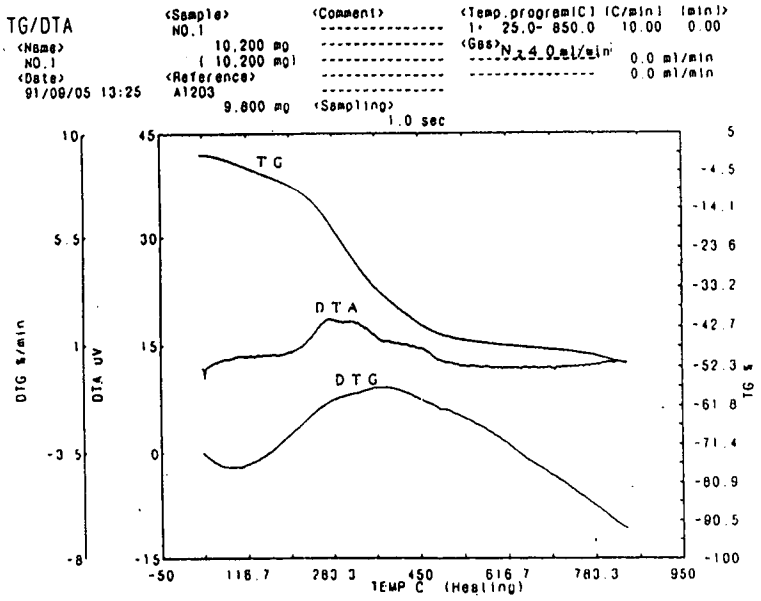


FIGURE 3 Thermogravimetry (TG,DTA) of sewage sludge (sample 1)

TABLE 3 Characteristics of activated carbon from sewage sludge

AC-S No.	Specific surface area (m^2/g)	Pore volume (ml/g)	Average pore radius (nm)	Iodine number (mg/g)	MB decoloring ratio (%)
1	97	0.13	2.66	185	40.6
2	55	0.07	2.48	143	17.7
3	7	0.03	8.28	71	2.1
4	7	0.02	5.69	255	37.2
5	54	0.06	2.09	93	13.4
6	78	0.10	2.52	151	25.8
7	69	0.07	1.93	115	22.7
8	48	0.05	2.27	105	17.9
9	50	0.07	2.67	123	17.9
10	39	0.05	2.58	60	12.8
R	<5	<0.01	-	<10	<0.1

AC-S: Activated carbon from sewage sludge
MB: Methylene blue R: Ignition residue

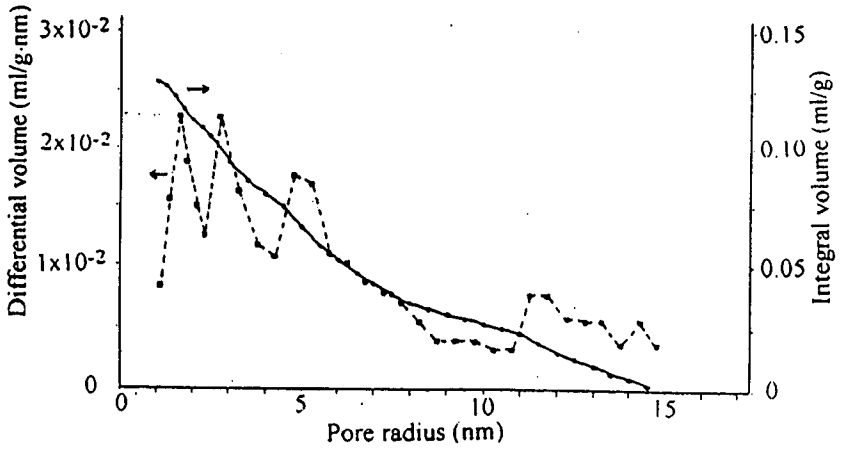


FIGURE 4 Pore size distribution of activated carbon from sewage sludge (sample 1)

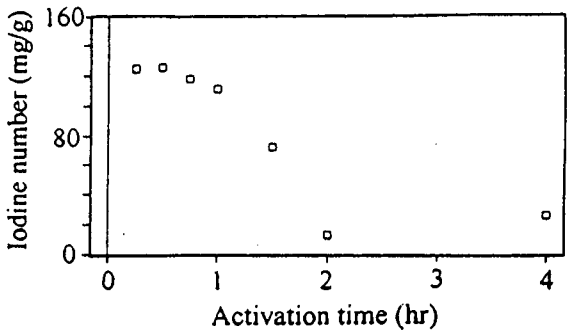


FIGURE 5(a) Relationship between activation time and iodine number (activation temp. :850° C)

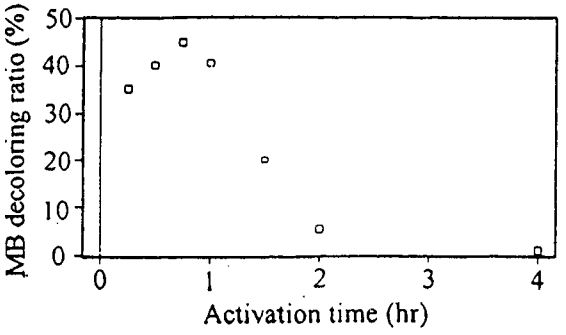


FIGURE 5(b) Relationship between activation time and methylene blue (MB) decoloring ratio (activation temp. : 850° C)

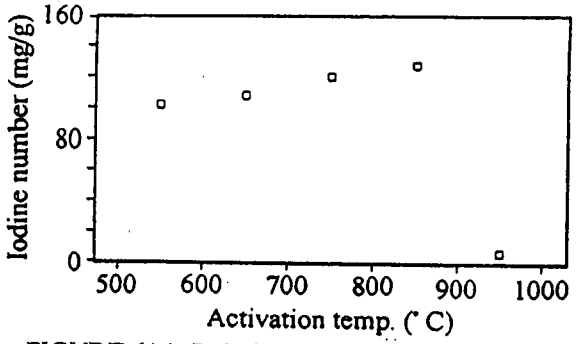


FIGURE 6(a) Relationship between activation temperature and iodine number (activation time : 1 hr)

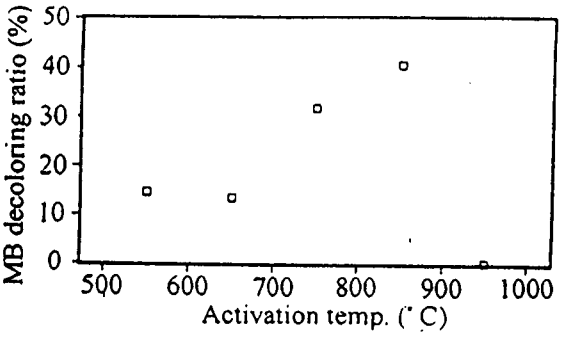


FIGURE 6(b) Relationship between activation temperature and methylene blue (MB) decoloring ratio (activation time : 1 hr)

TABLE 4 Freundlich's adsorption constants on activated carbon from sewage sludge (25℃)

Color Index	AC-S-1		AC-A	
	k	1/n	k	1/n
Acid Red 88	37.5	0.0971	219	0.139
Acid Orange 7	27.1	0.0696	227	0.0848
Direct Violet 51	21.1	0.122	71.4	0.153
Reactive Blue 2	15.8	0.0455	25.9	0.295
Reactive Red 221	9.05	0.212	<0.01	>10
Basic Blue 9	20.0	0.0397	231	0.0953

AC-S-1: Activated carbon from sewage sludge sample 1
AC-A: Commercial activated carbon

Vacuum dewatered sludge had relatively low carbon and high ash content because they contained ferrous sulfate or lime as dewatering agents. It was considered difficult to get high performance AC from these samples. Centrifugal dewatered sludge had relatively high carbon content because polymer type coagulant was used as dewatering agent. FIGURE 3 showed the characteristics of thermal analysis of sewage sludge sample 1. The sharp decrease of sample weight at 200-350℃ suggested high volatility and low fixed carbon content compared with those of conventional raw material of AC. The properties of AC-S were shown in TABLE 3. Activation was performed at 850℃ for 60 minites in this case. Compared with ignition residue of the sample, AC prepared from sample 1 (AC-S-1) revealed a significant adsorption capacity by activation. Considering on the results of specific surface area, pore volume, iodine number and methylene blue decoloring ratio, adsorption capacity of AC-S was about 1/10 level compared with that of commercial AC-A. Judging from TABLE 3, properties of AC depended on the conditioning process of the sludge. AC-S prepared from digested sludge by centrifugal dewatering using polymer-type coagulant showed relatively desirable values as AC.

Pore distribution curve on AC-S-1 was shown in FIGURE 4. Micropore (radius <2nm) which was generally much developed in commercial AC did not develop sufficiently, but the mesopore (radius 2-10nm) relatively developed and pore distribution curve shown broader peak compared with that of commercial AC.

FIGURE 5 and 6 showed the effect of activation time and temperature on iodine number and methylene blue decoloring ratio. Optimum condition for activation was not so clear but was considered the temperature was about 850℃ and the time was about 45 minutes.

Application to the Wastewater Treatment

TABLE 4 showed the Freundlich constants K and 1/n on adsorption 6 dyestuffs at AC-S-1 at 25℃. FIGURE 7 showed the adsorption isotherm on C.I. Acid Red 88. Judging from the K value as an index of adsorption capacity, AC-S-1 revealed adsorption capacity ranged from 1/2-1/11 as large as that of AC-A. And it was worth noting that AC-S-1 could adsorb C.I. Reactive Red 221 more effectively than commercial AC-A. It was supposed that this was resulted from the relatively high mesopore volume of AC-S-1.

FIGURE 8 showed the change of adsorption spectra in visual region on secondary treated sewage wastewater. In case of AC-A, the color of wastewater is fully removed by 100mg/L addition, while in case of the AC-S-1, it needed more than 300mg/L to remove color sufficiently.

On the improvement of COD removal in the aeration basin, COD removal rate was measured in the batch reactor as shown in FIGURE 9. After 24 hours effluent COD

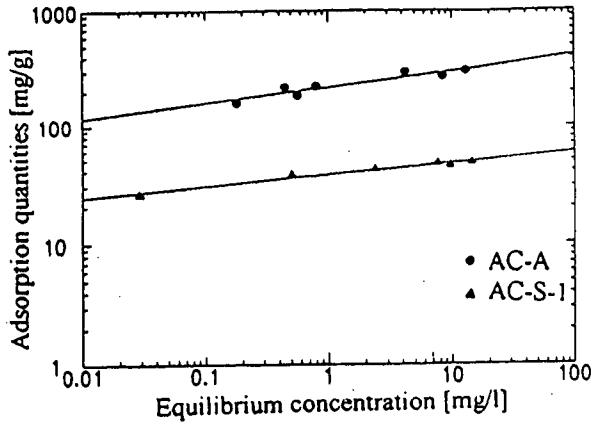


FIGURE 7 Adsorption isotherm of dye (C.I. Acid Red 88) on activated carbon from sewage sludge (25° C)

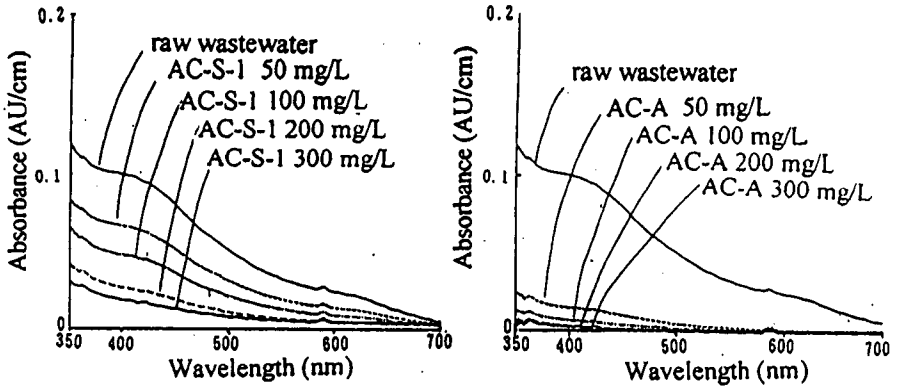


FIGURE 8 Decoloring of wastewater by activated carbon from sewage sludge

AC-S-1: Activated carbon from sludge sample 1
AC-A: commercial activated carbon (A)

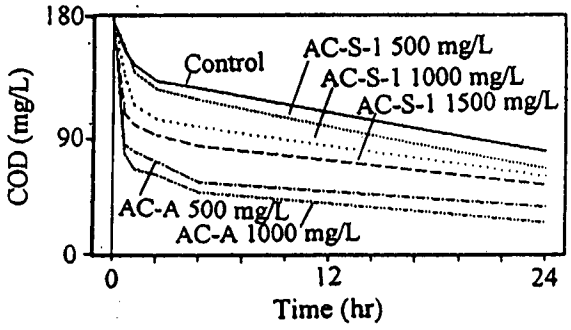


FIGURE 9 Improvement of COD removal by activated carbon

AC-A: commercial activated carbon (A)
AC-S-1: Activated carbon from sludge sample 1

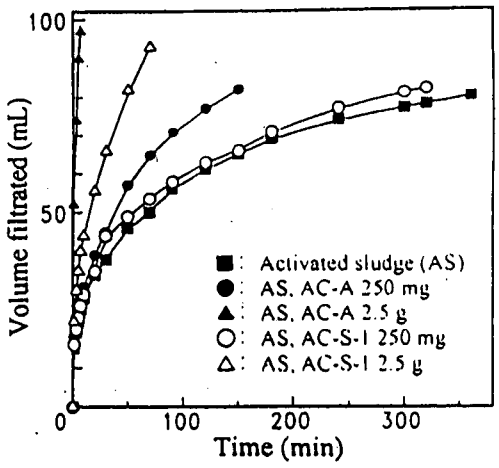


FIGURE 10 Improvement of filtration rate on surplus sludge by activated carbon (MLSS ≒ 2000 mg/L)

AC-A: commercial activated carbon (A)
AC-S-1: Activated carbon from sludge sample 1

TABLE 5 Removal ratio of odorous substances by activated carbon from sewage sludge (comparison with commercial adsorbents) unit (%)

adsorbents / odorous substances	AC-S-1	commercial activated carbon			
		coconut shell based	impregnated A	impregnaged B	impregnated C
ammonia	89.6	75.6	96.4	-	95.8
acetaldehyde	72.0	71.4	-	-	-
trimethylamine	58.0	89.1	98.2	-	98.3
methylmercaptan	85.9	95.0	99.4	-	99.2
dimethyl disulfide	23.1	79.0	85.6	-	73.3
hydrogen sulfide	81.7	90.0	100.0	-	98.2
benzene	75.6	96.6	86.7	99.0	98.1
styrene	81.3	88.9	88.9	64.7	55.0
acetic acid	86.7	-	-	94.4	96.2
propionic acid	87.5	88.5	85.7	90.0	88.0
n-butyric acid	76.7	54.8	-	-	-
iso-valeric acid	60.0	72.2	60.0	75.0	45.0

AC-S-1: Activated carbon from sewage sludge sample 1

decreased less than 1/2 of that of the initial COD concentration when activated sludge was 2500mg/L and AC-S-1was 500mg/L, while it decreased the level of 1/2 of the initial COD only by activated sludge. The addition of AC was considered effective for upgrading the effluent water quality of COD.

Time-course of the filtration rate of sludge sample were shown in FIGURE 10. By adding AC-S-1 or AC-A, the filtration time to get cake was considerably shortened. It suggested that AC-S-1 worked as a dewatering agent, while the improvement of dewatering rate was not so effective as that of AC-A.

On the removal of odorous substances, adsorption chamber test was performed on each substance and the residual percent of odorous substances after 60 minutes were shown in TABLE 5. AC-S-1 could adsorb various kind of odorous substances to some extent which were acidic or alkaline, compared with a reference sample. This means that AC-S-1 was relatively suitable for odor control from sewage treatment plant, which contained various kinds of odor.

SUMMARY

1. Preparation of AC from organic waste sludge was performed, using only wastes sludge and surplus energy from municipal sewage treatment plant.

2. AC from sewage sludge had a capacity to remove color in wastewater and improve COD in conventional treatment. AC from sewage sludge could also be useful for improvement of sludge dewatering charasteristics and for odor control.

3.The adsorption capacity of AC from wastes sludge were not so high. It was about 1/5 ~1/10 as large as that of commercial AC. High ash content and low fixed carbon content were considered main reason of low adsorption capacity.

4.This process could be evaluated as global warming control technology, because the organic content of the waste sludge was not converted to carbon dioxide or methane but partly fixed as carbon.

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PREUSSAG
NOELL

Gasification - the Thermal Processing for Sludge Treatment without Residues

7th Japanese-German Workshop on Waste Water and Sludge Treatment
Kyoto, Japan, December 10-12, 1997

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0 INTRODUCTION

The Preussag Noell Group is one of the major suppliers of enviromental protection technology in Europe. We offer processes for controlling water, air and soil pollution, for waste treatment and recycling and we also construct the relevant plants worldwide.

The Noell-KRC Energie- und Umwelttechnik GmbH is responsible for an important part of our wide range of enviromental technology services. We develop construct advanced waste processing systems for the biological, mechanical and thermal treatment of waste and residual materials. Furthermore we build plants for cleaning flue gases that result from the incineration of waste and residual materials.

Noell-KRC has extensive eyperience in the area of the conventional thermal treatment of sewage sludge, waste and residual materials, and can supply numerous references for the construction of incinerating systems.

1 THE THERMAL RECOVERY OF SEWAGE SLUDGE BY GASIFICATION

Approximately 60 million tons of sewage sludge (total solids approx. 5%) are produced in the Federal Republic of Germany every year. Only small quantities of these sewage sludge undergo thermal recovery treatment - the majority continues to be disposed of in landfill sites or is be used in the agrculture. The disposal of sewage sludge through usage in agriculture is possible only conditionally, and is steadily decreasing in acceptance due to the large concentrations of hazardous substances contained in some sludges. Sewage sludge is often contaminated by heavy metals and hazardous organic compounds as well. The problems of waste disposal will no longer be solvable in the future without the use of thermal recovery methods.

The primary goal of thermal recovery processes for sewage sludge is the safe disposal of hazardous substances. In particular, this refers to the destruction of organic compounds such as dioxins and furans, as well as the inerting of slags. This means that the mineral sewage sludge components contained in the slags are melted during thermal treatment to the extent that the non-volatile substances (heavy metals) are bound in the non-leaching mineral matrix. A further aim of the sludge disposal is the utilization of sewage sludge to generate electrical energy or thermal energy and to produce residual materials which can be introduced to materials recovery/recycling systems.

Although modern sewage sludge incineration plants are able to meet current requirements of the BImSchV, there are conceptual disadvantages in the

implementation of the aforementioned goals. The NOELL CONVERSION PROCESS was developed based on the increasingly strict standards for environmentally-safe waste sewage sludge recovery (Fig. 1). This process combines a mechanical/thermal conditioning process with pressurized gasification. While large quantities of flue gases are produced during the incineration, pressurized gasification produces only a small amount of synthesis gas. This means much smaller tank size requirements for gas cleaning, for example. Desulphurization of the synthesis gas produces an easily marketable product - sulphur - instead of the gypsum that is produced by the flue gas cleaning processes used for incineration plants.

At the high gasification temperatures of 1400 - 1700 °C, a slag is produced which can be used in building materials, like the slags produced with slag-type firing processes. Although this type of incineration plant is rarely being built or operated at the present, the demand for this type of material still exists - the utilization of this type of slag is therefore guaranteed.

A further advantage of the high temperatures is the complete destruction of hazardous organic substances such as dioxins and furans. The lack of oxygen in the synthesis gas as well as the rapid passing of the critical temperature window during gas cooling prevents DeNovo synthesis of the dioxins and furans. Therefore we accepted a high emission standard given by the local government in our permission to build and run the plant (Fig. 2).

2 DESCRIPTION OF THE GASIFICATION TECHNOLOGY

The term "gasification" is understood in theory as the conversion of every carbon atom in the fuel to CO. In contrast, with incineration processes theoretically every carbon atom is converted to CO_2.

The basic chemical reactions for the gasification of carbon are as follows:

(1) $C + O_2 = CO_2$

(2) $C + CO_2 = 2\ CO$ Boudouard Reaction

(3) $C + H_2O = CO_2 + 2\ H_2$

as long as methane or other hydrocarbons are not formed (Fig. 3).

An environmentally-friendly gasification process should have a high conversion rate of the input fuel. The conversion is represented by the efficiency of gasification carbon and is calculated as follows (Fig. 4):

$$Carbon\ conversion = 1 - \frac{carbon\ in\ gasification\ residue}{carbon\ in\ solid\ feedstock}$$

Processes for gasification of solid carbonaceous materials may be classified according to the method of bringing solid and gaseous reactants into contact. Types of gasification reactors are based on a fixed bed, a fluidised bed, an entrained flow or a molten bath.

2.1 Fixed-Bed Processes

The beginning of the fixed bed gasification in the previous century was closely associated with the metallurgical industry. The gas produced by gasification is used to heat hearth refining plants and coke plant furnaces, as well as for the conditioning of coke oven gas to manufactured gas (Fig. 5). The requirements placed on the input fuels - with regard to grain size, good flow properties of the bulk material, and thermal stability - limit the range of application of fixed bed gasification.

2.2 Fluidised-Bed Processes

The development of fluidised-bed processes with the Winkler generator eliminated the weak points of fixed-bed gasification and led until very recently to the construction of large gasification units at high gasification pressures, such as the development of the HT-Winkler process at Rheinbraun beginning in 1970, for example (Fig. 6). The limiting factor in the technical implementation of the fluidised-bed gasification is, however, the necessity of remaining at temperatures below the ash softening point. The necessarily low gasification temperatures result in a poor conversion of carbon, which makes the secondary incineration of residues necessary.

2.3 Entrained-Flow Processes

The disadvantages of the aforementioned processes are eliminated with entrained-flow gasification. The large-scale introduction of this gasification principle took place in 1950 with the Koppers-Totzek process, which was used in a number of plants (Fig. 7). The entrained-flow gasification process was developed further by Texaco, Krupp-Koppers, Shell, Dow, and Preussag Noell. The minimal requirements with regard to fuel properties, the obtainable synthesis quality and the transformation of inorganic components contained in the fuel into a non-leaching vitreous granulate prove that the entrained-flow gasification process has clear advantages over other processes.

2.3.1 The Gasification Reactor of the Noell Conversion Process

The gasification reactor is designed to comply with the special reaction conditions of the Noell Conversion Process (Fig.8). The reactor consists of a pressure-bearing external shell and an internal refractory-lined cooling jacket. The refractory-lined cooling jacket forms the contours of the reaction space and protects the external shell from the high-temperature flue gases. The inner surface is equipped with anchors for the silicon carbide refractory lining. This funnel serves as the transition to the slag discharge chamber, and the connection to the downstream plant component.

The actual gasifying process, i.e. the partial oxidation with technically pure oxygen in a flame reaction, occurs within a cylindrical reaction space, the contours of which are formed by a water cooled wall. Organic substances are decomposed in a flame reaction, producing a gas rich in CO and H_2 and free of high order hydride carbons.
The molten mineral compounds of the feed stock coats the refractory lining of the cooling jacket, forming a thin, protective layer. This coating both the refractory lining and tube walls against damage and wear.
The liquid slag and the crude synthesis gas jointly leave the reaction chamber trough a central opening located at the base. In the quench zone, located beneath the reaction chamber, the gas and the slag are cooled directly by quench water injected via nozzles.

3 PILOT PLANT FREIBERG

3.1 Testing Design in Freiberg, Germany

To demonstrate the capabilities of this type of plant, Preussag Noell has built a pilot plant in Freiberg/Germany that operates according to the NOELL CONVERSION PROCESS (s. Fig. 9).

The plant was designed for a throughput of 0.5 Mg/h of sewage sludge or municipal waste (based on concentration of total solids). Freiberg/Saxony was selected as the location since the existing infrastructure from an older pilot plant could be used for this new plant.

The development of the NOELL CONVERSION PROCESS is based on years of experience with pressurized entrained flow gasification used for the refining of low-grade brown lignite and the pyrolysis of hazardous waste at Salzgitter.

Gasification takes place at high pressure under the addition of technically pure oxygen. The pilot plant at Freiberg was designed for a pressure of 2.6 MPa or 0.6 MPa.

3.2 Acceptance, conditioning, feeding and gasification of sewage sludge

As the first step of the thermal recovery process, the initially dewatered raw or digested sewage sludge is dried and ground to a grain size of < 500 m before it is fed to the entrained flow gasification (Fig. 10).

The fully automatic dust feeding system of the gasifier functions according to the principle of the dense phase pneumatic conveying developed by Noell. The essential characteristic of this process is the transportation of large quantities of dust (250 - 450 kg/m^3) with small quantities of carrier gas and low rates of abrasion.

The gas first falls from the first funnel-shaped tank into a pressurized lock until it is filled. The dust is then flushed with inert gas. The dust then falls into a conveying hopper at the same pressure, in which the base of the container forms a fluidized bed through the injection of inert gas. The dust is conveyed continuously to the burner at the head of the gasifier reactor via a conveyor pipe which reaches into the fluidized bed.

Dust as well as oxygen is fed to the top of the pressurized water-cooled burners. The reactive elements are ignited by a pilot burner flame as the enter the gasification space, and are converted in a heterogeneous, autothermal flame reaction.

A reducing atmosphere is present as a result of the substoichiometrical introduction of oxygen, which results in the formation of a raw gas rich in CO and H_2. Sulphur is converted into H_2S and COS; chlorine forms HCl; fluorine forms HF; and the nitrogen introduced with the other substances forms N_2, NH_3 and HCN.

The use of technically clean oxygen for gasification - instead of air - has the following advantages:

- the exclusion of environmental nitrogen results in the thermal relief for the downstream process stages and therefore savings in energy and the improvement of efficiency levels;
- the volume of gas to be cleaned is reduced considerably, which in turn reduces the operational and investment costs required for gas cleaning.

The hot raw gas and liquid slag enter the quenching space through a reduced opening; the gas is quenched to a temperature of approx. 200 °C via water injection.

The slag falls into a quenching water bath at the base of the tank. The temperature shock causes the slag to form a glass-like granulate which settles in the form of a sediment, and which is discharged from the reactor at regular intervals. The washed and dewatered slag granulate can be utilized further as a high-quality substance due to its mechanical and chemical stability.

The raw synthesis gas, which is saturated with water steam, is discharged continuously from the reactor, together with excess quench water and the fine-grain slag.

3.3 Gas and water cleaning systems

In the subsequent scrubbing system the raw gas is separated from the solids-laden water and passes through a scrubbing stage consisting of a Venturi scrubber and hydrocyclone. In a second scrubbing stage, the solids are removed from the water and the water is returned to the quenching reactor.

For the desulphurization process, it is necessary to convert the trace COS in the raw gas cyclically within a fixed bed hydrolysis reactor to form H_2S, since COS cannot be removed in the subsequent cleaning stages. Likewise, any nitrogen contained in the raw gas in the form of HCN reacts in the hydrolysis reactor to form NH_3.

The desulphurization of the raw gas takes place using a direct oxidation process. After cooling and removal of the ammonia via water injection, the raw gas flow is directed to a contact reactor, where the H_2S is oxidized to form elementary sulphur using an iron chelate solution.

The clean synthesis gas is removed at the top and fed to the steam generator. The scrubbing solution is released in a regenerator, and the wet sulphur settles as sediment. After filtration, a high-quality sulphur cake is formed.

Due to the size of the plant, the pilot plant at Freiberg is not currently designed for wastewater-free operation. Hazardous substances precipitate out or are destroyed in several wastewater cleaning stages. The recovered water is fed to the sewage system if not needed for other purposes.

The ammonia contained in the fume concentrate from the sewage sludge drying process is removed with steam in a stripping column. The resulting NH_3-enriched water (25% NH_3) can be utilized in industrial plants. The quantities of NH_3-enriched water produced at the pilot plant in Freiberg are so low, however, that it can be returned discontinuously to the gasification process.

Metals, heavy metals, cyanide and ammonia are found in the quenching and scrubbing water from the gasification process, all of which must be removed in a wastewater cleaning stage. The following steps are carried out:

Fe (II) ions are oxidized continuously to form Fe (III) ions by introducing air; metals and heavy metals are precipitated out by adding precipitating agents; cyanide is detoxified to ammonia and carbonate via the batch-wise addition of oxidation agents.

The precipitates are discharged and filtered, and the sludge cake which has formed is emplaced in a special landfill site as the single unrecyclable substance.

4 EXPERIENCES IN THE OPERATING OF THE PILOT PLANT

Various sewage sludge types have been investigated since Autumn 1996 with respect to sewage sludge disposal by means of gasification while producing virtually no residues and ensuring the greatest possible recovery of energy.
The main areas of investigation were:

- Emissions
- Quality of the products
- System performance

The types of communal sewage sludge investigated covered a range of between "high concentrations of heavy metals" to " usable in agriculture " (Fig. 10). A dioxine load in the sludge clearly excludes agricultural applications.

4.1 Emissions

The investigations in the area of emissions were based on fulfilling the strict limiting values for dioxines and furans and mercury emissions as specified by the license. The values determined within the scope of an official acceptance measurement proved that the Noell Conversion Process maintains emission levels below the relevant limiting values without requiring expensive flue gas cleaning systems.
In three comparison measurements made at the stack, all measured levels were well below the officially stipulated dioxine limiting value (TE) of 0.01 ng/m^3 STP. The mercury emission levels (at < 0.001) were well below the required limiting value of Hg < 0.005 mg/m^3 STP (Fig. 10).

4.2 Quality of the products

The quality of the Noell Conversion Process products depends primarily on the synthesis gas and the glassified slag. The composition of the gas produced is of a purity that allows it to be used without restriction for power applications in gas motors, gas turbines, gas boilers, or as a raw chemical (Fig. 13).
The glassified slag is of high quality and can be used as a concrete additive in the building materials industry (Fig. 14). Relevant building material products show its good properties.
Since sulphur is present in the sewage sludge (approximately 1% mass, based on the total solids), it is also viewed as an essential product of the Noell Conversion Process. The sulphur qualities produced during the gas cleaning process are also utilizable (Fig. 13).

4.3 System performance

In addition to statements on the suitability and operational safety of individual components, investigations were also carried out under the aspect of system performance, i.e. which practical applications exist for improving the overall energy balance. The possibility of the energy-related coupling of various heat generators and heat consumers was investigated intensively. One area of emphasis during these investigations was the coupling of the sludge drying stage with the waste heat flow from the gasification reactor. Currently available results with selected sludge drying units show that almost the entire energy required for drying can be provided by the waste heat from the gasification process. Detailed results will be presented at the conclusion of the project in June 1998.

5 CONCLUSION

Based on the large-scale pilot plant constructed at the Freiberg site as well as previously completed investigations, it was possible to show clearly that the following results can be obtained through the thermal treatment of different sewage sludge types by means of the Noell Conversion Process:

- Destruction of organic compounds
- Emission of PCDD/F (TE) < 0.01 ng/m^3
- Heavy metals bound in a non-leaching glassified matrix
- Emission of Hg < 0.001 mg/m^3
- Sulphur recovered in usable quality
- Synthesis gas can be used in gas motors, gas turbines in boilers or as raw chemical substance

As an innovative thermal treatment process, the Noell Conversion Process has laid the basis for the mid-term replacement of current treatment processes.

6 APPRECIATION

We would like to thank the BMBF for their financial support of the project "Entwicklung eines geschlossenes Konzeptes zur thermischen Verwertung von Klärschlämmen mittels Flugstromvergasung" [Development of a closed design for the thermal recovery of sewage sludge using entrained flow gasification]- Research project 02WS9426/0.

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7.2 Figures

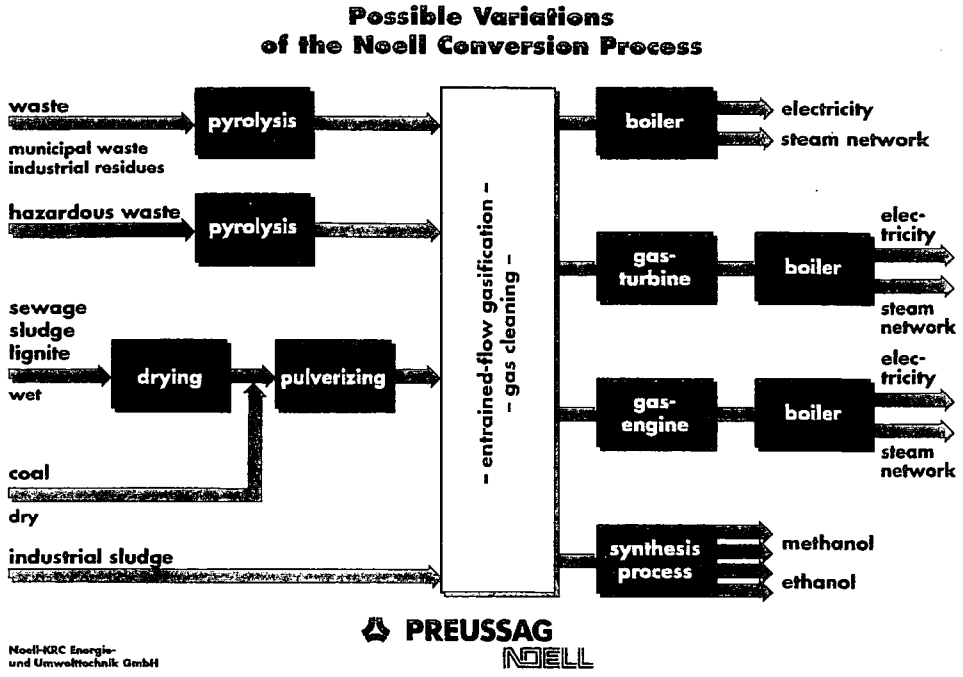


Fig. 1: Variations of the Noell Conversion Process

Development of Emission Values in Germany

Components	Emission Limits referring 11% O2 in the flue gas			
	TA - Luft 1974	TA - Luft 1986	17. BImSchV 1990	NCP -Freiberg 1995
Dust mg/m^3	100	30	10	10
Hg mg/m^3	20	0.2	0.05	0.005
CO mg/m^3	1000	100	50	50
Total C mg/m^3	--	20	10	10
HCl mg/m^3	100	50	10	1
SOx mg/m^3	--	100	50	50
NOx mg/m^3	--	500	200	200
PCDD/F (TE)	--	reduction in general	0.1 ng/m^3	0.01 ng/m^3

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Fig. 2: Development of Emission Values in Germany

Basic Chemical Reaktions for the Gasification of Carbon

(1) $C + O_2 = CO_2$

(2) $C + CO_2 = 2\,CO$ (Boudouard Reaction)

(3) $C + 2\,H_2O = CO_2 + 2\,H_2$

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Fig. 3: Basic Chemical Reaktions for the Gasification of Carbon as long as Methane or other Hydrocarbons are not formed

Efficiency of Gasification Carbon

$$\text{Carbon conversion} = 1 - \frac{\text{carbon in gasification residue}}{\text{carbon in solid feedstock}}$$

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Fig. 4: Efficiency of Gasification Carbon

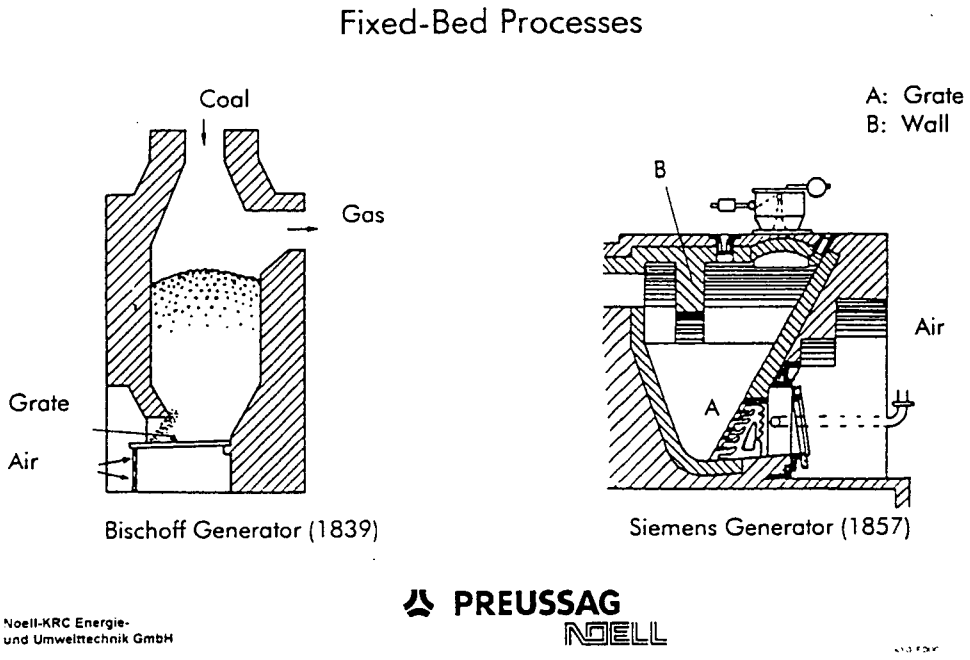


Fig. 5: Fixed-Bed Processes

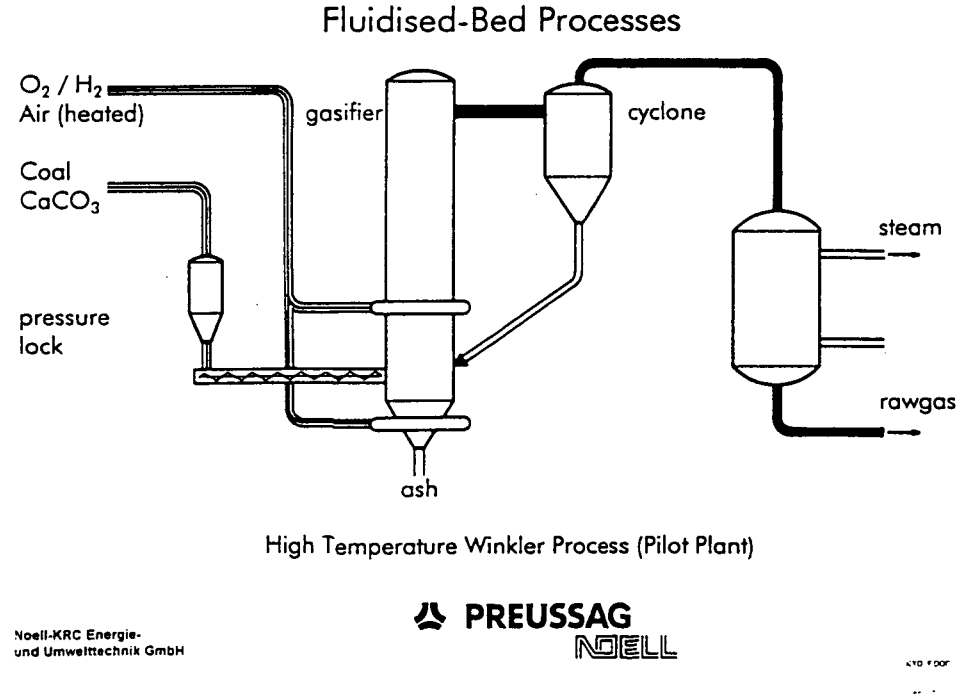


Fig. 6: Fluidised-Bed Processes

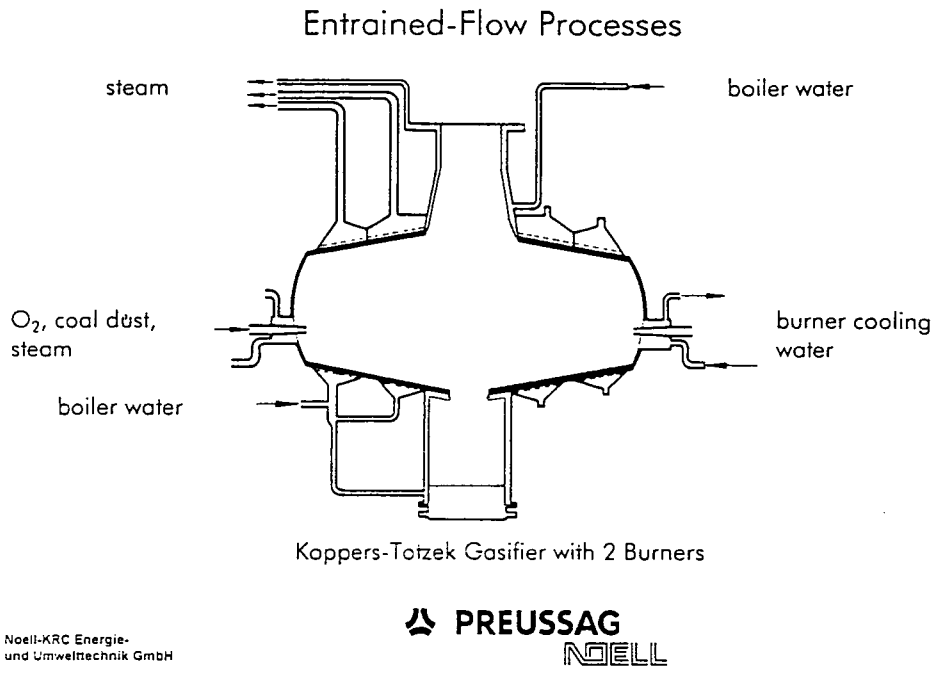


Fig. 7: Entrained-Flow Processes

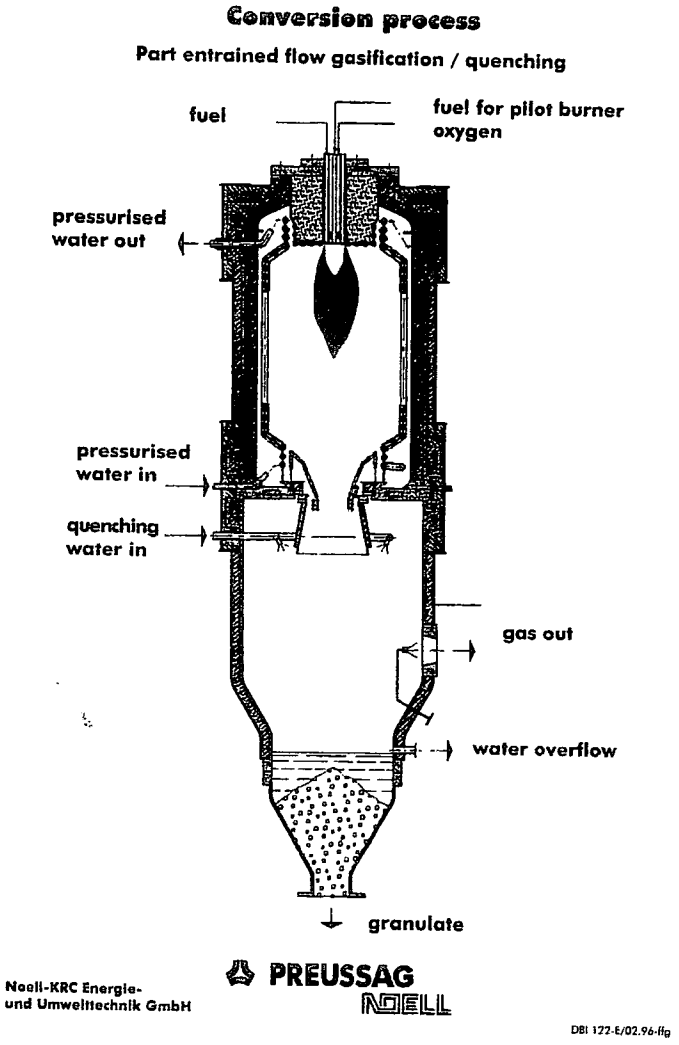


Fig. 8: The Gasification Reactor of the Noell Conversion Process

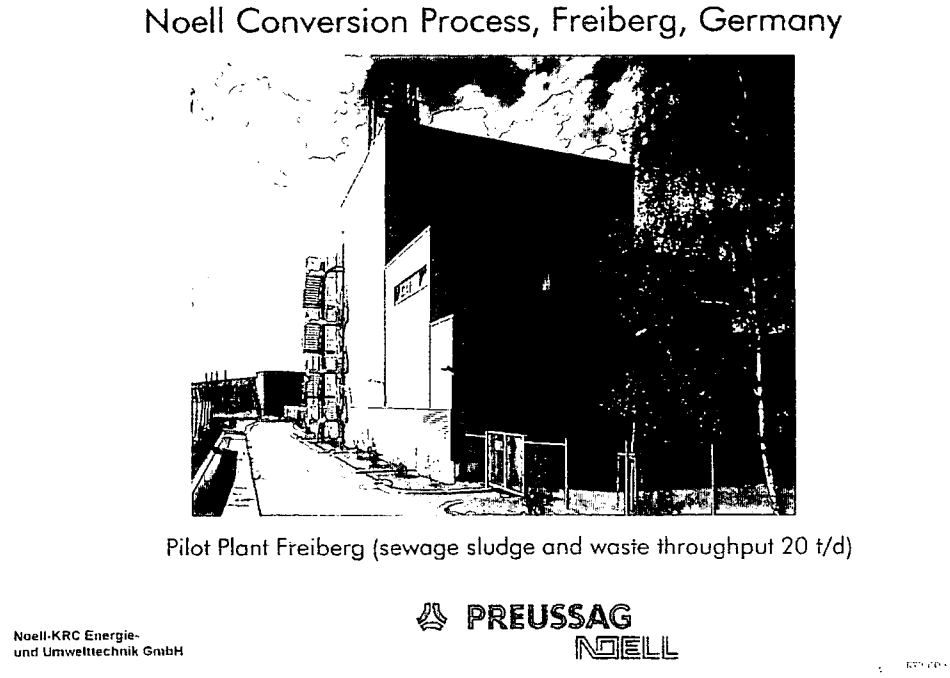


Fig. 9: Noell Conversion Process, Pilot Plant Freiberg, Germany

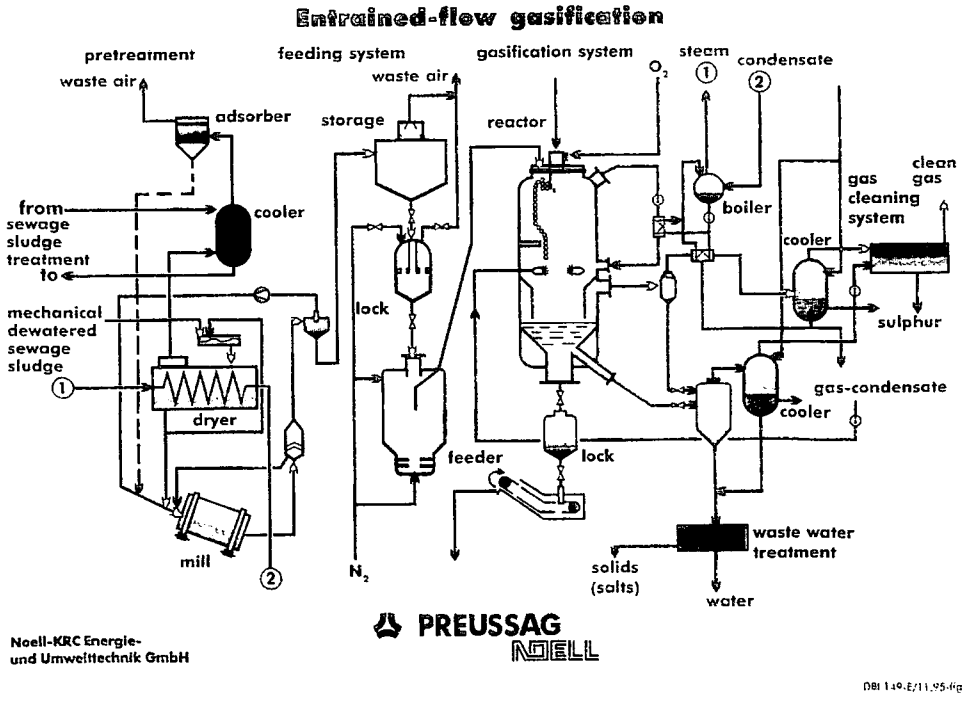


Fig. 10: Flow Diagram of Entrained-Flow Gasification

Analysis of Different Sewage Sludges

Components	Limits, §4 AbfKlärV 15.04.1992	A1	A2	F7	K1	K2
Pb mg/kg	900	59	60	779	460	160
Cd mg/kg	10/5	1.2	1.3	47	24	7
Cr mg/kg	900	55	50	252	77	70
Cu mg/kg	800	274	274	413	170	140
Ni mg/kg	200	29	27	n.a.	150	49
Hg mg/kg	8	1.4	1.6	3.3	3.6	2.8
Zn mg/kg	2500/2000	932	925	3980	2200	1400
Mn mg/kg		206	206	n.a.	240	190
Ti mg/kg		105	98	n.a.	n.a.	n.a.
Tl mg/kg		1.5	1.1	n.a.	<0.06	<0.06
PCDD/F (TE) ng/kg	100	n.a.	n.a.	n.a.	570	770

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Fig. 11: Analysis of Sewage Sludge

Emission Values after Boiler

Components	17. BImSchV 1990	Limits for NCP Freiberg, 1995	Measurement October 1997
Dust mg/m^3	10	10	<1
Hg mg/m^3	0.05	0.005	<0.001
CO mg/m^3	50	50	42
Total C mg/m^3	10	10	3
HCl mg/m^3	10	1	<1
SOx mg/m^3	50	50	11
NOx mg/m^3	200	200	84
PCDD/F (TE)	0.1 ng/m^3	0.01 ng/m^3	<0.001 ng/m^3

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Fig. 12: Emission Values after Boiler

Analysis of Synthesis Gas

Components vol.-%	Raw Gas *	Clean Gas * SulFerox Process	Expected Values in an Industrial Plant
H_2	23.5	23.5	32
CO	35.8	35.8	49
CO_2	18.1	18.1	12
N_2	22.8	22.8	6,7
O_2	0.3	0.3	< 0.1
CH_4	1.1	1.1	< 0.1
H_2S	0.19	< 0.003	0.28
COS	0.012	< 0.003	0.02

* Test in the Freiberg Plant October 1997

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Fig. 13: Analysis of Synthesis Gas

Leachability of Granulated Slag

Element	Limits Dumping Class 1 mg/l	Eluate Concentration mg/l (test no. 5)
Cu	< 1	0.04
Cd	< 0.05	0
Co	--	0.01
Ni	< 0.2	0.03
Cr	< 0.05	0.01
Pb	< 0.2	0
Zn	< 2	0.05
Mn	--	0.01
Hg	< 0.0005	0

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Fig. 14: Leachability of Granulated Slag

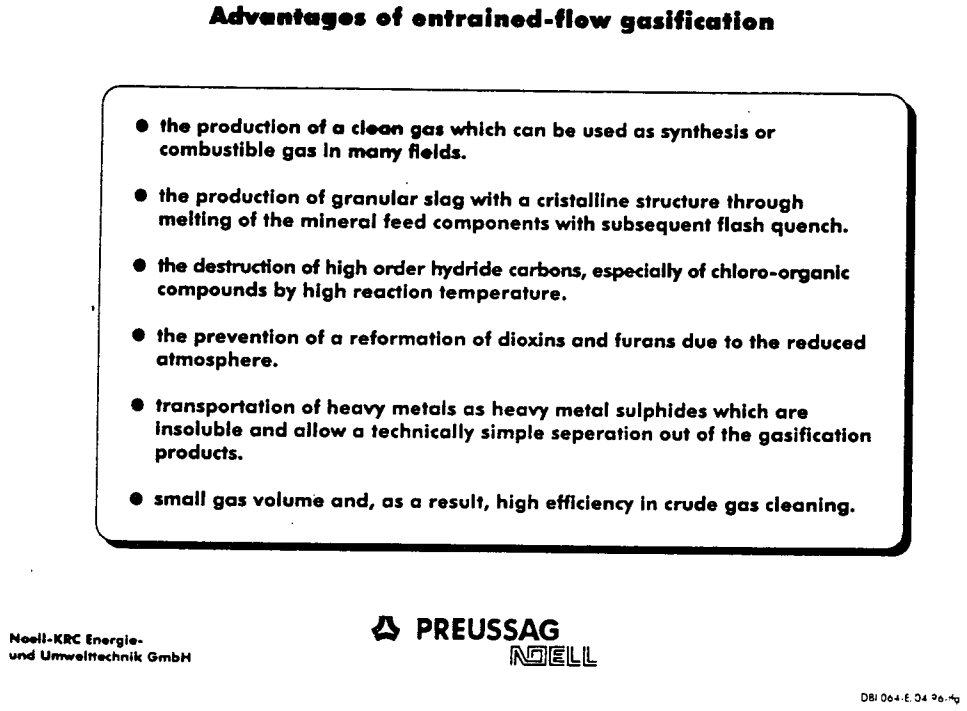


Fig. 15: Advantages of the Noell Conversion Process

Improvement of Excavated Soil Using Lime-added Biosolids Ash

Toshihiko Asano

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Construction Department
Sewerage Bureau, City of Nagoya

Abstract

In September 1996, the City of Nagoya commenced operating the Narumi Soil Improvement Center as part of a project for recycling biosolids ash. The Center is designed to produce improved soil by mixing lime-added biosolids ash (produced at Hojin Sludge Treatment Plant) with soil excavated during sewer construction works. This improved soil, with enhanced physicochemical properties, is used again for backfilling in sewer construction works. An excellent feature of this process is the creation of a new beneficial product by combining two kinds of waste, i.e. biosolids ash and excavated soil. The use of improved soil has positive effects in all aspects of sewage works, including reduction of the amount of pit sand conventionally used for backfilling, and in turn contributing to environmental conservation, construction and maintenance cost curtailment, and enhancement of the public image of sewage works as a whole.

Prior to establishment of the Center, studies were conducted for three years from 1987 as to the practical applicability of improved soil. These studies yielded data indispensable to plant construction, operation and management, including data verifying that lime-added biosolids would be usable as a soil improvement additive, and that the proportion of ash can be controlled by excavated soil water content.

After the opening of the Center, a follow-up study was conducted to confirm the quality, workability and durability of improved soil in actual sewer construction. The results confirmed that improved soil has sufficient properties as a backfilling material, and satisfies standards stipulated by the road management authorities. The results show that improved soil quality is equal to or better than the quality of pit sand.

Keywords:

Recycling, Lime-added biosolids ash, Soil Improvement Center, CBR (California Bearing Ratio)

Introduction

In Japan most of biosolids generated in wastewater treatment have been routinely disposed by sanitary landfill or coastal reclamation, following quantitative reduction and qualitative stabilization treatment through thickening, dehydration and incineration processes. In recent years, however, the diminishing availability of disposal sites and increasing disposal costs have become serious problems. Therefore, Nagoya and other cities have to reduce the volume of biosolids and promote beneficial use of biosolids in the ways most suitable to the respective locales.

The City of Nagoya has long been actively promoting the beneficial use of biosolids. However, the volume of biosolids is expected to increase year by year due to the introduction of full-scale advanced wastewater treatment and other factors. Accordingly, further efforts must be undertaken to expand the scope of biosolids use and raise the ratio of beneficial use by taking advantage of technical innovations.

Background of Biosolids Treatment and Beneficial Use

The City of Nagoya's sewerage system has a history of about 90 years, going back to the commencement of sewer construction in 1908. As of March 1997, about 96% of the City's population of approximately 2.15 million are served by the public sewerage system. The City's 15 wastewater treatment plants produce biosolids at a total rate of approximately 23,000 m^3/day. Biosolids are transported to three sludge treatment facilities, located in the southern part of the City, for thickening, dehydration, and finally incineration. Biosolids ash generated by the treatment process, amounting to 19,500 tons/year, is disposed of in landfills, excepting a portion set aside for beneficial use. Recently, the amount of biosolids ash disposal has been declining due to the introduction of entire volume incineration of dehydrated biosolids, and beltpress filters using a polymer coagulant (Fig. 1).

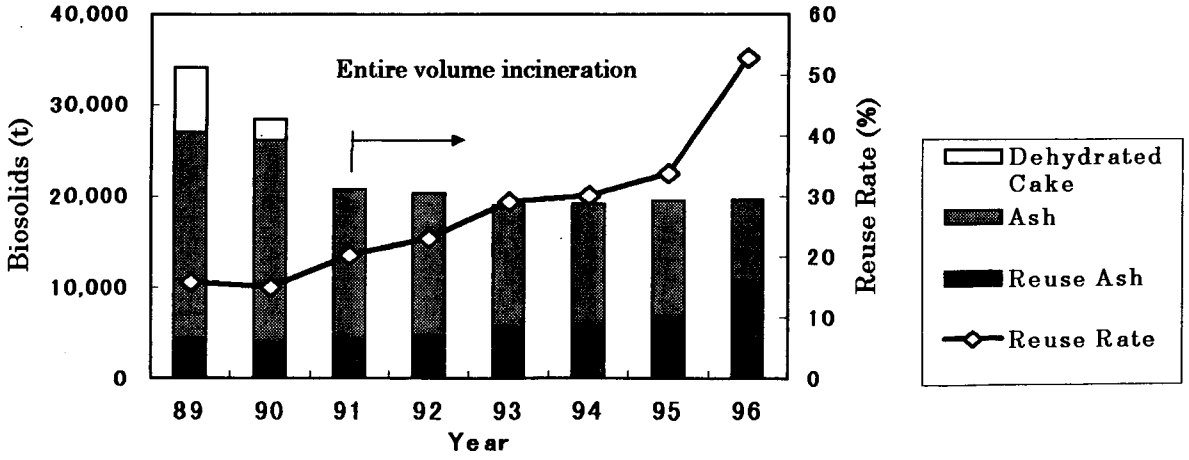


Fig. 1 Biosolids Disposal

The beneficial use of biosolids in the City of Nagoya began in 1933, with the production and sale of "Activated Biosolids Manure Made in Nagoya" at Tenpaku Sludge Treatment Plant. The production of this manure was terminated in the 1960s as its sales shrank. Today, biosolids ash is mainly put to beneficial use by turning it into construction materials. In Nagoya, biosolids ash has differing properties, depending on the type of coagulant added in the conditioning process of biosolids dehydrating. For this reason, different uses are adopted to suit different properties. For example, lime-added biosolids ash, to which slaked lime and ferric chloride are added in the conditioning process, is used as a soil improvement additive for backfilling and as a special manure, while polymer-added biosolids ash, to which a polymer coagulant is added, is used in construction materials (Table 1).

Table 1. Reuse of Biosolids Ash (1996)

Use	Type of Biosolids Ash	Proportion of Ash mixture (% by weight)	Amount of reused Ash (ton/year)
Ceramic Pipe	Polymer-added Biosolids Ash	1	100
Permeable Brick		50	1,000
Tile		1～10	200
Colored Brick		15	100
Cement Material		0.2	4,200
Manure	Lime-added Biosolids Ash	70～100	2,600
Soil improvement additive		5	2,100

Practical Application of Improved Soil

Soil improvement involves mixing excavated soil from sewer construction works with lime-added biosolids ash produced at Hojin Sludge Treatment Plant as a soil improvement additive. This improved soil, with enhanced physicochemical properties, is used again for backfilling in sewer construction works. An excellent feature of this process is the creation of a new beneficial product by combining two kinds of waste, i.e. biosolids ash and excavated soil. The use of improved soil has positive effects in all aspects of sewage works, including reduction of the amount of pit sand conventionally used for backfilling, and in turn contributing to environmental conservation, construction and maintenance cost curtailment, and enhancement of the public image of sewage works as a whole.

The amount of excavated soil generated in sewer construction works in Nagoya totals approximately 200,000 m^3 each year. Without treatment, excavated soil cannot meet the standards set by the road management authorities, nor be used as a backfilling material, due to poor manageability. Meanwhile, the fact that lime-added biosolids

ash has a 40 to 50% quick lime content by weight suggests the possibility of using this substance as a soil improvement additive. The City of Nagoya therefore commenced a study with the Public Works Research Institute of the Ministry of Construction in 1987, for the purpose of using lime-added biosolids ash as a soil improvement additive. The study proved that lime-added biosolids ash is usable as a soil improvement additive, and that it enables quick, easy and assured excavated soil improvement regardless of soil properties, when the water content of the target soil is controlled.

The Narumi Soil Improvement Center commenced operation in September 1996, after a sludge treatment facility at Narumi Treatment Plant located in the southeastern part of Nagoya City had been renovated into a recycling facility. The Center's production capacity is set at 100,000 tons per year (500 tons per day) in consideration of the supply-demand balance between excavated soil and biosolids ash, as well as factors related to operation management. Lime-added ash used as a soil improvement additive is transported from Hojin Sludge Treatment Plant by special trucks and directly discharged into stock silos. There are three silos in total, one of which is equipped with a quick lime-adding facility for backup. The soil improvement additive production process is composed of grading, crushing, sorting and mixing, with foreign matter removal and adjustment of grain size conducted in stages (Fig. 2).

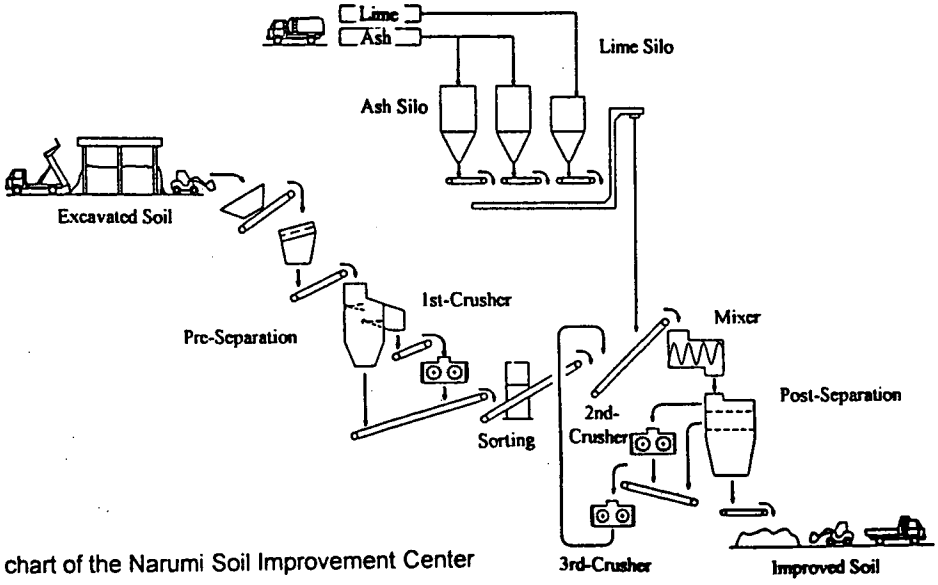


Fig.2 Flow chart of the Narumi Soil Improvement Center

Quality of Improved Soil Produced at Narumi Soil Improvement Center

Survey details

After the opening of the Narumi Soil Improvement Center, a follow-up study was conducted to confirm the quality of improved soil produced at the Center. For this study, two sewer construction work sites were chosen, where two-dimensional

improvement was being conducted; three locations per work site, i.e. six locations in total, were designated for measurement. The study was carried out both in the laboratory and in the field. The laboratory study aimed to evaluate the quality of soil around the concerned backfilling location, material properties of improved soil at the time of backfilling and improved soil potential for re-excavation and reusability after backfilling. The field survey involved various bearing capacity tests at subgrade and sub-base, and measurement of settlement, both at the time of backfilling and 1 - 2 months after backfilling.

Survey results

Quality of improved soil at the time of backfilling

(1) Comparison between excavated soil and improved soil

Table 2 indicates the physical properties of excavated soil and improved soil at the time of production and backfilling. "Improved soil at the time of backfilling" refers to improved soil placed in on-site storage temporarily for about three days after production at the Soil Improvement Center, and sampled at the time of backfilling work. In comparison with excavated soil, improved soil at the time of production demonstrated physical improvements, including lower water content, higher liquid and plastic limits and complete passage through a 26.5-mm sieve. In addition, its immediate CBR value increased considerably from that of excavated soil, and at this stage met the road management authority standards (CBR value should be over 10% for backfilling). The CBR value of improved soil at the time of backfilling was roughly the same as at the time of production, which indicating that temporary on-site storage does not significantly deteriorate quality.

Table 2. Physical properties between excavated soil and improved soil

		Excavated Soil	Improved soil	
			At production	At backfilling
Water content	%	16.3	14.0	13.6
Liquid limit	%	30.8	35.0	32.6
Plastic limit	%	21.9	24.5	24.2
Maximum grain size	mm	40.6	26.2	26.5
CBR (immediate)	%	2.6	28.4	20.3
CBR (standard)	%		48.7	47.7

(2) CBR properties of improved soil

Fig. 3 indicates the CBR properties of improved soil at the time of backfilling. The immediate CBR values are greater than 20% except for Location No. 3, which shows a difference of about 4% between natural and optimum moisture content. The CBR value increased as the number of curing days increased, for example 1.5 - 2.5 times the

immediate CBR on the fourth day and 2.0 - 3.6 times on the 10th day (standard CBR). On the 30th day, however, there was no considerable change from the standard CBR , which indicates short-term soil improvement effects such as hydration reaction are completed roughly within 10 days. Therefore, it is possible to determine the bearing capacity of improved soil after a 10-day curing period. Incidentally, data collected up until last year suggest that the CBR value of improved soil increases gradually as times passes, under the influence of Pozzolanic reaction.

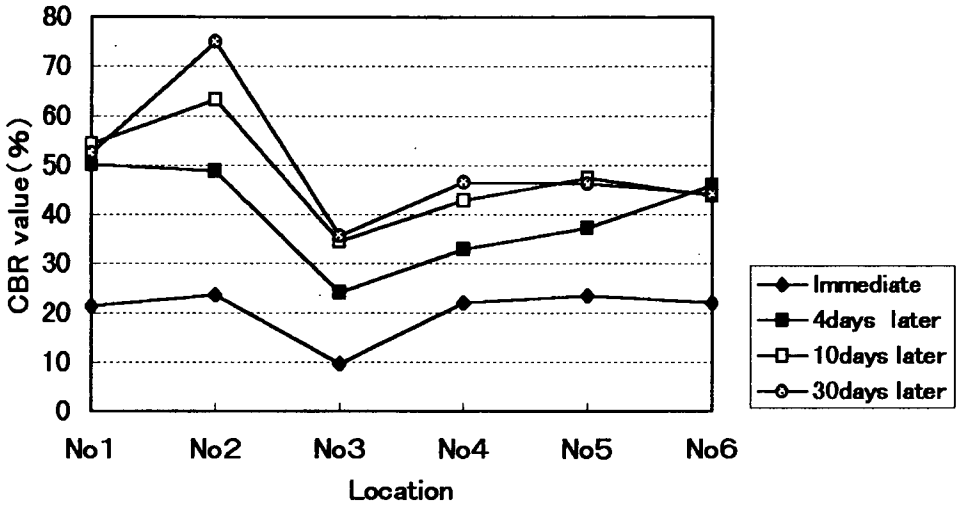


Fig. 3 CBR properties of improved soil

(3) CBR value in the field

Fig. 4 shows changes in field CBR values at the subgrade. While Locations NO. 4 - 6 show relatively high field CBR values at the time of backfilling, values at all locations are greater than 10%. Field CBR values at re-excavation conducted 1 - 2 months after backfilling are 1.3 - 2.9 times higher than at the time of backfilling.

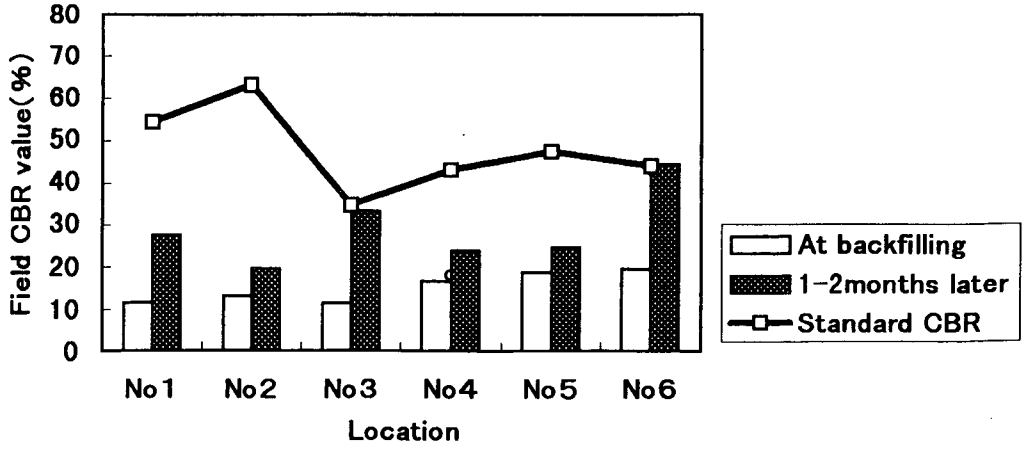


Fig.4 Changes in field CBR values at the subgrade

Workability and durability of improved soil

(1) Degree of compaction

Fig. 5 shows changes in the degree of compaction at the subgrade, based on a field density test conducted by the sand replacement method. Here, degree of compaction refers to the ratio of field density to the CBR density (3 layers, 42 times). The degree of compaction at the time of backfilling is 90% or higher at the medium subgrade layer at all survey locations, and 95% or higher at the subgrade surface, that confirms sufficient compaction by the conventional rolling compaction method. At re-excavation conducted 1 - 2 months after backfilling, the degree of compaction at the subgrade did not increase more than 2% at maximum, compared to the value at the time of backfilling. This is presumably because a high degree of compaction was already achieved at the time of backfilling, and because the ground became firmer as a result of chemical bonding, unlike in the case of other materials, such as pit sand, whose density increases by compressed settlement.

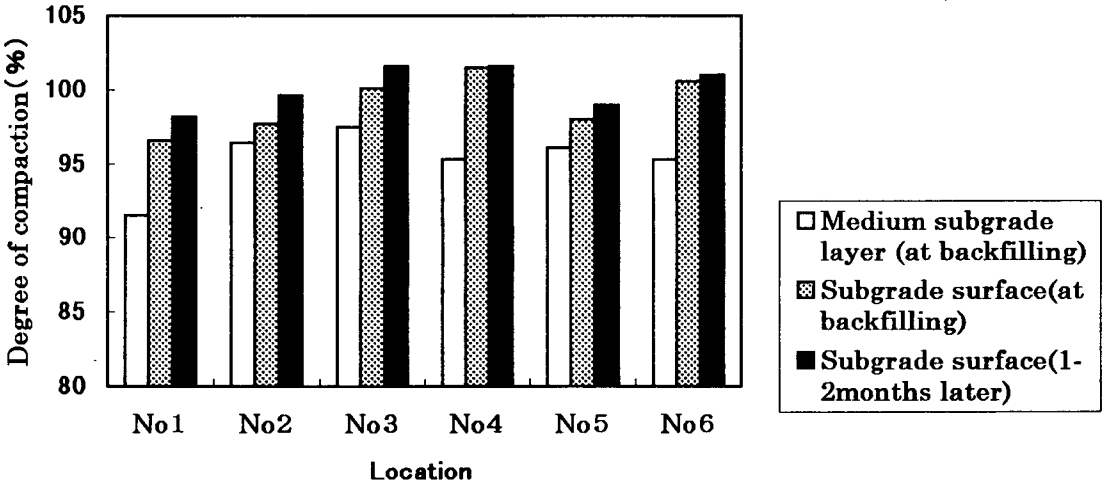


Fig.5 Changes in the degree of compaction

(2) Subgrade and road surface settlement

Fig. 6 indicates changes in the amount of settlement at the subgrade and surface. The amount of settlement at the road surface at the time of re-excavation 1 - 2 months after backfilling is extremely small (1 mm or less) at all survey locations, regardless of excavation depth and the amount of traffic. Settlement at the subgrade, on the other hand, is greater than at the road surface at Locations No. 3 and No. 5, which show about 8 mm of settlement. This is believed to have been caused during paving after subgrade backfilling and sub-base construction, and therefore is not caused by the passage of time, since no void was found between pavement and subbase at the time of re-excavation. Accordingly, it is assumed that no or little road surface settlement occurs, and traffic and other external conditions have no impact, if the field CBR is 10% or higher, as in the case of this survey.

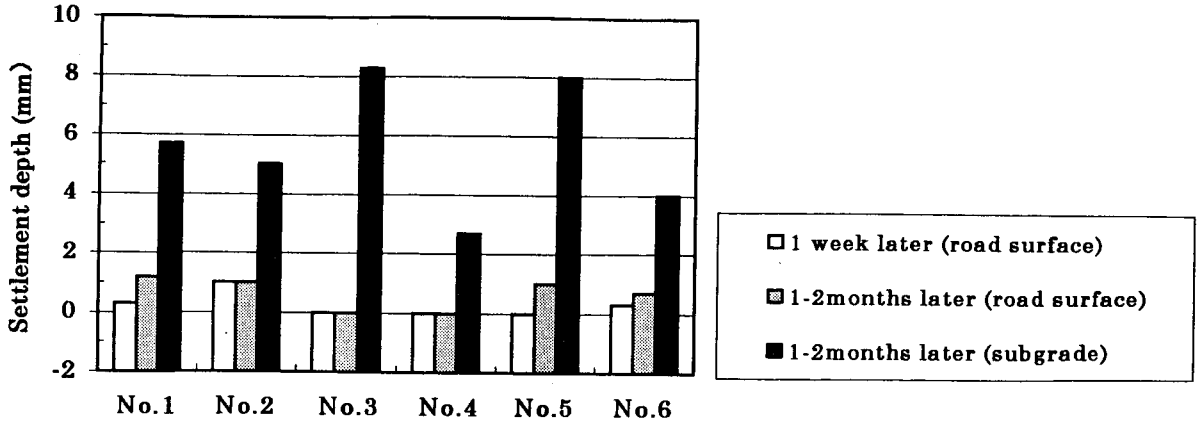


Fig.6 Changes in the amount of settlement

Re-excavation and reuse of improved soil

We sampled improved soil at Locations No. 5 and No. 6 at the time of re-excavation, to examine the CBR properties. Improved soil had almost no hardened mass and we could collect samples by hand. Fig. 7 indicates changes in CBR values of re-excavated improved soil. The immediate CBR value of samples taken from both locations was about 30%, roughly 50% higher than at the time of backfilling. The CBR value of re-excavated improved soil increased gradually as time passed. From this we conclude that re-excavated improved soil can be used without modification in backfilling for lateral pipe, following sewer construction work.

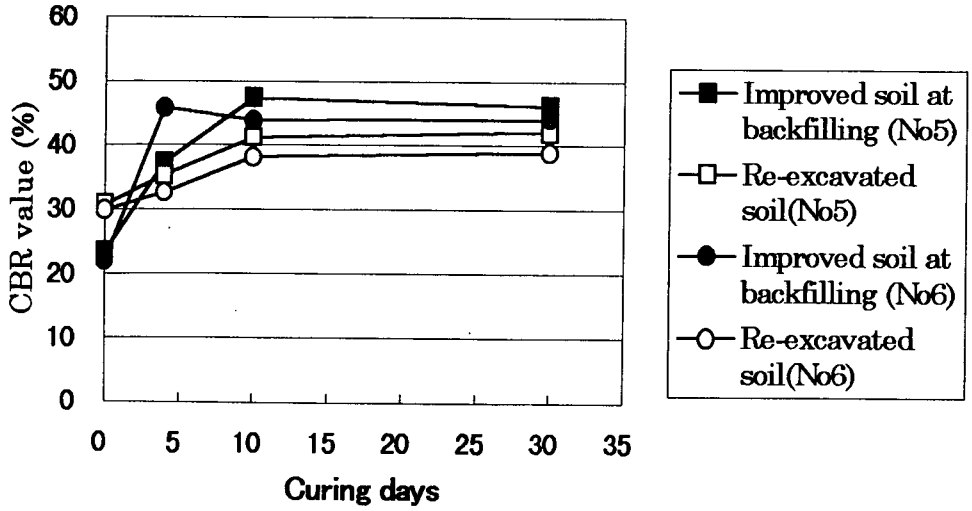


Fig7. Changes in CBR Values

Safety of improved soil

Prior to using improved soil in sewer construction works, its potential impact on

natural soil and ground water was examined on the premises of a treatment plant, to confirm safety. In the current study, a leachate test was conducted regarding biosolids ash and improved soil. Results confirmed that ash and improved soil both meet environmental quality standards related to soil pollution, and have no adverse impact on the environment.

Conclusion

In the study described above, suitable properties of improved soil produced at Narumi Soil Improvement Center have been confirmed, such as the fulfillment of road management authority standards, and high degrees of field workability and durability. Armed with this positive result, the Sewerage Bureau of the City of Nagoya intends to continue to help realize a recycling-oriented society, by reducing wastes through promoting beneficial use of sewerage-related resources such as improved soil, in addition to our original role of protecting the water environment.

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Session 4

Cost Reduction

"Possibilities for Cost Reduction in Municipal Waste and Waste Water Treatment "
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"Cost Reduction for Sewer Pipe Works"
K. Sasabe -174

"New Developments in the Remediation of Leaky Sewers"
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Possibilities for Cost Reduction in Municipal Waste and Waste Water Treatment

Vera Rabelt
BMBF-Project Agency for Waste Management and Abandoned Hazardous Sites
Federal Environmental Agency
Germany

1. Introduction

In the first half of the 1990s some DM 25.2 billion was invested in water supply and more than DM 32 billion in local waste water treatment facilities. Rough estimates of the cost of investment in waste disposal in the same period are around DM 20 billion.

Positive results of the expense and effort invested in the past include
- a substantial improvement in the quality of water courses;
- a substantial reduction in air, water and soil pollution resulting from waste disposal;
- a very high standard of drinking water supply, waste water and waste disposal in international terms; and
- a high quality of german environmental protection technology.

On the other hand, local authorities' supply and disposal costs have risen disproportionately. Not only investment and operating costs increased, but total cost of special burdens such as charges for drawing-off water has also been increasing in recent years. In the costs for environmental protection the regular expenses exceeded with 53% the costs for investments in 1993 for the first time.

Table 1 shows some average figures in waste disposal costs. Waste disposal costs where incineration is used average around DM 420 per tonne. The remuneration burden for drinking water supply is around DM 150 per capita per annum, for waste water disposal around DM 210 per capita per annum, and for waste disposal around DM 144 per capita per annum. As a result of this high costs, the average drinking water price is currently for example DM 3.14 per m^3 and the average waste water disposal charge DM 4.56 per m^3.

Table 2 shows waste water charges in some communities depending on a different number of inhabitants in 1996.

The burden placed on the population at large by the so-called "third rent" levy increased disproportionately. Between 1991 and 1995 water prices rose by an average of approximately 35%, waste water charges by around 60%, and waste disposal charges by over 80%. In the same period the overall cost of living rose by only around 20% in comparison.

The example of the average water price in the "old" federal states of West Germany makes this above-inflationary trend clear. From 1963 (DM 0.40 per m^3) to 1993 (DM 2.90 per m^3) the price rose more than seven-fold. It seems reasonable to suppose the reason for such an increase lies in the increased cost of water recovery, treatment, purification, discharge, and similar operations.

Type of costs		Average (*Figures in German Mark per capita per year*)	
Waste disposal from private households:	total	144	
*disposal of residues		84	
*organic waste		19	
*bulky refuse		12	
*printed products		8	
Range of costs	100		170
Supply of drinking water		150	
Waste water disposal		210	
		(*Figures in DM per ton waste*)	
Municipal solid waste incineration before landfillig		420	
Range of costs	190		650
Landfilling		200	
Range of costs	50		350

Table 1: Cost structure in municipal waste and waste water disposal

Communities in number of inhabitants up to	Average charge in DM/m³	Range in DM/m³
5 000	3,12	0,74 - 9,32
10 000	4,06	1,00 - 11,20
20 000	4,38	1,03 - 11,05
50 000	4,82	1,60 - 10,63
100 000	4,31	2,10 - 7,95
more than 100 000	4,63	2,13 - 7,06
Total	**4,56**	**0,74 - 11,20**
East Germany	4,98	1,28 - 10,63
West Germany	4,38	0,74 - 11,20

Table 2: Waste water disposal charges of private households
Source: Survey carried aout by the German Association for Water Pollution Control, 1996

Though these increases are very high of more significancy seems to be the enormous range of costs and in the sequel the prices and charges (see Tabel 1 and 2). A german study in the federal state of Bavaria gives a an extreme price-margin only between the bavarian disposers of 2 500% per ton of disposed waste.

2. Reasons for Increase of Costs

The reasons in the rise of costs, and thus in the prices and charges passed on to consumers, are not generally made clear in detail to the consumer. The reason for this may be for example in the waste water disposal that, although the waste water charges are calculated on the basis of fresh water procurement, there is in Germany a strict separation of drinking water supply and waste water disposal.
One factor in terms of increased cost may be seen to be the additional investment which became necessary in order to meet increased environmental requirements. In the last five years requirements have not risen to the same extent as costs, however, and so other reasons must be to blame.

In analyzing the costs and charges situation, and the measures to reduce them, attention needs to be paid to regional specifics as well as to cost structures in the investment sector in particular. Thus, a distinction needs to be drawn

- in general terms for example, between water/waste, "old"/"new" federal states, rural/urban areas, topography and connection density;
- in the area of water supply and waste water disposal, between need for purification based on the properties of the water and waste water, the structural condition of the supply and disposal facilities, and pipe and sewer length;
- in the area of waste management, between existing and new, regionally differentiated, concepts of waste management;
- in the different administration structures within the communities;
- in the kind of calculation the costs: communities use very different methods of depreciation and assessment of running time of a plant;

Subsequently the range in costs and charges may stem from the lack of a uniform national calculation base for costing, which alone results in a substantial freedom of pricing and charging for the local authorities, and which can lead to considerable localized differences.

The Federal Environmental Agency is carrying out at present a study to identify all aspects and reasons of cost increase in waste water and waste disposal. Though the finally results are still not available some reasons for cost explosion are already known. A significant proportion of total cost is attributable to maintaining, refitting and developing supply and disposal facilities. For example, in the water industry some 60% of production/acquisition cost is expended on the distribution and sewer network. The same applies to the collection and transportation of waste. Depending on the waste management concept, the cost share in that sector is between 20% and 90%.

Especially in waste management the cost structure is of high complexitiy due to the multifolded technological, organisational and logistical possibilities of ways to treat and

dispose waste. Concerning the cost differences for incineration of municipal solid waste (see table 1), for example, the type of technology which is used and the capacity utilization play an important role for the cost structure. There are large differences in the capacity utilization rates of plants currently in operation in Germany for the thermal treatment of residual municipal waste, hazardous waste treatment as well as mono- and co-incineration of sewage sludge. Capacity utilization at the various plants evidently strongly depends on the regional waste management conditions (duration of waste management contracts, size of catchment area, quantity of waste subject to mandatory delivery, cost of acceptance and treatment). Precise plant-related data are not available. General estimates assume most plants to operate at 60 to 80% of their design capacity.

A number of reasons are cited why thermal treatment plants are not working to capacity:

- the efforts made over the last few years to avoid and recycle waste are beginning to show an effect and are causing the quantities of residual waste to be treated to drop;
- due to the general cost increases in the communities some of the waste (e.g. commercial waste similar to household waste) is directly sent to landfill (due to lower cost of 50 DM/t to 350 DM/t) in order to use the landfills'remaining operational time to fill them until 2005 in respect to the „Technical Instructions on Waste from Human Settlements" (TA Siedlungsabfall);
- for the future it can be expected that wastes which hitherto have been disposed of will be dealt with as "wastes for energy recovery". This is partly due to an unintentional effect of the new definiton of waste in the german "Waste Avoidance, Recycling and Disposal Act" from 1994 (Kreislaufwirtschaftsgesetz).

As the costs for thermal treatment are essentially fixed costs which could not be dropped by a decreasing amount of waste cost reduction is not possible with less waste.

Another reason of high costs of waste management concepts is the collection and transportation of waste. With increasing separation of waste like paper, glass and organic waste different container and transport systems have to be used which also cause higher costs.

The population at large and industry increasingly regard the rise in water prices and waste water disposal charges as burdensome. In particular because the general public is unable to understand that environment-conscious behavior such as water conservation or waste separation brings about additional increases in costs and levies. A reversal of the trend is required here.

3. Measures and Activities Eligible for Support

The BMBF will announce a competition of ideas how to reduce costs and charges in waste water and waste disposal simultaneously with optimized implementation of environmental reqirements. The aim is to exploit cost-saving potentials in supply and disposal systems and to promote the development of innovative technologies in order to safeguard lasting cost-effectiveness while maintaining performance in supply and disposal. This is a decisive factor in ensuring the most favorable solutions for tax-payers and a rapid reduction in levies.

Furthermore, the development of more cost-effective environmental technologies can be expected to strengthen the international competitiveness of german suppliers.

Within the framework of existing legal requirements relating to water and waste, the bundling of synergistic measures in particular is a key prerequisite for rapid and far-reaching reductions in costs and charges. Areas where savings potentials can be exploited are to be found in the plant and operations areas, as well as in organization and cost accounting.

The following factors may for example serve to exploit savings potentials and to implement more efficient and cost-effective methods and strategies in the water and waste management industries (the specific tasks to be formulated by the institutions involved in competition):

- New investments which are amortized within a very short period of time on the basis of substantial reductions in operating costs, and which thus bring about a real reduction in cost.
- Demand-oriented solutions for existing plant and equipment.
- Exploitation of operational potential for rationalization in drinking water treatment, waste water and sludge treatment and waste processing and recycling facilities.
- Increased operational reliability and efficiency of plant.
- Infrastructural concepts.
- Modern organizational forms and management methods in planning, financing, constructing and operating facilities, as well as in cost controlling.

4. Conclusions and Outlook

Cost reduction in waste water and waste disposal is one main issue in the environmental policy of the German government. Of course do environmental protection reqirements cause costs. These are necessary investments in our and our childrens' future for a sustainable society which is not to obtain for nothing. But, as was shown in this paper, in Germany there are big potentials of reducing costs which still have to be worked out. This should be reached with the announcement of the idea competition of the BMBF and with further research in this field.

COST REDUCTION FOR SEWER PIPE WORKS

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ABSTRACT

The national policy required the cost reduction by more than 10% on public works at the Ad hoc Cabinet Council for Cost Reduction on Public Works January 1997. In order to reply this requirement, a lot of concrete measures are issued by central and local governments or related groups to the sewage works. Described at the beginning of this paper is the cost reduction concept by the Ad hoc Cabinet Council and the action program by the Ministry of Construction and the Sewerage and Sewage Purification Department. The feasibility study and the research and development on the concrete measures of the action program are conducted by the Public Works Research Institute (PWRI), the Japan Sewage Works Agency, metropolitan cities and other municipalities, and relevant groups. The Wastewater System Division, PWRI, focuses on the wastewater collection and transport system, of which cost accounts for 70-80% of the total sewage works including the treatment works. The cost reduction ideas for sewer pipe works and their effectiveness are mainly discussed in this paper.

KEYWORD

Sewer pipe works, Cost reduction, Morphological analysis, Soil covering, Slope, Manhole

INTRODUCTION

The national average of sewer service population by public sewerage system reached 54% in 1995. The service rate averages 97% in 11 metropolitan cities with population over 1 million, but only 17% in smaller municipalities with population of less than 50,000. In these smaller municipalities, the sewered population is only 5.83 million with total population of 35.32 million. National policy for the sewage works has been shifting from the bigger cities to the medium- or small-sized municipalities which have less financial and technological abilities. On the other hand, the cost reduction on the public works is strongly required by the central government because of the nationwide fall of economic and financial circumstances. This paper presents the overview of the cost reduction scheme on the public works and the sewage works. In the cost reduction scheme the sewer pipe works is focussed in this paper because the sewer pipe works account for 70-80% of the total sewage works.

OVERVIEW OF COST REDUCTION FOR SEWAGE WORKS

In early 1997, the Ad hoc Cabinet Council for Cost Reduction on Public Works issued the action guidelines addressing to reduce the cost of public works by more than 10 percent in three years. The reduction concept consists of following four phases:

- review and revision of present project and design
- development of efficient contracts
- cost reduction of construction materials and equipment
- alleviation of restrictions on construction practice

Responding to this requirement, the Ministry of Construction (MOT) revised the action program for cost reduction on public works which had been issued December 1994 . The revised action program is categorized as follows:

review and revision of present project and design

- review of planning methods
- revision of technological standards
- review of design methods
- promotion of research and development
- rationalization of cost estimation

development of efficient contract

- periodical equalization of contracts
- review of contract unit
- review of contract systems
- efficient construction management
- electronic information transfer of complicated procedures

cost reduction of construction materials and equipment

- efficient production and transportation of construction materials
- unification and simplification of material standards and specifications
- education for skilled technical workers
- efficient use of construction machines

alleviation of restrictions on construction practice

- simplification and enhancement of safety working environments
- integrated works and simplifying procedure on road practice
- mitigation of public nuisance
- recycle system of construction wastes
- efficient research of buried cultural heritages
- speedup and simplification of regulatory procedures on fire protection law and

building standards law

At the same time, the Sewerage and Sewage Purification Department, MOT, organized the action committee for cost reduction on sewage works issuing the concrete measures according to the cabinet and MOT requirements. These measures are followings:

review of planning methods

- review of treatment areas and design flows
- alternative wastewater collection system
- activation of stormwater storage and infiltration facilities
- co-combustion of sludge with solid waste
- centralized sludge treatment
- central management of various small wastewater treatment works

revision of technological standards

- revision of sewer pipe slope
- revision of the covering standard of pipes under the ground
- modification of manhole installation
- clarification of permits for sewers under the river
- standardization of the design and equipment for small scale wastewater treatment plants

review of design methods

- adoption of small diameter sewer pipes
- standardization of the bore for pipe jacking methods
- improvement of shield tunneling methods
- promotion of pre-fabricated oxidation ditch facilities
- facility construction above the ground
- simplification of grit chamber
- post grit chamber on pumping stations
- long siphon type pumping station
- wide use of materials and equipment putting on the market

research and development

- long distance pipe jacking method
- long distance shield tunneling method
- removal of the secondary lining on shield tunneling
- low cost activated sludge process with membrane separation in the reactor

rationalization of cost estimation

- unification of construction cost estimation standards

efficient construction management

- simplification of start-up test systematic operation of equipment
- simplification of product inspection of equipment

electronic information transfer of complicated procedures

- simplification of procedure papers

COST REDUCTION FOR SEWER PIPE WORKS

In order to conduct the cost-effectiveness analysis, it is crucial to realize the characteristics of the sewer networks. It is very difficult to realize the networks visually, because they are installed under the ground and arbitrarily spread in the drainage district. Firstly analyzed is the characteristics of the sewer networks by application of Strahler's stream order concept and morphological stream laws in the river engineering. Second, standard drainage district model is formulated with the result of the morphological analysis and the statistical analysis of twelve "Prefectural Master Plan for Appropriate Wastewater Collection and Treatment". Third, cost effectiveness analysis is conducted with the standard drainage district model and the result of cost analysis of sewer pipe works. The cost effectiveness analysis for manholes are separately conducted.

MORPHOLOGICAL ANALYSIS OF SEWER NETWORKS

Strahler's stream orders

Though the sewer networks are artificial structures, the sewers are designed chiefly by gravity flow and affected by geological features, and then the morphological analysis of natural streams in the river engineering is applicable. Strahler defined the stream order shown in Fig.1: the first order stream is a segment from a riverhead to the first junction; if two streams of the first order join, the stream segment is called as the second order; the order number of the segment increases in the same way.

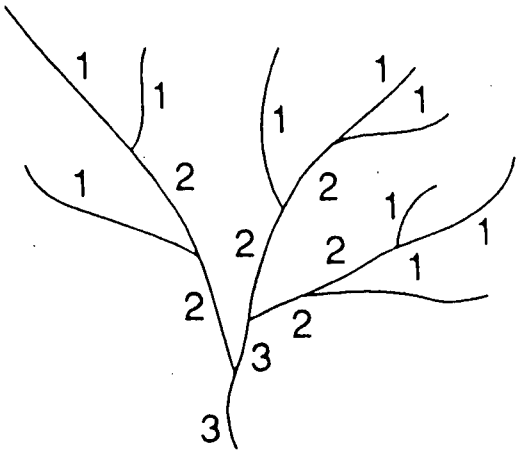


Fig. 1 Strahler's stream orders

Four morphological laws of stream

Four morphological laws based on the Strahler's stream orders have been theoretically and statistically confirmed;

- Law of the number of the streams $N_i = R_b^{k-i}$ ($R_b = N_i/N_{i+1}$)
- Law of the stream length $L_i = L_1 R_l^{i-1}$ ($R_l = L_{i+1}/L_i$)
- Law of the basin area $A_i = A_1 R_a^{i-1}$ ($R_a = A_{i+1}/A_i$)
- Law of the stream slope $S_i = S_1 R_s^{1-i}$ ($R_s = S_i/S_{i+1}$)

Where: N_i ; the number of the streams of the order i, L_i ; the mean stream length of the order i, A_i ; the mean basin area of the order i streams, k ; the highest rank of the order, Rb, Rl, Ra and Rs are the bifurcation ratio, the stream length ratio,the basin area ratio and the stream slope ratio respectively. These ratios are proved to have almost constant values, and theoretical values are:

$$R_b = 4, \quad R_l = 2, \quad R_a = 4 \quad \text{and} \quad R_s = 2$$

Application of the morphological laws on the actual drainage districts

Five drainage districts, which are less than 200 ha of the area and have less pumping stations, were selected to analyze the morphological characteristics. The highest rank of the stream order of the pipeline is 5 with an exception of a treatment district of the order 4. The average length of the first order pipeline is 90m and the average drainage area is 0.47ha. The total length of the first order pipeline accounts for 50 – 60% of the overall length of the sewer network, and the stream number of the first order pipeline makes up about 70% in the overall stream number. The pipeline length of each stream order and four morphological ratios were analyzed as shown in Table 1. From the result of Table 1, the average value of the bifurcation ratio, stream length ratio, basin area ratio and stream slope ratio are calculated to be 3.60, 1.75, 4.03 and 1.51 respectively.

Table 1. Morphological characteristics

	Natural Rivers	Drainage District No.1	No.2	No.3	No.4	No.5
Area (ha)	---	112	92	57	190	49
Population	---	8,180	3,000	1,600	4,100	1,700
Population density		73.0	32.6	28.1	21.6	34.7
Bifurcation ratio (Rb)	3.80 ~ 4.61	3.91	3.39	3.94	3.87	2.87
Stream length ratio (Rl)	2.00 ~ 2.58	1.74	1.40	2.18	1.80	1.61
Basin area ratio (Ra)	3.99~ 5.00	3.98	3.65	4.74	4.39	3.37
Stream slope ratio (Rs)	2.09~ 2.75	1.36	1.25	1.83	1.22	1.90

THE STANDARD DRAINAGE DISTRICT MODEL

The mean size of the small scale drainage district

Identified in the survey of the twelve "Prefectural Master Plan for Appropriate Wastewater Collection and Treatment" were 7,435 drainage districts comprising publicly owned municipal sewage works, rural sewerage systems and privately owned household sewage treatment (Jokaso) under the jurisdiction of the Ministry of Construction, the Ministry of Agriculture, Forestry and Fisheries and the Ministry of Health and Welfare respectively. The service population of the public sewage works, the rural sewerage systems and the Jokaso are 83%, 10.7% and 5.6% respectively. The number of the drainage districts of the public sewage works and the rural sewerage systems are 21.4% and 72.5% respectively. Assuming the drainage district with service population of less than 10,000 to be a small scale, the average of the service population, the drainage area and the population density in this small scale public sewage works are 2,766, 126ha and 30 persons per hectare respectively.

The standard drainage area model

From the results of the morphological analysis and the mean size analysis, the standard drainage model is described as Table 2. Assumptions in this model are followings: the drainage area the maximum stream order is five; the mean length of the first order pipeline is 90m; the mean area of the first order drainage sub-district is 0.47ha; the gradient of the first order pipeline is 3‰; the minimum soil covering is 1.2m. The number of the higher order pipeline is calculated by the stream length ratio. The area of the higher order pipeline is also calculated by the basin area ratio and the gradient is calculated by the stream slope ratio. The pipe diameter is dimensioned by the service population in the corresponding drainage area.

Table 2 Standard drainage district model

Order of pipelines	1	2	3	4	5	Total
Number of pipelines	168	47	13	4	1	233
Average length (m)	90	158	276	482	844	--
Sub-district area (ha)	0.47	1.89	7.63	30.76	123.97	--
Total length (m)	15,120	7,426	3,588	1,928	844	28,617
Pipe diameter (mm)	200	250	300	400	500	--
Slope (‰)	3.0	2.0	1.3	0.9	0.6	--
Covering (m)	1.34	1.63	1.97	2.36	2.83	--
Construction cost (Million Yen)	1,403	784	431	271	140	3,029

COST ANALYSIS OF SEWER PIPE WORKS

The branch sewer comprises pipelines, manholes, laterals and inlets. The cost portion of these branch sewer components are analyzed from eight actual estimations for the contracts. Excluded the cost for restoration of pavement or other compensation works, the cost portion of pipelines, manholes, laterals and inlets are 74.8%, 17.3%, 5.8% and 3.0% in average respectively. The costs for pipelines and manholes extend to 92% of the total cost and it is accordingly realized that these two components are crucial for the cost reduction. The material costs of the pipelines and the manholes are very low or 2.4% and 5.0% respectively in the total cost. In the construction works, the costs of the foundation and installation, the excavation and sheathing, and the compensation works are 31.1%, 51.6% and 17.3% respectively. The foundation and installation costs or the compensation works costs are difficult to reduce. The excavation and sheathing costs are seemed to be the crucial element for the cost reduction.

COST EFFECTIVENESS ANALYSIS

Shallow laying of sewer pipes

It is prescribed by the Road Construction Ordinance that the minimum of the soil covering under the roads is three meters and is permitted to be one meter in unavoidable case. The depth of the soil covering is dependent on the traffic volume and the importance of the road. The road administrators have site specific rules for the soil covering, which mostly prescribe to be deeper than 2 to 3 meters under the national or prefectural roads. In the case of the municipal roads, the soil covering is commonly deeper than 1.2m, which is normally deeper than the location of the tap water lines. The experiment for the shallow pipe laying is conducted at the pavement test field in the PWRI, on the covering conditions of 40,50,60,70 and 80cm in depth with the centrifugal reinforced concrete pipes, the PVC pipes, the ductile cast-iron pipes and the polyethylene pipes. The prescription of the Ordinance for the soil covering are going to be amended in near future from the result of this experiment. The effect of the shallow pipe laying on the cost reduction is estimated by the above mentioned standard drainage district model. If the pipelines are shallower laid by 50cm, the cost reduction of 7.8% is expected.

Flattening the pipe slope

It is desirable to lay the pipe as flat as possible in order to reduce the soil covering, but the sediments are likely accumulated at the bottom of the pipe. In the design guideline for the sewerage facilities, it is prescribed that the minimum velocity should be greater than 60 cm/sec to prevent deposition of suspended solids for the design flow. The Wastewater System Division is conducting the experiment to realize the transportation of the solid excreta in the branch sewer. The results show that the main force to convey the solid excreta is not the flushing toilet water but the daily maximum flow from bathing or laundering. The results also show that the slope of the branch sewer is not crucial factor to transport the excreta. A trial calculation shows that the cost reduction of 5% is expected by flattening the pipe slope from 3‰ to 2‰.

Modification of manhole installation

In the design guideline for the sewerage facilities, it is prescribed that the manholes should be installed at the upstream ends, the bends, the conjunctions and the drops, and the recommended spacing of the manholes is less than 50m for the pipe diameter of less than 300mm. The survey on nine small scale drainage districts is conducted, in order to clarify the current state of the manholes. The average spacing of 3,400 manholes is about 30m and the maximum spacing is 50m in accordance with the design guideline. Fig.2 shows the distribution of the manholes classified by the objectives of installation. The bending manholes accounts for fifty percent and are crucial parts for the cost reduction. Fig.3 shows the distribution of the bends manholes classified by the bending angles. The manholes with bending angle of less than 30 degrees accounts for 66%. It is very cost effective, if these bends manholes are eliminated without any trouble.

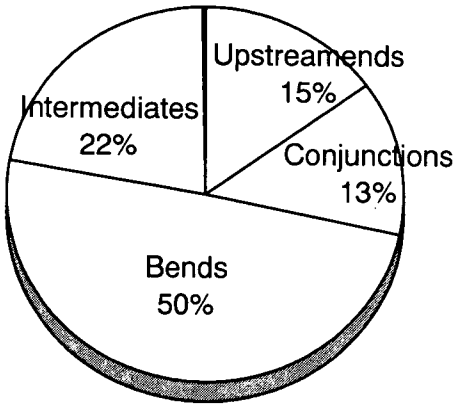


Fig.2 Roles of Manholes

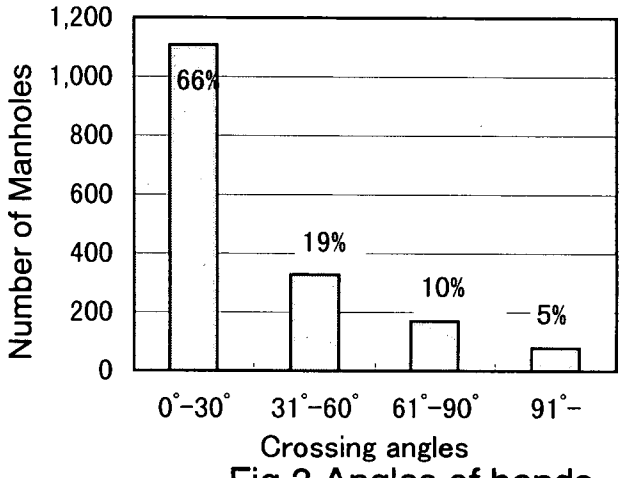
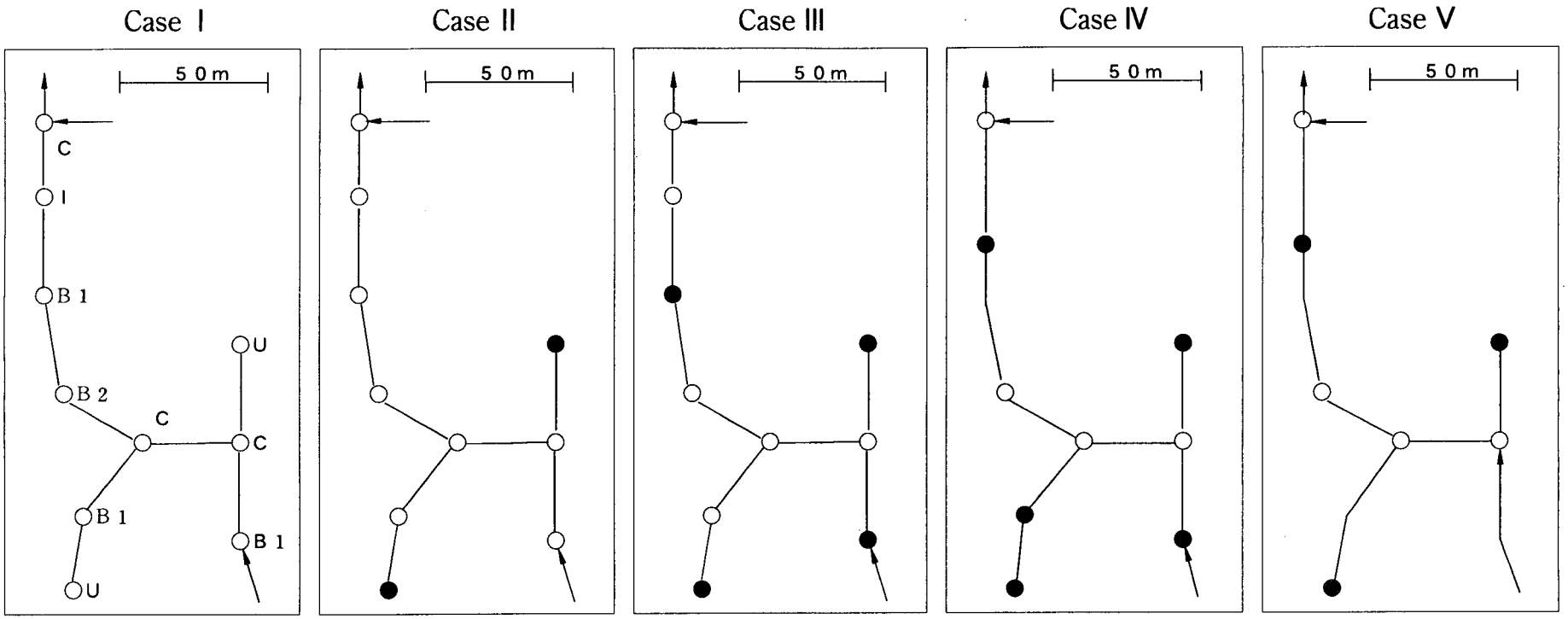


Fig.3 Angles of bends

The small diameter PVC manhole, in which man cannot enter and then call it "machine hole", was authorized in 1996 by the Japan Sewage Works Association as a standard material for sewage works. The machine holes are appropriate for branch sewers and have lately begun to apply in small scale drainage districts. No trouble has been found out even in the case of cleaning or TV inspection from the machine holes.

In order to reduce the cost for manhole installation, two methods are picked out: first, to reduce the number of installation; second, to substitute machine holes for manholes. A cost effectiveness study is conducted, assuming the drainage district which has one thousand manholes. The distribution of the manholes is assumed to be as shown in Fig.2 and Fig.3. Four cases are estimated at the condition of shown in Fig. 4. Case Ⅰ is the control design in accordance with the present design guideline. In case Ⅱ, machine holes are introduced at the upstream ends. In case Ⅲ, machine holes are alternately installed at the bends and the intermediates on the linear segment satisfying the maximum spacing of 50m. In case Ⅳ, the



○ : Manholes ● : Machine holes
U : Upstream ends B 1 : Bends with angle of less than 30 degrees B 2 : Bends with angle of more than 30 degrees
I : Intermediates on the linear section C : Conjunctions

Fig. 4 Schematic diagram of each case

manholes or machine holes at the bends with less than 30 degrees of the crossing angle are eliminated unless the spacing exceeds 50m. In case Ⅴ, the maximum spacing of 100m is assumed. By introducing the machine holes in case Ⅱ, the manhole installation cost is estimated to be reduced by 8% compared with the control design in case Ⅰ. Cost reduction of 30.2% is estimated by the alternate installation of the machine holes in case Ⅲ. The cost is possibly reduced by 51.6% in case Ⅳ by some elimination of bends manholes, and by 62.5% in case Ⅴ by further elimination of bends manholes. The life cycle cost analysis should be conducted in actual practice, because the additional maintenance costs are not considered in this estimation.

CONCLUSION

The following conclusions are drawn from this study:

- The first order pipelines account for 70% in number and 50% in length of the total sewer pipelines from the result of the morphological analysis of sewer networks.
- The construction cost for the first order pipelines accounts for 46% of the total cost, and it is accordingly cost effective to make effort to reduce the first order pipelines cost.
- The cost for the excavation and sheathing accounts for 51.6% of the total construction cost from the result of the cost analysis of pipe works. It is very cost effective to reduce the soil covering.
- The cost reduction of 7.8% is expected by laying the sewer pipe shallower by 50cm.
- The cost reduction of 5% is expected by flattening the pipe slope from 3‰ to 2‰.
- It is very cost effective to introduce the machine holes, eliminate the bends manholes with the crossing angle of less than 30 degrees and prolong the spacing, but the life cycle analysis should be conducted to eliminate the maintenance troubles.

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New Developments in the Remediation of Leaky Sewers

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1. Introduction

A strong ecological consciousness and increasing qualitative and quantitative requirements on modern infrastructures make the topic of "Pipeline Construction" gain political importance both nationally and internationally. All over the world, towns and regions face the challenge to ensure a reliable supply of water, gas and electricity and provide for modern communication facilities as well as a sustainable waste management. The sometimes very old pipe networks in the industrialized countries have to be maintained, remediated, extended and modernized consistently. Each year, sewers in Germany transport about 9 billion m^3 of sewage from households and industry to more than 10 000 sewage treatment plants. The value of reprocuring the entire public sewer network is about 350 billion DM. Sewers were and are made of various materials and designs. Economic aspects as well as the technical progress made resulted in certain materials not being applied any longer or in special cases only. This applies to clinkers which have been used for the construction of a considerable part of the sewer network in German cities. The sewer network of our cities is very old sometimes and often leaky for various reasons and due to various influences. According to a poll of the Sewage Technical Association (ATV), more than 20% of the sewers are damaged. The resulting need for remediation by far exceeds 60 billion DM. The fraction of damaged private sewers is estimated to be more than 50%.

Previous experience gained from groundwater accidents has shown that a very high expenditure is required for exact studies and a reliable investigation of the causes of damage. As far as soil and groundwater contamination by leaky sewers is concerned, there is a considerable lack of methods, studies and knowledge allowing a reliable assessment of the hazard potential to be made as a function of the various boundary conditions, such as the type and scope of the sewer damage, the geomorphology of the sewage properties and the duration of impact. There is no method available up to now for

the determination of the damage with suitable techniques and criteria. An evaluation scheme for the assessment of the environmental hazard and particularly soil and groundwater contamination caused by damaged sewers is still missing. Quantitative statements exist neither for the amount of sewage released from the leaky sewers nor for the infiltrating amount of groundwater.

2. Causes of Sewer Damage

The causes of sewer damage are of various nature, as sewers are subjected to externally and internally acting mechanical, chemical, and biological impacts that may lead to wear and eventually to the destruction of the sewers. Besides qualified planning and appropriate material selection, the construction quality and other factors, such as the sewage composition, temperature and humidity fluctuations, changing water levels, static and dynamic loads and mechanical stress due to sewer cleaning processes are of crucial importance for the service life of sewers. In most cases of damage, several factors combine. Many destructions are caused by war-induced damage or due to other sources, e.g. leaks caused by deviating positions or relocations. The damage may cover a large sewer length or occur locally only. Sewers consist of pipes, seals, fittings and ducts. Failures or damage may occur in any part. The quality or tightness of a sewer depends on the functionality of all four elements (service life is determined by the weakest element of the chain!).

The construction of sewers has always been accompanied by design and material failures since the beginning of modern sewerage technology, although efforts have been made constantly to use materials or components of best quality only and to install them according to the current state of the art.

3. Problems Caused by Leaky Sewers

The sewer network existing in the Federal Republic of Germany reflects all development stages. The network is rather heterogeneous with a multitude of pipe materials, pipe connections, pipe ducts, construction principles and draining methods employed.

The public sewerage system is a major instrument for the protection of our water bodies, both groundwater and surface waters. This protection function can only be fulfilled, however, if the entire sewer system is tight. Damaged sewers may adversely affect the

environment in many respects. If sewage emerges from the leaks, the soil and the groundwater are contaminated by the sewage constituents. This is mainly the case when the damaged sewer lines are located above the groundwater layer. Such a situation may considerably impair the drinking water supply. By the increasing use of solvents and other substances which are hazardous to water in both households and industry, a contamination of groundwater and soil by hazardous toxic substances is possible.

Entry of extraneous water adversely affects the decomposition efficiency of sewage treatment plants and, hence, the economic efficiency of sewage treatment. Usually, this water is not contaminated, but it equally affects the sewerage system, pumping stations and sewage treatment facilities. The latter are overloaded hydraulically and functionally, as they are only designed for a certain maximum amount of water. Consequently, efficiency of the treatment may be reduced considerably. The amount of extraneous water has already been found to exceed that of the sewage by a factor of four!

The actual scope of the environmental hazard caused by leaky sewers has not yet been determined completely. A few cases are known, however, where significant groundwater and soil contaminations were caused by damaged sewers.

Without functioning sewage facilities, i.e. facilities for the collection, discharge, treatment or elimination of sewage, modern civilization is no longer conceivable. The construction of sewage treatment or removal facilities and their continuous improvement in the past decades were in the interest of environmental protection and especially water protection. As a result of these activities, a high degree of connection of the sewers to the sewage treatment plants of nearly 95% has been achieved.

4. Main Activity "Sustainable Technologies for the Remediation of Leaky Sewers" Supported by the BMBF

In contrast to this, the facilities for sewage collection and discharge, i.e. the sewerage systems, were not always given the attention required.

It is therefore necessary to solve these environmental problems by means of technical innovations and to cover the need for economic and sustainable construction methods. As no standard requirements have been made on damage recognition methods and the technologies and materials to be used for the remediation of sewers, considerable uncertainties exist as to which are the appropriate methods to be applied for the solution of specific problems. To improve the situation, the Federal Ministry for Education, Science, Research and Technology (BMBF) established the main activity of "Sustainable Technology for the Remediation of Leaky Sewers" in 1989 already. In October 1991, this main activity was extended to cover the new federal states as well. The following priorities have been specified:

- Development and testing of new detection methods for determination of the damage of leaky sewers,
- methods for the determination of the environmental hazard caused by leaky sewers, their classification and evaluation,
- prototype demonstration of the state of the art of sewer remediation,
- development of novel technologies for the new construction and extension of sewer networks.

Within the framework of this main activity, a total of 45 projects in the amount of about 45 million DM have been granted since 1990. In accordance with the requirement of damage recognition as a prerequisite for damage remediation, highly sensitive optical, acoustic and geoelectric detection methods have been developed. Special investigation and test methods allow reliable statements to be made with regard to the tightness of pipelines and seals and, hence, to perform object-related controls of public and industrial sewers, e.g. for the determination of the sewer status at a certain time as well as for the estimation of its remaining service life. Development in the field of remediation technology

focused on methods for passable and unpassable sewers. Technologies for the reconstruction of damaged household connections from the ground surface, from buildings or from within the sewers are of crucial importance. By means of telemanipulator systems, sewers that are in danger of collapsing and therefore cannot be entered by persons can be remediated. Other important developments focus on carrier vehicles for the installation of detection and/or remediation systems.

Within the framework of this main activity, a number of developments was launched and sometimes implemented rapidly in practice. Hence, a major contribution was made to the solution of an acute environmental problem.

5. Project Examples

On the occasion of this workshop some examples of successful projects of the following main topics will be presentend:

- Detection methods for determination of damage
  - Ultrasonic sewer inspection
  - Impact vibration analysis
  - Satellite inspection system

- Sanitation methods
  - Multi-segment sewer robot platform
  - Sleeve rehabilitation using prestressed injection sealing
  - Controlled propulsion of connecting pipes
  - Special packer for sewer renovation

- New construction methods
  - Replacing existing, non-passable pipes
  - In-situ replacement of pipes

Ultrasonic sewer inspection

- State of the art inspection of sewer lines is done by video camera. This technology gives no information from inside the pipe-wall. Even cracks are sometimes hard to find or, on the other hand, scratches are classified as cracks. Therefore the Fraunhofer-Institute Biomedical Technology has developed a system for ultrasonic detection of flaws in sewer lines.
- The first prototype coupled the ultrasonic transducers by a water-film to the pipe wall and the inspection was done stepwise and took a lot of time. To overcome this problem, the next version was built with wheel transducers for a fast and continuous inspection.
- Flaws like reduced wall thickness due to corrosion or crack are detected automatically without a worker.
- The overall results of an inspection are shown in a projection of the pipe wall and stored in a file, ready for further evaluation with common sewer maintenance software.

Impact vibration analysis

The device is able to detect cracks, material and structural defects in pipes and is further able to determine the quality of the embedment of pipes.

The device consists mainly of two acceleration transducers to pick up the pipe wall vibrations on opposite sides of a pipe and a pneumatic hammer that is impacting the pipe.

A first prototype has been constructed to test possible components and after good experience in a test pipe the components have been fixed on a carrier able to operate in 50 m pipes of 12" to 16" diameter. Because of the good performance of this tool, it was covered for usage in operated municipal pipes. New developments are carried out for industrial pipes.

Satellite inspection system

The satellite inspection system provides remote control technical facility for cleaning, inspection and recording the state of the full length of the lateral. The system operates from the main public network. By employing the principle of repulsion the system can be actuated regardless of the environmental structure. Obstacles, such as broken fragments of pipe, dislodged pipes or in-grown roots only represent a minor hindrance, unlike in cases where traction systems are used. Once the highly integrated inspection head (satellite) reaches a side inlet, it goes inside. The inspection head can be moved around freely inside the space by its inherent power vector control. The inspection satellite uses high-pressure water, which is partly pulsed through special micro-valves. The satellite can go for up to 30 m in the narrowest of pipes, acquiring a comprehensive picture of the state of the pipe by means of an integrated CCD camera. It can penetrate up to three times deeper than conventional systems.

Tube-relining process with manufacture of house connections

- Tube-relining method

The purpose was to develop and test a tube-relining system for sewers with diameters of 300 mm 800 mm, which satisfies the structural strength requirements and stress values for prefabricated products and shwos a ductility of > 10%. This expansibility is intended to guarantee a tight-fitting connection of the tube to the wall of the pipe, even in the case of large deviations in the tolerances of the nominal pipe diameters.

- Robot system

The robot system consists of two self-propelled components for nominal diameters of 150 mm to 250 mm and for nominal diameters 250 mm to 600 mm. The aim was that the technical equipment should be mounted on one carrier vehicle and function autonomously. The drives were mainly hydraulic and in part electromechanical. The robots are fitted with a videocamera, so that monitoring during the work is guaranteed. The supply cables are mounted on a hydraulically-operated drum. The maximum length of the hose and cable bundles used is 85 m. The carrier vehicles can be equipped as cutting robots and with a few modifications be turned into robots for making repairs to feeder pipes.

Multi-segment sewer robot platform

To help make sewer inspection more effective, the aim here is to build the prototype of a cable-less sewer robot platform. The intended features are:

- for pipe diameters 300 mm - 600 mm
- able to follow bends and steps
- allows for adding payload (e.g., damage sensors).

Wireless transmission of data from and to the platform is possible, but due to its foreseeable lack of reliability, the platfrom must basically be operable fully autonomously.

„Platform" here means that it is not intended to build a fully functional sewer inspection robot, but a device providing the space and control capacity to carry and employ, e.g. damage sensors autonomously in a sewer.

The platform is intended to be both more autonomous and more maneuvrable than state-of-the-art sewer equipment. Maneuvrability requires high kinematic flexibility, which will be achieved by a multi-segment architecture with active, controllable joints (3 degrees of freedom per joint) and independent propulsion per segment. Autonomy requires the ability to perceive important features in the environment (landmarks, obstacles), to navigate according to a given sewer map, and to provide hardware and control interfaces to work units, such as damage sensors.

Achieving these features under the conditions inside a sewer (lack of space, lack of energy, difficult and different sensor conditions, dirt, slip, water) requires dedicated robotics research.

Sleeve rehabilitation with prestressed injection sealing

- Material

A new type of polyurethane system has been developed for the process whose most important material characteristic values are comparable to those of current compression seals. The result of the material development is a two component polyurethane system. The initial substances are extremely hydrophobic so that the material can be worked under water without forming foam.

- Increase in volume

The material experiences a definite increase in volume following hardening which creates a pre-stressing in the injected seal ring. The increase in volume is independent of the chemical reaction. A further special feature of the new injection material is the creation of pre-stressing through increase in volume. The increase in volume sets in after the material has hardened, i.e. it can take up mechanical stresses. The creation of the desired stressed condition is thus independent of the leakiness of the connection to be rehabilitated.

- Position of the seal

The seal produced lies in the annular ring of the pipe connection. The surrounding earth remains almost unaffected, the pipe cross-section is not decreased.

- Operation of the Seal

The seal produced with the new process functions in four ways:

1. Pre-stressing
2. Adhesion
3. Positive closure
4. Lateral strain

The functions are independent from each other.

- Mixing technique

A dynamic mixing device, integrated in the packer is employed to prepare the sealing material. This ensures that only correctly mixed material leaves the mixer head. Thus a constant high material quality is achieved.

- Material usage

By monitoring the application efficiency and the injection pressure the complete filling of the sleeve gap is ensured. At the same time the multi-stage cut-off criteria limit the material usage to the volume necessary for the seal.

Controlled propulsion of connecting pipes

With this machine, small collectors with nominal widths of up to 500 mm can be laid underground. A special feature of the machine is the very short set-up und dismantling times as well as ist intensitive, sturdy design. Furthermore, emphasis was placed on simple user-friendly handling. Considerably lower investment costs as well as easy and quick set-up and removal at the construction site, compared to conventional micro tunnel machines, result in lower construction costs.

Up to now, pilot rods with inclined tips were used to control the machine. The rods were pressed through the soil in a controlled manner and monitored by a camera. A prerequisite for this kind of control is a displaceable soil, free of obstacles, and the presence of a target chamber.

In order to eliminate these drawback to control with pilot rods, an entirely new controlling technique was developed. The pilot step, formerly indispensable, can be together eliminated. Essential elements that were already part of the equipment when controlling with pilot rods (camera with inclinometer and monitor) were integrated into the new controlling technique. The following is a description of the new controlling technique:

- The bore press device is set-up in the starting ditch.
- The CCD camera is mounted onto the machine frame or onto a separate post in the starting ditch. The camera is set to the nominal direction and the nominal inclide, and the monitor is mounted to the wall of the chamber within the equipment operator's field of vision.
- The boring is carried out as a normal clearing boring with a hollow boring worm.
- The boring head is a worm boring head with an inclined control surface with a diode traget field attached to it.
- During the boring, the position and location of the worm boring head is continuously monitored by the camera through the optical channel in the hollow boring worm conveyor, and is displayed on the monitor for the operator.
- If a deviation of the diode target field from the specified axis is displayed on the monitor, the machine operator can turn the worm boring head with the control surface in such a way that, when further pressing ahead with turning, a control movement occurs towards the desired direction.

- The controlled boring is driven along the specified axis.
- After having reached the target point, the desired product pipes are pushed in from the starting ditch, and the protective steel pipes are removed in the target ditch.

The advantages of the new controlling technique can be summarized as follows:

- While the soil must be displaceable and free of obstacles during a pilot boring, boring with the steering worm conveys the soil. The soil does not have to be displaceable under all circumstances and individual rocks up to a size of approximately 70 mm will be conveyed by the hollow boring worm.
- The placement of the diode target field at the control tip, almost at the foremost point of the boring head, indicates the current location of the boring head at all times. The effects of steering corrections are therefore immediately visiable with their full impact without any time delay. Therefore, deliberate over compensation based on the time delayed reactions of the boring head is unnecessary.

Special packer for sewer renovation

The aim was the technical construction of a device for the purpose of trenchless renovating the area around the main-sewer-pipe and laterals connection. It consists of two parts:

- Sturdy steel construction - rigid understructure - sliding steel carriage (approx. 80 cm long) with two bellows as integral parts of it which serve to elevating the packer-plate to any position whichever you want to choose.
- Packer-plate (= alloy steel fitted into a sealing rubber-cushion) rigidly fixed to the a/m described bellows to put it into the final renovating position by means of a rotary unit.

In the middle of the packer-plate a small special-piston-packer is fitted to be charged with 2,0 bar compressed air to keep free the laterals from penetration of sealing material. On the top of that smaller packer a selv developed tiny surveillance camera is fitted.

Pneumatically acuated bellows guarantee an optimum of adjustment of the packer-plate to the interior of the wall of the sewer-pipe covering the following diameters:

Main-sewer-Pipe: DN 250, 300, 400, 500 mm

Laterals: DN 150, 200 mm

All motions of the packer-plate (attached smaller packer as well) are fully controlled by three cameras (two of them rigidly fixed at the undercarriage of the packer-plate / 1 in front, 1 at the rear of it).

The sealing material applied should have an adhesive strength, shouldn´t foam up and after curing period to have a certain resilience.

Replacing existing, non passable pipes

The aim was the development of an easy-effective technology in order to change existing sewers of the same line with a remaining or larger cross section in the non- man-sized nominal width area (800 mm).

The excavating behavour of the cutting wheel was improved decisevely by using a pneumatic hammer which is integrated in the machine. The material transport is effected pneumatically by the exhaust air of the hammer in the area of the cutting head. In the machine pipe the soil is passed onto screw conveyors in the direction of the launching shaft. The fine-grained soil can be transported out of the launching shaft with the help of a bucket.

Via a forward pilot head which is centred in the old pipe a technically complicated guidance was not necessary. The driver of the machine can operate the tunnelling machine directly out of the jacking pit by means of simple motor hydraulics. A hydraulically operated gear displacement simplifies the handling when changing a pipe and therefore reduces the assembly time considerably.

Advantages of this new trenchless technology are:

a) Low prime and operation costs for the machine; simple site equipment; little operation personnel.
b) Fast advance by high bore speed (for jacking and pipe changing about 5 m/h) with a jacking length up to 80 m.
c) Controlled installation of the new pipe in same position of the old pipe by forward running and thus centering pilot head.
d) Application for traditional pipe materials like clayware and concrete; new pipe could consist of plymeric concrete, GRP, clayware (reinforded) concrete or ductile cast iron.
e) Ground conditions can be sandy or cohesive; groundwater level should not be much higher than top of the pipe.
f) Useful method for protecting the environmental resources by reducing impacts on vegetation, traffic and pavement and minimizing costs and problems; the crusched old pipe (pieces of 40 - 50 mm) and the surrounding soil are removed via new pipe, leaving no material as wate in-situ.

In-situ replacement of pipes

Microtunnelling today relies exclusively on the pipe jacking technique. In this method the force required to advance the tunnelling machine is transferred from the launch shaft, through the product pipes to the machine itself. The force required to advance the machine increases with the length of the tunnel due to frictional resistance to the pipe movement. Interjack stations are installed in long pipe jacks to reduce the maximum thrust required.

The tunnelling machine is designed in modular units as detailed below:

- Tunnelling machine

This section resembles current micro tunnelling machines consisting of a steering head incorporating a clutterhead and conical crusher type drive unit, and a machine pipe housing steering and slurry circuitry.

- Trailing tube

Containing installations for main drive and measurement.

- Finishing unit

Contains the thrust ring and thrust rams, the drive for the transport unit, and tunnel section handling cylinder.

- Tailskin

For lining erection and backgrouting of lining units.

- Transport

For transport and installation of the individual tunnel sections following the quick-look procedure. Using this expandable tunnel elements are transported through the previously constructed pipe into the tailskin area where they are enlarged to the final lining diameter by means of a rack and pinion drive and the locked in position.

- Transport system

For transport and injection of annulus grout.

77963 Schwanau 2, Dec. 1997
Werner Suhm / mta

Microtunnelling under economical aspects

ECO 97; (Kyoto,Japan)

1. Information on Messrs. Herrenknecht

- In 1977 Martin Herrenknecht founded the company **Herrenknecht**.
- Mr. Herrenknecht himself has worked as responsible machine engineer at the Selisbertunnel in Switzerland, where he got accustomed to the basics of tunnelling work.
- Engineer-office and fabrication is in Schwanau.
  At present: 600 employees.
- Since 1991 supplier for steel-girder construction in Dresden (200 employees)
- Subsidiary with sale and service in USA, South Carolina,
- Subsidiary with sale and service in England
- Subsidiary with sale and service in Thailand for Asia
- Further subsidiaries in the Netherlands and in Switzerland

1.2. Product range of Herrenknecht GmbH

- Excavators and roadheaders
- Mixshields
- Hard Rock TBMs
- Earth-pressure balance shield (EPB-shields)
- Tunnelling equipment (data recording systems, segment moldes conveyor plants, logistical accessories and tunnel measuring system)
- Microtunnelling machines

1.3. Aim of Herrenknecht GmbH

Our aim is to build all kind of tunnelling machines from NW 100 mm up to 14 m diameter and for all geologies, with:

- high service quality / availability
- friendly service
- easy assembly
- high jacking speed
- high efficiency
- high safety standards

At present, Herrenknecht is worldwide the only manufacturer of tunnelling equipment who is able to offer for tunnelling work machines of all systems and sizes.

2. Development of microtunnelling

For the development of new technologies subsidiaries, used for exact purposes, are advantageous. They allow to start developments found out to be advantageous. The first development and test of tunnelling systems for non-accessible cross sections in Germany started this way. This step was necessary in order to start some sort of initialization process. However, the establishment of a new construction procedure on the market depends afterwards on the competition.

Any subsidiaries would not only be wrong but even detrimental as they would not challenge enough the clients' readiness for innovations which is imperative for the technical evolution by pratical experience. Experience in-situ and a permanent communication between owner, user and manufacturers of machines and pipes can only be centralized and effective if there are sufficient chances for the companies to realize the corresponding projets.

Only if there are large volume orders of public and non-public clients, the industry is challenged to achieve low prices with new techniques.

In the beginning, the closed-type construction was very critically compared with the open-type technique. In 1984, the economical breakthrough of Microtunnelling in Germany was achieved by the Waterworks of Berlin with the development of the "Berlin construction method (shaft lining".

The initial thought was to reduce the number of road openings. The opening and reconstruction alone cost 31 % of the channel construction costs in open-type construction. Another 39 % have to be invested in the lining, the excavation, the soil exchange and the filling of trenchs. This partial costs are not involved in the channel laying itself and are very critical concerning economics as they can be reduced drastically in the closed-type construction.

The "Berlin construction type (shaft lining)" consists of the consequent application of controlled pipe-jacking for road and connection channels in an interval procedure for nominal widths of ND ≤ 600 launch and reception shafts.

The necessary shafts for the excavation of road channels serve also as a basis for the excavation of house connection channels. Star-shaped drive of the channels to the properties. During this procedure several properties can be reached without overlengths for house connection channels or an undercrossing of external properties. It only is important that the position of this shafts is optimized.

As for the "Berlin construction type I (shaft lining)", the properties which cannot be reached from the launching or reception shafts are - equally in star-shaped drive - developped from "auxiliary shafts". In the "auxiliary shaft" the connection channels are relied with the public channels by means of vertical support devices and form pieces.

At the end of the tunnelling works, the launch and reception shafts are constructed as access shafts with the normal dimensions. This can naturally be effected as shaft in the shaft, a solution, which is applied for 3.20m wide launch shafts for thrust pipes larger than 400 ND. All auxiliary shafts are converted into access shafts when applying the "Berlin construction type 2 (shaft lining)".

The "Berlin construction type (shaft lining)" results in a totally different division of the partial cost groups in comparison to the open-type mode. The reduction of costs for road opening and reconstruction from 31 % to 8% is significantly.

The breakthrough of the technology was accelerated as the machine manufacturers supplied machines for small diameters from ø 250 - 1200 and simultaneously machines for the following house connections with a diameter of ø 100 - 150.

3. Requirements of the microtunnelling machines

With regard to the universal field of application the following characteristics were required from tunnelling machines:

- exact control,
- operation in all loose and hard grounds as well as in groundwater
- largest possible advance lengths.

In order to be competitive with the conventional channel construction it was also necessary that the machines fulfilled the following requirements:

- short dimensions for launch and reception shafts,
- sufficient advance lenghts,
- small expansion of jobsite equipment,
- few operation works and low fault liability,
- cutterheads with extension possiblities for one basic equipment.

Generally, German machine manufacturers were able to improve and complete their systems in many ways due to the application possiblities and the high flow of information as well as the research and development works. This concerns the automatic tunnelling control with an electronic laser system (ELS) and Fuzzy Control (FC) as well as the permanent addition of excavation devices for a variety of geological situations.

4. Applications of the microtunnelling technique

If you summarize all applications the following tasks can today be carried out by means of the environmentally friendly Microtunnelling:

a) Sewerage technique

- Underground production of channels and pipes in order to extend drainage networks.
- Refurbishment of channels and pipes by means of the underground laying in free lines. The systems which are to be refurbished serve to continue the current operation until the connection change.
- Refurbishment of channels and pipes by driving over defectuous headings (pipe-eating u. crush-lining).
- Additional underground production of connection channels including the underground connection within an existent heading.

b) Other

- Laying of pressure lines like gas, oil and long-distance energy pipelines under constructions like roads, airports etc. as well as rivers.
  Partially, the product pipe is jacked directly or pulled in a previously jacked protection pipe.
- Pre-supporting arch in connection with tunnelling measurements with a low cover or constructions jeopardized by settlements in the area of the tunnel route.
- Drainage lines in depots.
- Protection pipes for communication and supply lines.

5. Economical aspects

The construction costs for channel measurements depend on many situations, administrative requirements and secondary conditions. Naturally, the local price level and the conjuctural sitation play an important role.
Supply and demand - in form of order volumes by public customers as well as the number of rival contractors have a direct impact on the construction costs.

Evaluations of the direct and indirect costs are up to now often unconsidered respectively only partially considered in the economic comparison of the open and closed construction type.

This are advantages whose values can be exactly figured and be recognized as economic saving.

Direct costs:

- Loss or limitation of lowering of ground water.
- Reduction of line relayings.
- Decrease of of street and carriageway break ups.
- Upholding of the drainage.
- Measurments of traffic diversions.
- Hand shaft lining in the area of tree roots.
- Loss of excavation material and delivery and elimination of huge ground quantities.

Advantages which mainly result of the ecological and social sector and whose value is quite difficult to figure.

Incirect costs:

- Noise emission by traffic influence and building implements.
- Impairment of the retail trade by reduction in turnover.
- Detoriation of accident risk for local residents and staff.
- Loss of stoppage periods due to weather conditions.
- Avoidance of damages on the surface vegetation and buildings.
- Reduction of the exhaust and dust emission.
- Change in value of road surfaces.
- Limitation of traffic impairment.

When comparing the economic contemplations, the costs which can mainly be assigned to the social sector are at present generally not yet considered in favour of the microtunnelling. This means that the trenchless solutions, which are only cheeper when considering the "social costs" are not chosen, as the balance can nowhere be figured.

It is in the interest of the conservation, the fair competition and the taxpayer that decisions are immediately taken. Charges for the obstruction of carriageways depending on size and duraton which are orientated on the actually resulting and determinable "social costs" would be one possibility.

However, up till now no one thought on bringing this into relation with the line construction. Bearing this option in mind and orientating the charges on the actually resulting expenses for the national economy, an equality in the competition of the different construction types could be ensured.

6. Advantages of Microtunnelling under the aspect of process technology

- High quality of the building works due to little tolerances of the jacking pipe, high laying precision and high-quality jacking pipe.
- Undisturbed pipe bearing.
- Damages become directly obvious during the jacking process and can not be hidden.
- No interference zone above the pipe which might for instance be caused by bad packing (compression) of the pipe trench.

7. Recommendation for the promotion of the economy

- Microtunnelling is not only suitable for short undercuttings of dams trackways, waterways or intersections. The longer a jacking job site the more economic the relatively high expenses for this sophisticated technology can be splitted. In addition, many and huge projects are a sign for the contractor, that it is worth investing in a modern technology.
- Future comparative economic calculations for the open and close construcion type in the planning period. In this situation, all influences have to be considered, meaning especially regarding the expenses for the open construction type all factors have to be objectively considered. For instance even taffic light installations, provisional and definite street recoveries, pipe re-layings, ground exchanges, ground water reach (levels) and the times of construction. In case of almost equal expenses of these contemplations, the economy should lead to a decision on alternative detailed estimates of the market.
- Due to the standarization of the start- and end-shaft and their later integration in to the sewage net/system the customer can contribute to the rationalisation. Especially pre-manufactured cylindrical start shafts of reinforced concrete have proven to be a good investment.
- The operator should restrict himself to a certain number of nominal widths (diameters); spaces such as DN 350,450, 700 or 900 should be avoided if possible. Beneficiary of such a rationalisation contribution are all persons involved; machine and pipe manufactuerers, building companies and operators do not have to produce and store an unnecessarily high number of nominal diameters.
- Samples of detailed estimates and standard capacity books have to be adjusted to the technic conditions and be completed by the jacking works.

- Jackings of single distances such as house connecting channels should be added to general agreements for permanently recurring smaller projects and generalisations, whenever possible, in order to simplify the clearing business.

8. Facts at the example of Berlin

Until the end of 1996 the waterworks of Berlin have constructed underground by means of microtunnelling approximately 250.000 m sewage channels and lines on a much more economic way with the extensive application of the Berlin construction type. Thus they were able to realise savings of more a good 40 millions DM.

Break up and recovery of approximately 348.000 m^2 carriageway surface could be avoided. More than 640.000 m^3 must not even be digged out, transported and topped up again as thanks to the pipe jacking itself only a fraction of the ground has been displaced.

As a result it was possible to abstain from transports of more than 53.000 lorry loads of ground; thus a source of enormous pollutant emissions has been avoided. It was possible to considerably limit ground water reaches. Thus, there was no need to lower a good 56 millions m^3 of the precious ground water - a quantity that would be sufficient to provide the reunited city of Berlin with drinking water for more than two months!

9. Prospect

In Berlin meanwhile yearly a good 50 % or the pipe layings are done underground.
In spite of all these advantages and the success in Berlin, microtunnelling has at present a proportion of 5 % of the entire line construction in Germany. This is quite hard to understand as this proportion lies far behind the possibilities of this technology in the sector of line construction of sewage, long distance energy, gas, telephone and water.

The reasons for this are:

- Ignorance of the state of the achieved developments.
- Unsureness regarding questions of planning, request for tenders and building preparations.
- Suspiciousness in view of the success in case of difficult soil conditions.
- Caution of the companies regarding invesments, as the application frequency cannot be judged.

Microtunnelling allows to construct conservation-minded and over and above that often in a more economic way. Obviously this is not yet known to most offices, authorities and institutions as in the present official discussions on the subjects of cost saving in the sector of the sewage technology allusions to this trenchless construction type are almost never made.

Microtunnelling offers in many cases the possibiliy of saving money and to construct more and more conservation-minded. In a world of limited ressources this should be the highest aim of each technically high-developped country.

Session 5

Groundwater Preservation and Membrane

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Groundwater Pollution by Leaking Sewers

M. Dohmann, Aachen

1 Introduction

Ever since experts and general public worked on the assumption that sewers for centralized waste water transportation and premises drainage are and remain watertight after having been laid. But since sewers have been operated more carefully during the last 20 years, the knowledge on massive leakage of pipes and sewers has increased. For a long time it was already known that some sewage treatment plants received considerable amounts of infiltration water from leaking sewers lying in the groundwater; but no special importance was attached to this fact. Measures for continuous watertightness control were taken only in the case of a potential risk for the groundwater, such as laying of sewers in drinking water protection areas or sewers in industrial enterprises with critically loaded waste water. Only the suspicion of massive waste water exfiltration from sewers laid above the groundwater table gave the impulse for closer examinations. First investigations only allowed very rough estimations of the waste water volumes exfiltrating from the sewers. For the public sewers in West Germany a flat waste water loss of 300 [1] and 330 [2] millions m^3 per year was established. With approx. 55 millions connected inhabitants this would have meant a specific exfiltration rate of about 15 l per inhabitant and day, thus of more than 10 % of the whole domestic waste water volume. These investigations did not even consider the leaking sewers of the premises drainage plants, which are laid nearly exclusively above the groundwater table and, with this, are relevant for waste water exfiltration.

In recent years the knowledge on leaking sewers and its effects has considerably increased. This was due to

- extensive inspection of sewers and pipes in many German cities,
- research work on the environmental hazard with the help of emission measurements [3, 4], and
- study of groundwater pollution with the help of input measurements [5].

Now it is possible to make a better founded estimation of soil and groundwater pollution resulting from leaking sewers. However, due to complex peripheral conditions such as

- waste water composition at dry and stormweather flows,
- damages in sewers and the degree of leakiness linked with them,
- groundwater levels, and
- permeability of the soils,

simplifying assumptions are necessary if generalizing statements and comparisons with other pollutant input sources are to be made [6].

2 Exfiltration Volumes

Within the framework of research projects [3, 4] the exfiltration processes at leaking sewers were more exactly studied. Examining individual damages in the sewer under always the same conditions (degree of partly full flow, waste water composition) it was shown that the exfiltration volume decreases over the time. Figure 1 shows the results for a vitrified clay pipe with a longitudinal crack of 4 mm length in the bed. After some hours up to some days a state of equilibrium in the zone waste water - damage - soil turns up, which, however, easily can be disturbed, leading again to higher exfiltration rates. Disturbance may result from precipitations (pressure increase due to a higher degree of partly full flow, diluted waste water), high-pressure rinsing or impermeability tests. If the sewer is surcharged up to the interior of the shafts, the exfiltration rate rises exponentially.

By means of extensive investigations specific exfiltration rates were determined in real sewers for different sewer damages and conditions in terms of waste water technology. Table 1 shows some of the values used. Based on these findings the minimum and maximum exfiltration volumes were estimated with regard to damage types and frequencies [6]. The assumptions taken as basis are compiled in Table 2.

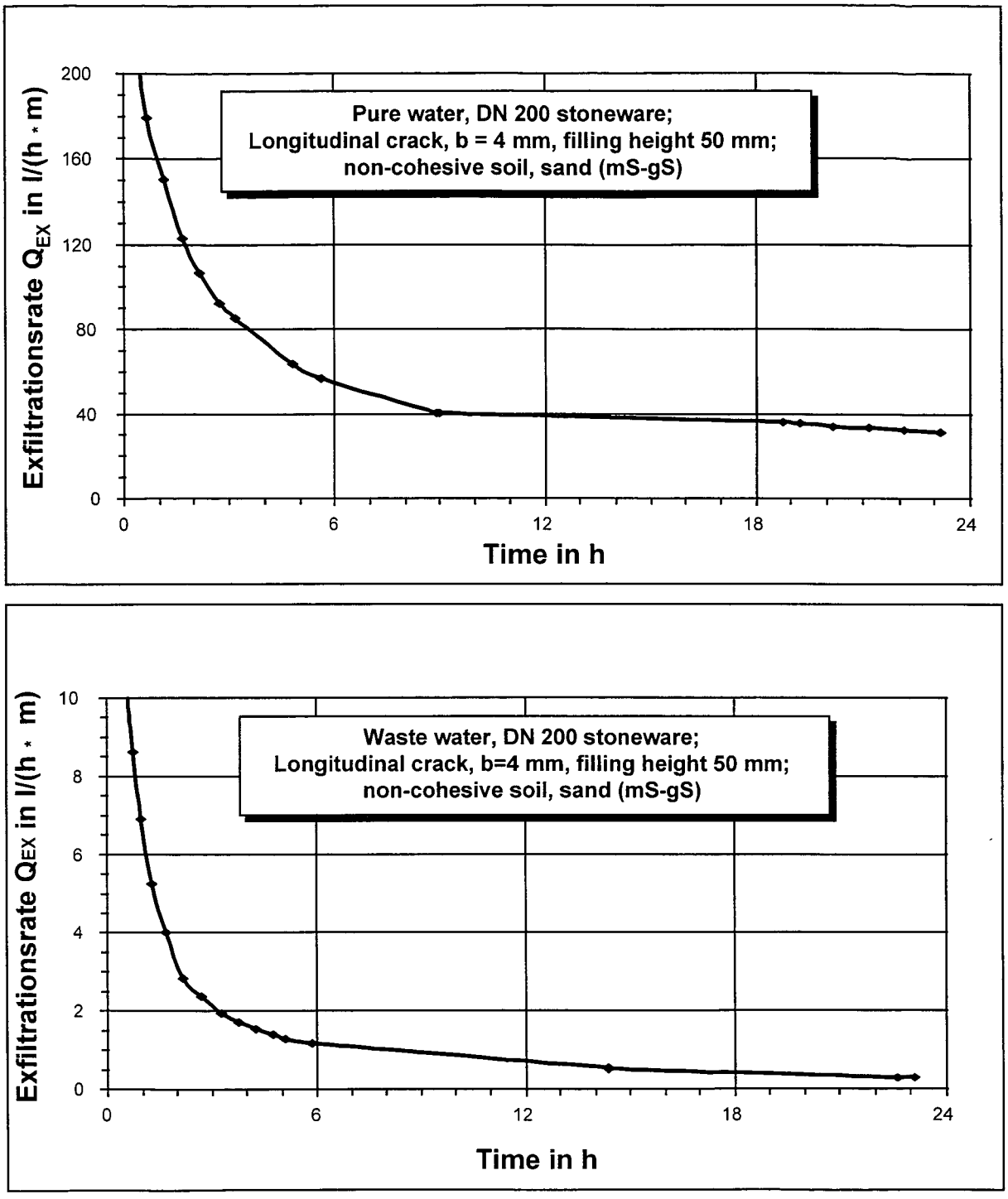


Figure 1 Exfiltration of pure water and waste water from a sewer with a longitudinal crack in the bed and partly full flow

The proportions of the waste water volumes exfiltrating under the varying discharge conditions and the proportion of exfiltration from combined and separate sewer systems are represented in Figure 2 for the minimum and the maximum estimation. For West German sewers the resulting waste water exfiltration volume is in a range of 33

- 440 millions m³ per year. The influence of the pressure head (stormwater flow with surcharge) on the exfiltration rate can clearly be seen.

Table 1 Values for the estimation of the minimum waste water exfiltration volume from leaking sewers

Damage	Damage frequency per km		Exfiltration l per h and damage		
	TW	RW	TW	RW I	RW II
Cracks	5.1	10.3	0.17	0,83	279.05
Joints	10.0	12.0	0.18	0.90	478.20
Cullets	1.3	2.5	0,18	0,90	410.50
Connections	0.0	12.0	0.00	0.90	358.36

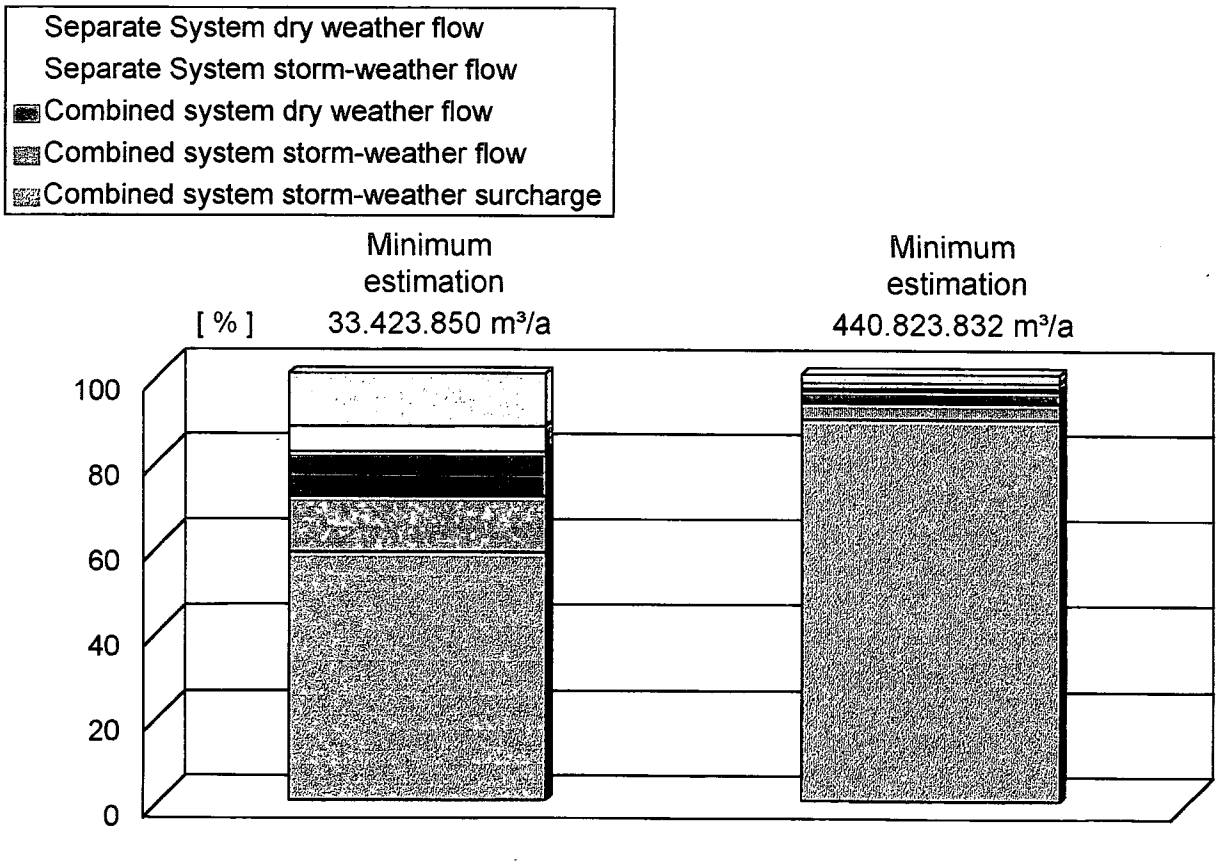


Figure 2 Minimum and maximum estimation of the waste water volumes exfiltrating from West German sewers, according to [6].

Table 2 Assumed values for the estimation of the waste water volume exfiltrating from leaking sewers in West Germany, according to [6]

	Minimum estimation	**Maximum estimation**
Types of damages considered	cracks joints cullets connections	
Damage frequency	according to Table 1	according to Table 1 frequency of permeable joints by five times increased
Length of damaged lines	1.00 m	1.90 m
Sewer length considered	combined system: 193 156 km separate system: 87 221 km (sewers)	
Exfiltration-effective sewer length (groundwater table below the sewer bed)	80 %	80 %
Discharge conditions - duration in % of annual hours	combined system	
dry weather flow	90 %	85 %
storm weather flow *(flooding)*	9.9 %	14.7 %
storm weather flow (surcharge)	0.1 %	0.3 %
	separate system (sewers)	
dry weather flow	90 %	85 %
storm weather flow *(flooding)*	10 %	15 %
- filling degree	combined system	
dry weather flow	DN/3	
storm weather flow *(flooding)*	DN	
storm weather flow (surcharge)	1.5 m above sewer bed	3.0 m above sewer bed
	separate system	
dry weather flow	DN/2	
storm weather flow (surcharge)	DN	

Tests concerning the influence of the soil showed that the cohesiveness of the bedding material or the surrounding soil strongly influences the exfiltration rate. A non-cohesive material, which is not silted up due to "self-sealing effects" of the waste water, allows exfiltration rates that are many times higher than for cohesive bedding material. Therefore the calculations also indicate the possible range of waste water exfiltration rates from leaking sewers resulting from the different soil types.

3 Study of the Emissions

If one starts from the assumption that in the case of waste water exfiltration processes the infiltration course of the waste water is more or less long until it reaches the groundwater, the substances transported will normally be submitted to changes. These changes have to be estimated in order to make statements on the input of substances into the groundwater body. Detailed examinations concerning the soil passage of exfiltrated waste water were carried out in [7]. Seven case studies were realized with regard to waste water composition and sewer damages as well as soil and groundwater. As expected, a biologically active layer appeared in the soil at the exfiltration spot. The thickness of this layer depends on the outcropping soil. The thickness in sandy layers was between 5 and 10 cm. In this layer especially the particular waste water components were retained, and "normal" organic substrate was degraded. Under corresponding oxygen supply conditions or if dissolved oxygen is lacking, nitrification and denitrification of the nitrogen compounds discharged may occur in this layer. Moreover, heavy metal compounds are accumulated. However, the largest part of metal cations and anions Cl^-, SO_4^{2-} and NO_3^- are transported into deeper soil layers. Figure 3 shows the pollutant input below a 60-year old leaking sewer, determined with the help of soil eluates.

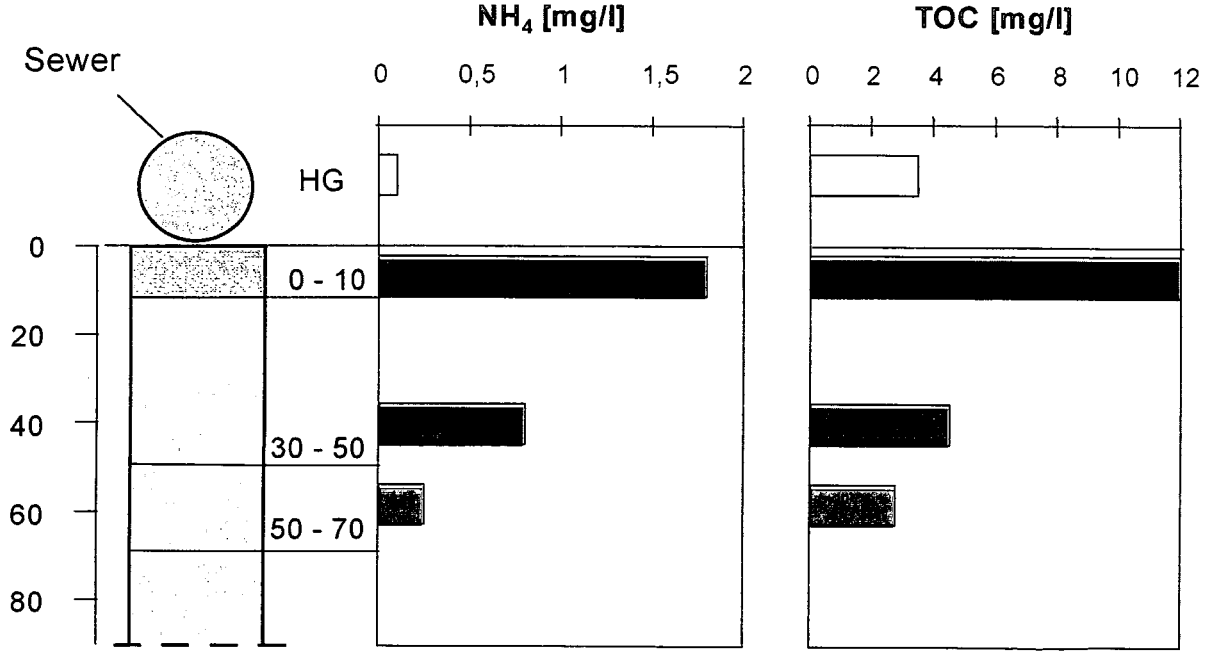


Figure 3 Pollutant input into the soil resulting from a leaking joint

In the cases studied no effects on the groundwater could be detected that might have resulted from leaking sewers. Damage-related analysis of the guide parameters in the soil and the soil eluate showed effects on the subsoil only in the case of serious damages in the sewer bed or leaking joints and defective connections. With slight damages as well as damages in the sewer crown and springing no accumulation of waste water components below the sewer bed was stated [7]. This means that input of substances into the groundwater due to waste water exfiltration has to be expected only in the case of serious damages in the sewer bed, at groundwater levels of less than 1 m below the sewer bed and with well-permeable soil.

4 Study of the Inputs

Within the scope of a research project carried out in the urban area of the city of Hannover, the water volumes exchanged between the sewerage system and the groundwater were determined, and the effects of these exchange processes on the groundwater were studied [8]. The following tasks were worked on:

- Balancing of the flows occurring in the different parts of the sewerage system,
- Determination of the water exchange between the sewerage system and the groundwater with the help of a groundwater model, taking into consideration the infiltration- and exfiltration processes,
- Calculation of the exfiltrated waste water volume by balancing the indicator substances sulphate and boron.

For the research area with a surface of 204 km², 5 - 8 millions m³/a of percolated waste water and 14 - 20 millions m³/a of infiltrated groundwater were established. With this, groundwater recharge is considerably influenced, resulting in groundwater tables changing up to 2 m.

For the studies carried out in Hannover, however, it was not distinguished between public and private sewers. Furthermore the inputs of substances from domestic sewage plants and small sewage treatment plants were neglected. Reducing these values correspondingly allows the comparison with the total amount of waste water exfiltrated from public sewerage systems in West Germany, which had been evalu-

ated before. It results in approx. 416 Mio. m^3/a, which is similar to the value of the maximum evaluation. The specific inputs of different waste water components into the groundwater in the urban area of Hannover are listed in Table 3. The calculated total input rates are compared to other pollution sources [5]. Figure 4 shows the pollution of the groundwater resulting from the sewerage system, from green spaces, forests, agriculture and allotments for the compounds sulphate, nitrate, chloride and potassium. However, it has to be pointed out that the inputs listed for the sewerage system also include the parts from premises drainage plants and domestic sewage plants.

Table 3 Specific input of substances from the waste water into the groundwater in the urban area of Hannover, according to [8]

Parameter	**Specific input in kg/(ha · a)**
Ammonium	39
Sulphate	160
Chloride	120
Phosphate	13
Potassium	20
Boron	1
Chlorinated hydrocarbons	$40 \cdot 10^{-3}$
Cadmium	$2 \cdot 10^{-3}$
Chromium, Nickel	$30 \cdot 10^{-3}$
Copper	$90 \cdot 10^{-3}$
Lead	$30 \cdot 10^{-3}$
Zinc	$220 \cdot 10^{-3}$

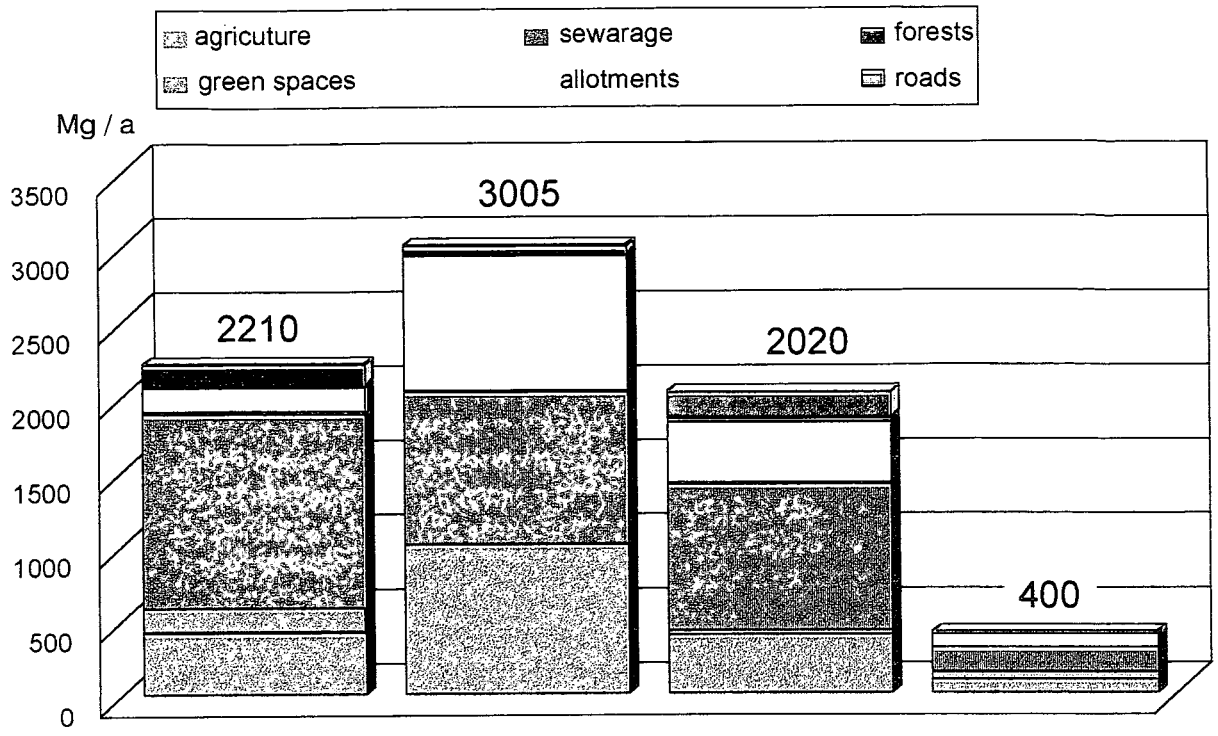


Figure 4 Input of substances into the groundwater in the urban area of Hannover, according to data in [5]

5 Pollution of Groundwater and Soil

Based on the specific exfiltration rates of leaking sewers established and the input of substances linked with them, a projection was made for the West German sewers. The parameters nitrogen, AOX, zinc and copper were chosen for the study because comparisons with other pollution sources of the soil and the groundwater were to be made.

In Table 4 the assumed substance concentrations in waste water and precipitation water are compiled. Since it is not possible to distinguish between lower or higher loaded partial waste water flows, these values must not be taken as universally valid. With the help of these substance concentrations a minimum- and maximum estimation of the pollution load exfiltrating from leaking sewers was carried out, which is summarized in Table 5. While the minimum and maximum exfiltration volumes vary by the factor 13, the range of the exfiltrated nitrogen- and AOX load is 1 : 7. This is due to the dilution effect caused by stormwater flow events.

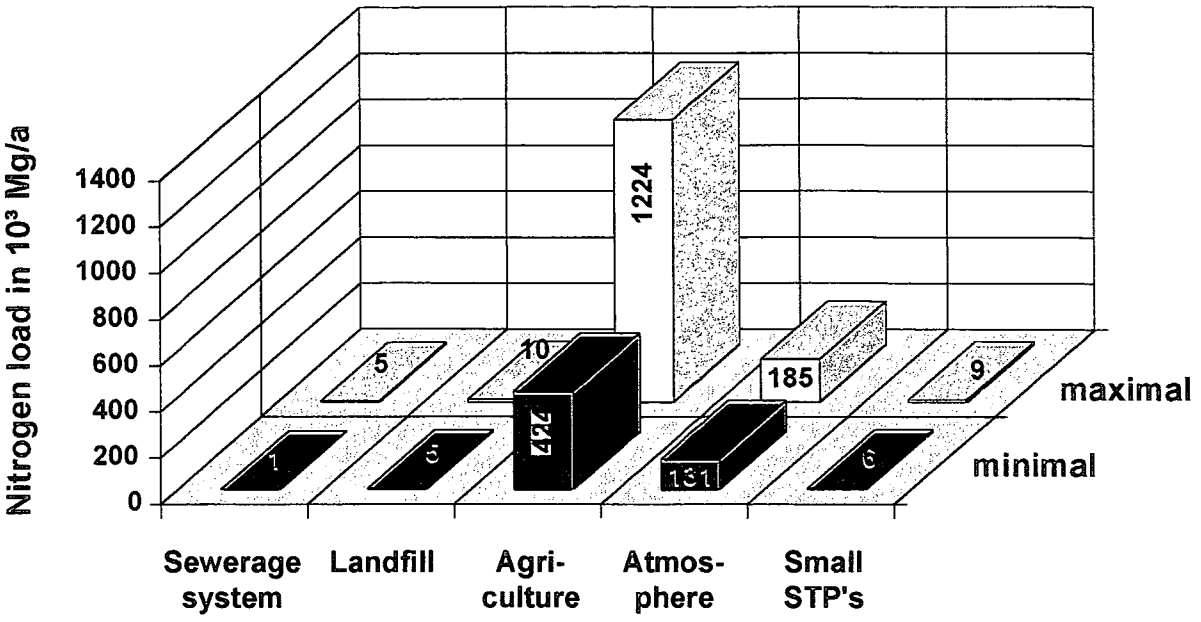


Figure 5: Nitrogen loads from various sources discharged into soils in West Germany

In [6] it was tried to estimate the nitrogen load discharged from various sources into the soil and the groundwater. Besides leaking sewers four other pollution sources were considered: landfills, agriculture, atmosphere and small sewage treatment plants. The result is represented in Figure 5. It turned out that in the case of nitrogen leaking sewers are of minor importance compared to other pollution sources, if the totality of the West German sewers is considered. However, it has to be remembered that each individual leaking point of a defective sewer represents a punctiform load for soil and groundwater. This means that the potential risk for groundwater and soil resulting from leaking sewers has to be assessed for each individual case. This is especially true in the case of industrial waste water with higher concentrations of hazardous substances.

Table 4 Assumed substance concentrations in waste water and precipitation water, from [4]

Parameter	Unit	Municipal waste water			Precipitation		
		min	max	chosen	min	max	chosen
TKN	mg/l	30	100	55	0.7	2.8	1.8
AOX	mg/l	100	300	200	-	-	0
Zn	mg/l	0.1	1	0.7	0.05	1.5	0.7
Cu	mg/l	-	-	0.15	0.007	0.2	0.1

Table 5 Pollution load exfiltrating from leaking West German sewers, according to [6]

	N [Mg/a]	AOX [Mg/a]	Cu [Mg/a]	Zn [Mg/a]
Minimum estimation	688.4	2.4	3.9	23.4
Maximum estimation	5079.4	16.1	48.1	208.6

6 Summary and Outlook

Within the scope of research projects [3, 4] the pollution of soil and groundwater emitted by leaking sewers was examined. The results are summarized as follows:

- Below the sewer bed a biologically active soil layer (about 10 – 15 cm) develops in the area of leaking damage spots where the components of the raw waste water are immobilized or eliminated to a far-reaching extent.
- Effects on the subsoil were only stated in the case of serious damages in the sewer bed or at leaking joints and defective pipe connections.
- Direct contamination of the groundwater could not be stated. However, with groundwater levels of less than 1 m below the sewer bed at least a temporary groundwater impairment is to be expected.
- Under constant conditions a certain self-sealing effect of the waste water occurs at a damage spot, which, however, may easily be compensated by external effects such as pressure increase (stormwater flow, impermeability tests), dilution of the waste water (stormwater flow) or high-pressure rinsing.

Within the scope of a maximum estimation the waste water volume exfiltrating from leaking sewers in the old Federal States was determined with 33 – 440 millions m^3 of waste water per year. Compared to other pollution sources such as landfills, agriculture, atmosphere and small sewage treatment plants, the pollution load of the totality of soils and groundwater in the old Federal States emitted by leaking sewers can be estimated as low. However, this estimation is based on the even distribution of the pollutant emission. A small-scale study related to parts of the urban area of Hannover showed that the pollution load in the groundwater resulting from waste water was much higher.

Private premises drainage plants are in a considerably worse state than public sewers [9]. In future they should be included to a higher extent into risk assessment studies concerning soil and groundwater. Assuming that the private sewers have three to four times the length of the public sewers, but normally are flown through with lower filling degree, a total exfiltration volume of the order of the public sewers can be estimated.

Flooding and surcharge events highly influence the exfiltrating waste water volume. If flooding or surcharge is planned within the scope of sewerage system management, it has to be taken care that the sewers in question are water-tight.

The existing knowledge on the pollution load of soil and groundwater resulting from leaking sewers makes clear that there is no area-wide pollutant potential. Under corresponding preconditions such as

- high share of industrial waste water,
- high hydraulic capacity utilization rate of the sewer,
- high damage density of the sewer,
- groundwater level 0 – 1 m below the sewer bed,
- highly permeable soil,

in individual cases there is the danger of considerable soil- and groundwater pollution.

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ANAEROBIC DEGRADATION OF CHLOROPHENOLS

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ABSTRACT

Effect of acclimation and degradation of chlorophenols by the anaerobic sludge were studied.

Dechlorination of pentachlorophenol (PCP) were observed in a non acclimated anaerobic sludge. After acclimation to PCP, its degradation rate increased about 7 times.

As the result of chlorophenols degradation study by acclimated anaerobic sludge, degradation rate and path were compared. Highly chlorinated phenols were more easily degraded than low one. Dechlorination was a main reaction on anaerobic degradation of chlorophenols. Chlorine at ortho position were removed more rapid than para and meta position. All the chlorophenols were degraded by PCP acclimated anaerobic sludge.

Anaerobic degradation is very effective to the dechlorination of polychlorinated phenols, but high loading of PCP or bad performance of reactor resulted in the accumulation of monochlorophenol.

KEYWORD

chlorophenols, anaerobic degradation, dechlorination, acclimation,

INTRODUCTION

Recently many manmade chemicals are used in industry and human life. Among them some chemicals, such as chloro-aromatic compounds are toxic and hard to degrade. They are used in the chemical industry, chemical products, such as pesticide, herbicide. Pulp mill effluent contains chloro-aromatics, due to chlorine bleaching process. These compounds are hardly removed by the conventional treatment process, such as chemical coagulation or activated sludge process. These compounds should be removed from effluents.

Chlorinated compound are toxic and resistant to aerobic degradation. Recently many report refer to the anaerobic degradation of Chloro-compounds. Even highly undegradable PCB were dechlorinated in anaerobic sediment. Anaerobic treatment has high potential for water pollution control.

Anaerobic degradation of chlorophenols were studied, in order to treat a chloro-aromatic compounds in industrial wastewater, such as bleached pulp effluent, chemicals effluent. Anaerobic sludge were acclimated to penta chloro phenol (PCP), most polychlorinated phenol. The acclimated sludge to chlorophenols seemed to be effective to the degradation of chloro aromatic compound.

In this report effect of acclimation and degradation of chlorophenols by the acclimated anaerobic sludge are summarized.

MATERIALS AND METHODS

anaerobic sludge

Digested municipal sewage sludge were fed by synthetic media of glucose in a 100 litter batch reactor in laboratory. This sludge were used as a control (non-acclimated) sludge. Acclimation of anaerobic sludge to pentachlorophenol (PCP) were carried out using a membrane separated continuous fed reactor of 2 litter. Control sludge and phenol acclimated sludge were mixed and fed continuously glucose media as a main carbon source. PCP, which were dissolved in methanol, were added intermittently two times a week, as the feeding concentration of 3.8 micromol (1mg-PCP/l). The PCP concentration were increased step by step in a month reached to 11.3 micromol.

anaerobic degradation

Anaerobic degradation of chlorophenols were tested in a 150ml serum bottle. Twenty-five ml of anaerobic sludge and defined volume of concentrated chlorophenols were injected. Methanol were added as the solvent of chlorophenols, so defined volume of methanol were added so as to the same quantity were added to each bottle. Total volume of methanol added to each

bottle were around 25 μ l, so it became the main source of methane formation of the test. Mixed liquor were purged by nitrogen gas and sealed by butyl rubber stopper and incubated in a water bath at 35 degree centigrade.

Gas and mixed liquor were sampled and measured.

analysis

Gas sample were analyzed by TCD gas chromatography. Formed methane volume were calculated from the ratio of nitrogen and methane of the head-space of serum bottle and corrected sampling loss.

Sampled mixed liquor were tripled by adding methanol, and separated by eppendorf centrifuge at 10,000rpm. Chlorophenols concentration were measured by HPLC, using a ODS column , gradient of methanol/phosphate and UV absorption at 220nm.

RESULT AND DISCUSSION

effect of PCP to anaerobic methane formation

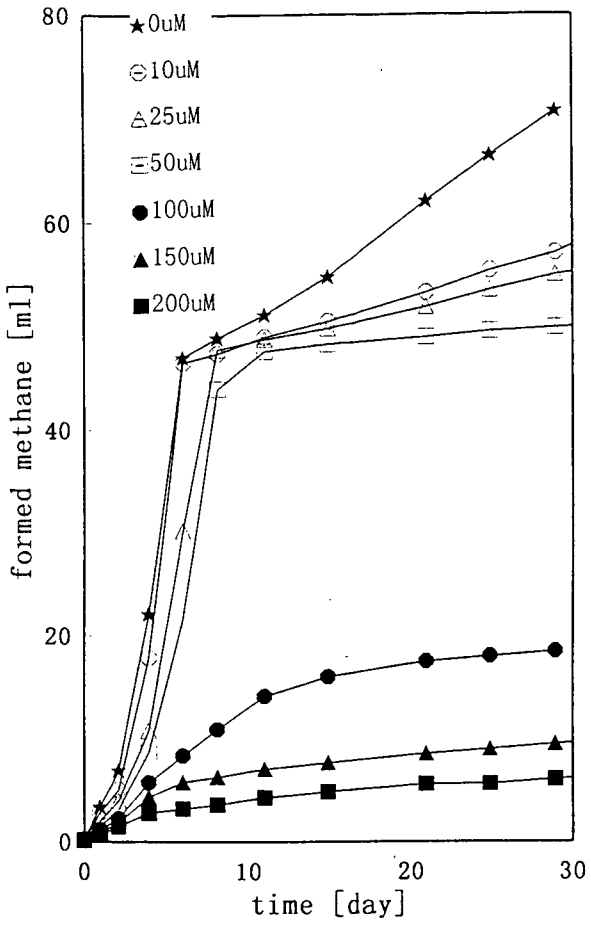
The effect of PCP addition to the control anaerobic sludge were shown in fig.1 and fig.2. In these test methane were formed mainly from methanol, that added with PCP. Most of the methane were formed within four days. It showed little decrease below 50 micromol addition. In case of above 100 micromol addition, methane formation were largely prevented, but even 200 micromol it were not completely stopped. PCP degradation were observed in all the bottle, and the degradation rate were similar, in spite of the toxic effect to methane formation of PCP.

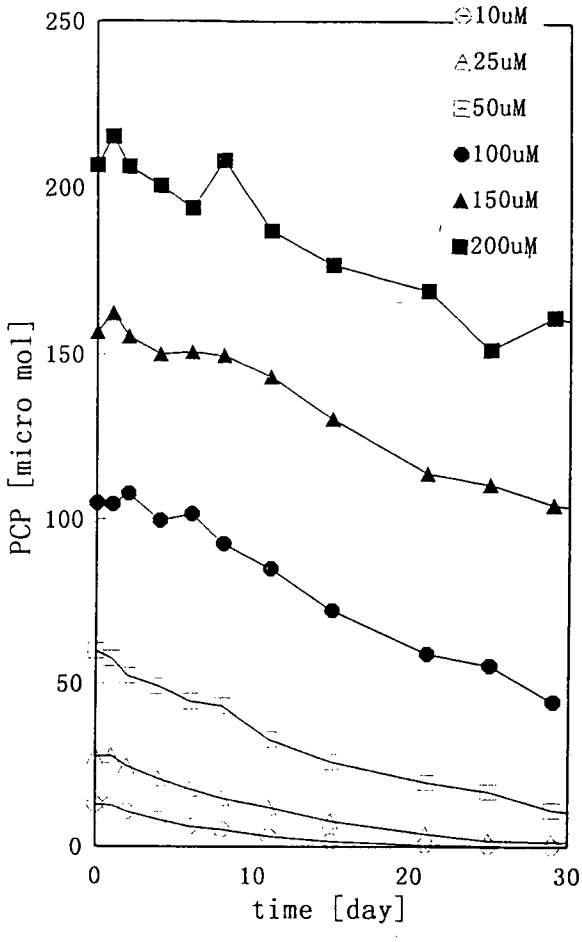
It shows the high potential ability of anaerobic sludge to degrade chlorophenols.

A few big peaks were appeared in HPLC chart in the time course of PCP degradation. Figure 3 shows one example. In case of no addition the peak was not observed. As the result of fraction separation and GCMS analysis, and from the similarity of retention time and UV pattern of standard, the peak was estimated para-cresol. Maximum concentration was about 100 micromol. The chemical is not the intermediate of PCP, it seemed to be formed as the toxic effect of PCP to anaerobic bacterial consortium.

effect of acclimation

PCP degradation rate and path were compared between control and acclimated anaerobic sludge. Figure 4 and 5 show the result. PCP degradation rate increased about 7 times after acclimation to PCP. In the case of control sludge PCP were degraded only through 2,3,4,5-tetra-chlorophenol, but in acclimated sludge by-path route through 2,3,5,6-tCP were developed. Acclimated sludge could





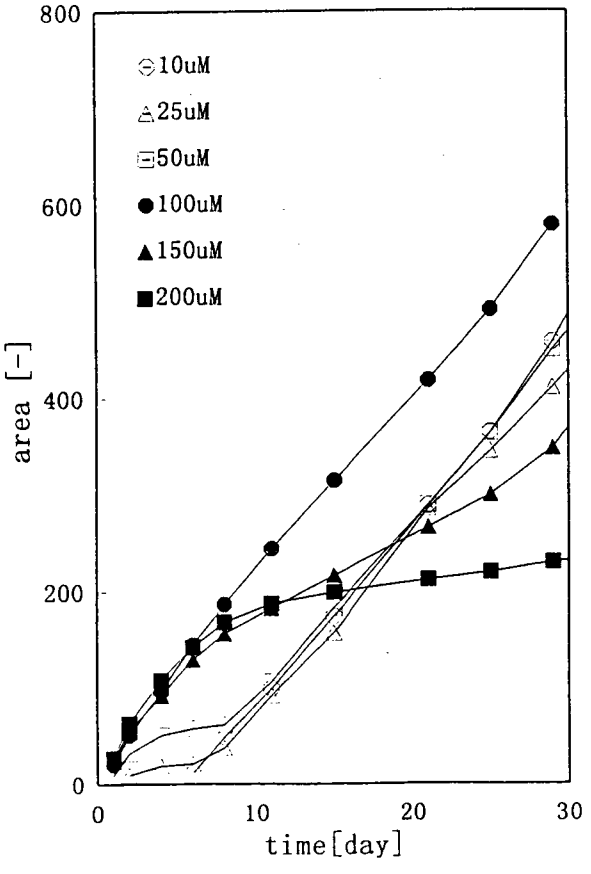


fig.1 Effect of PCP concentration to methane formation of non-acclimated anaerobic sludge (left up)

fig.2 PCP removal by non-acclimated anaerobic sludge (right up)

fig.3 Para-cresol formation due to the PCP addition to non-acclimated anaerobic sludge (left down)

scale: 640=100 micromol of cresol

common conditions

MLVSS: 10,400 mg/l

volume: 25 ml

PCP: 0-200 micromol/l

methanol: 100 micro l

expected methane: 46.8 ml

temperature: 35 degree C

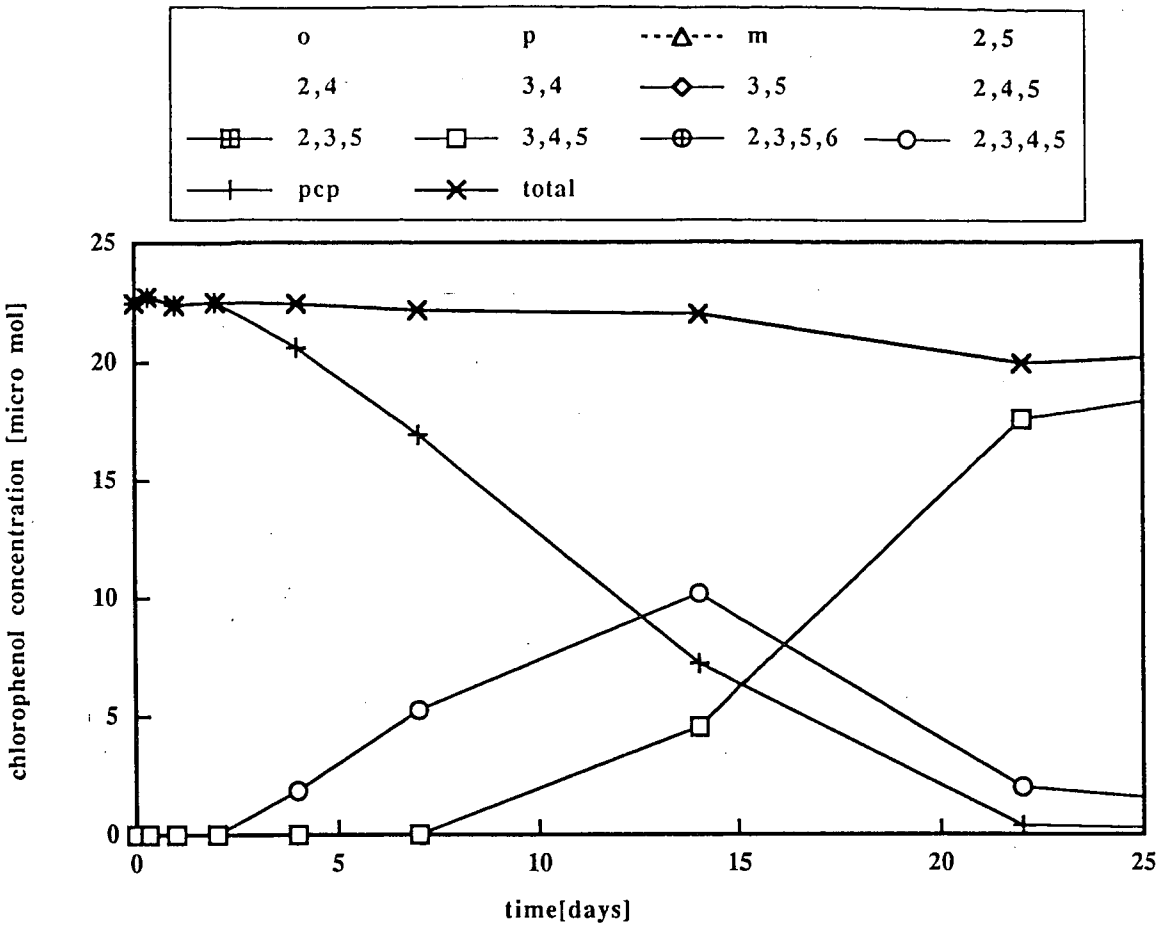


fig.4 PCP and chlorophenols formation/degradation by non-acclimated sludge.
MLVSS: 6,000mg/l, volume: 25 ml, PCP: 22.5 micromol/l, methanol: 25 micro l, temp:35C

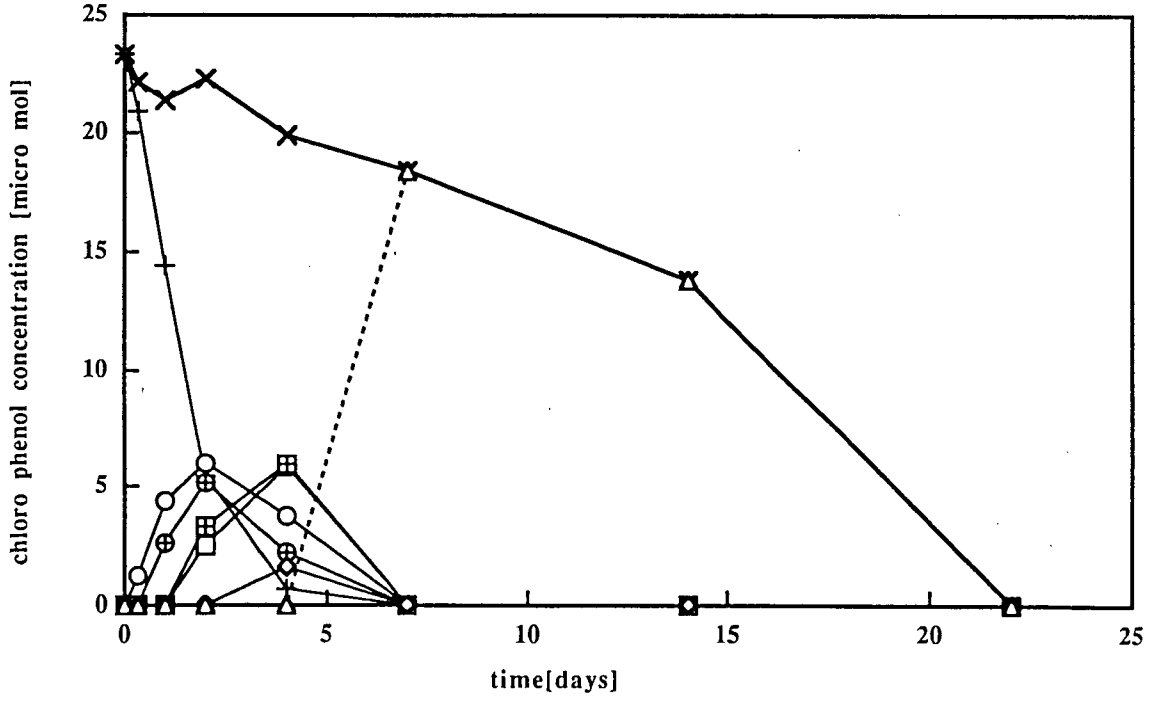


fig.5 PCP and chlorophenols formation/degradation by acclimated sludge.
MLVSS: 3,100 mg/l, volume: 25 ml, PCP: 22.5 micromol/l, methanol: 25 micro l, temp:35C

degrade PCP to mono-chlorophenol (meta-CP) within a week. And completely degrade within 3 week.

As the result of acclimation anaerobic sludge get a strong ability for degradation of the chemicals.

degradation of chlorophenols by acclimated anaerobic sludge

Chlorophenols have 19 group members, 1 penta, 3 tetra, 6 tri, 6 di and 3 mono. Nine-teen chlorophenols were added to the acclimated sludge and their degradation rate and degradation products were measured. Concentration of each chemicals was 20 micromol. The methane formation from the added methanol was same as the control. Each chemicals at the tested concentration did not show the toxic effect. Results of 6 di-chlorophenols were shown in fig.6. Removal pattern showed zero-order, first order (2,5-di 2,6-di), and logarithmic (2,3-di 2,4-di 3,4-di 3,5-di). Logarithmic growth pattern were often appeared at the low chlorinated phenols. This seemed to be caused, that such chemicals are not the intermediate of PCP and need acclimation period for degradation. However rapid degradation after a short period shows the high potential chlorophenols' degradation ability of the PCP-acclimated anaerobic sludge. Degradation rate of chlorophenols were compared using the initial zero order degradation rate constant. Relation between the chlorine number and the degradation rate were summarized in fig.7. The result showed that highly chlorinated phenols were more easily degraded than low one.

Degradation path of chlorophenols were estimated on the HPLC data of degradation products of 19 chlorophenols. In most of the degradation, molar concentration of chlorophenols were preserved, and new chlorophenol, one of chlorines of initial chemical was removed, was formed. Dechlorination was a main reaction on anaerobic degradation of these chemicals. In many case dechlorinated product were occupied by only one isomer. Dechlorination was related the position of chlorine on the aromatic ring. Order of ease was ortho >> para > meta. Similar order was observed in mono-chlorophenol degradation. Ortho-chlorophenol showed a fast and stable removal, while para and meta chlorophenol are hard to degrade.

Estimated degradation path of chlorophenols were summarized in fig.8. Main path of PCP degradation were from 2,3,4,5-tetra-chlorophenol, through 3,4,5-tri-chlorophenol, 3,5-di-chlorophenol to meta-chlorophenol. More than 80 % of added PCP were changed to mono-chlorophenol and mineralized. (see Fig.5). Chlorophenols, that are not belonging to intermediate of PCP degradation, such as 2,3,4,6-tetra-chlorophenol or 2,3,6-tri-chlorophenol were dechlorinated first at ortho position, and joined in the main path.

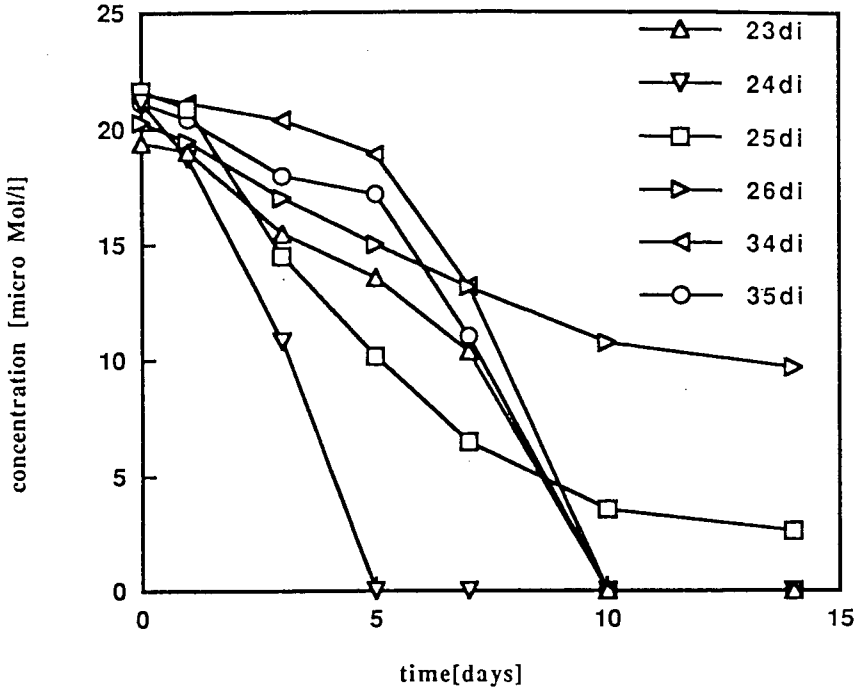


fig.6 Di-chlorophenols degradation by PCP acclimated anaerobic sludge
MLVSS: 2,900mg/l, volume: 25 ml, chlorophenol: 20 micromol/l, methanol: 25 micro l, temp:35C

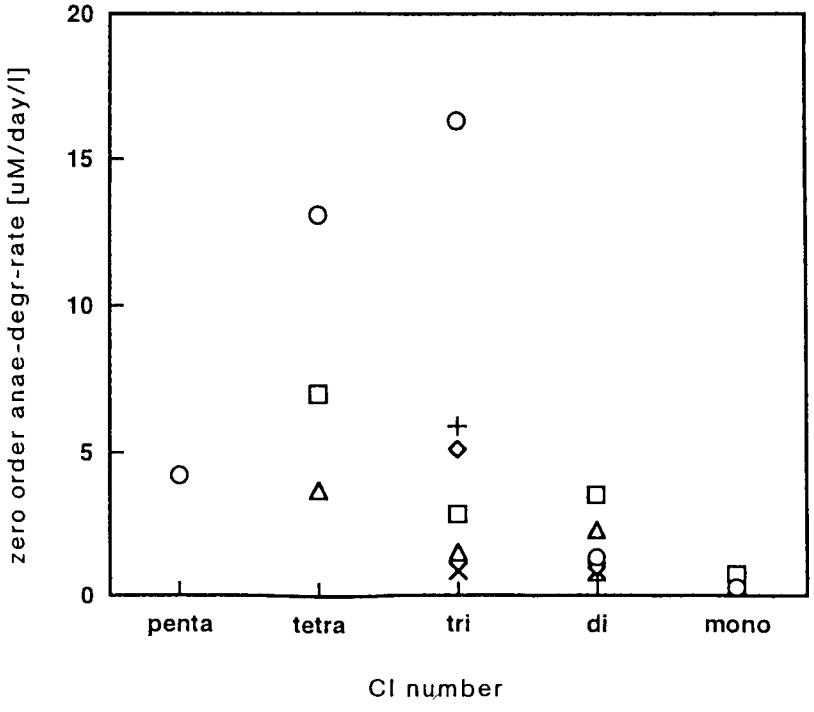


fig.7 Relation between chlorine number and zero-order degradation rate constant by acclimated sludge.

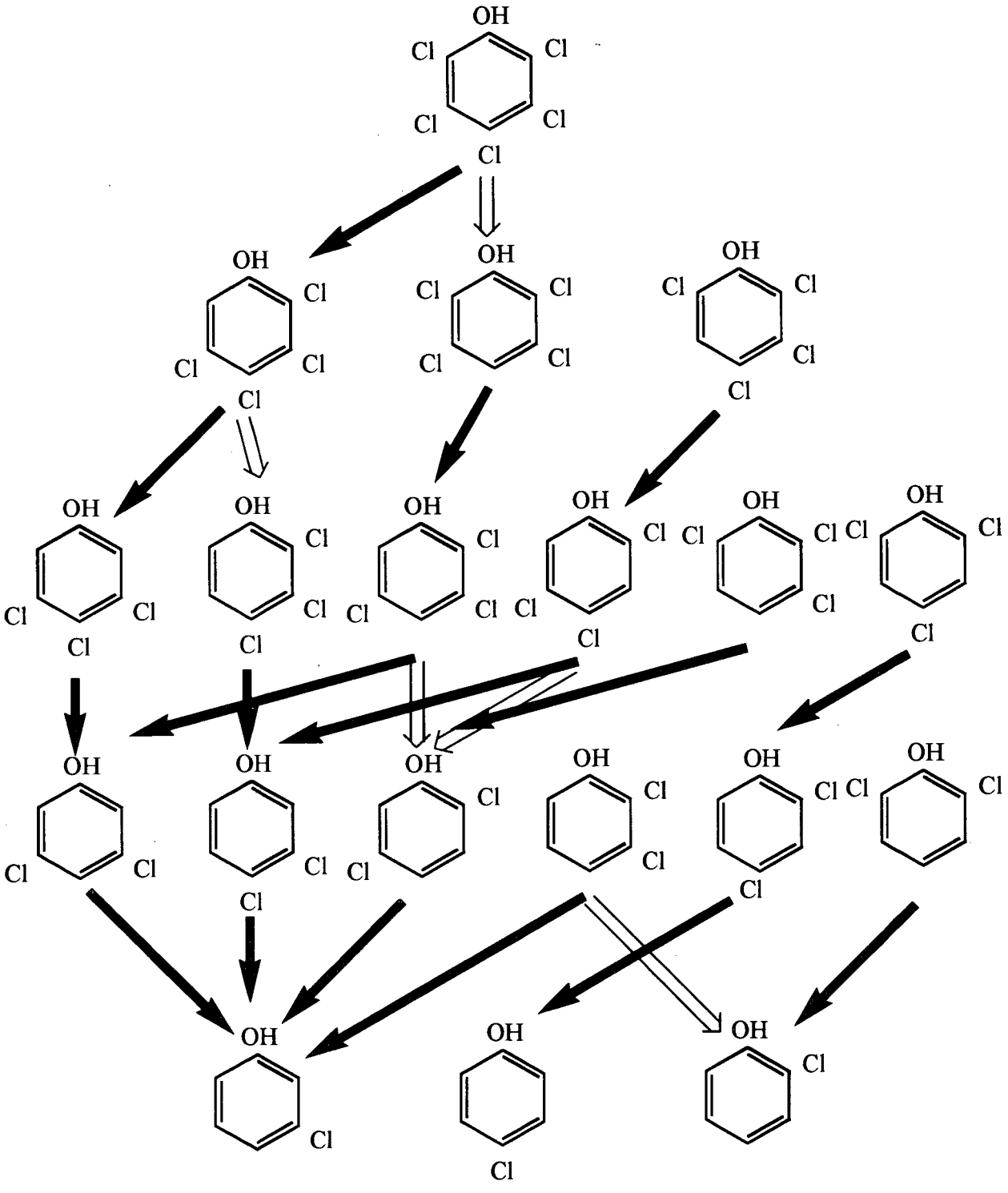


Fig.8 Degradation path of chlorophenols by PCP acclimated anaerobic sludge

main path 60-100%

sub path 20- 40%

As the result of anaerobic degradation of chlorophenols by acclimated sludge, poly-chlorinated phenols were successively dechlorinated and finally degraded through mono-chlorophenol, mainly metha chlorophenol. However, 20-40% of 2,3-dichloro, 2,5-dichloro and 3,4-dichlorophenol were degraded without formation of mono-chlorophenols. Finally mono-chlorophenol were disappeared. As accumulation of possible intermediate, such as mono-chlorobenzoate, phenol were not observed, they were seemed to be dechlorinated and rapidly mineralized.

It was concluded, that all the chlorophenols were degraded by PCP acclimated anaerobic sludge.

repeat addition of PCP to acclimated anaerobic sludge

To evaluate the high loading of PCP to anaerobic sludge, 20 micromol of PCP were added repeatedly at 2week interval. Result of five times addition were shown in fig.9. In the first addition, PCP were degraded to metha-chlorophenol on day 20. In the second addition, metha-chlorophenol were degraded at first, but accumulated after its concentration increased, due to the degradation of PCP. In the third and forth addition, polychlorinated phenol, such as PCP, tetra-chlorophenol, and tri-chlorophenols were degraded at the same speed, but mono-chlorophenol and di-chlorophenol were accumulated and total chlorophenol concentration became high.

Mono or di-chlorinated phenols were hard to degrade than polychlorinated phenol, as shown in Fig.7. So it is important to remove the low chlorinated products, for the complete degradation of chlorophenols in the reactor system. To degrade such a low chlorinated chemicals by aerobic system should be one of the possible counter measures.

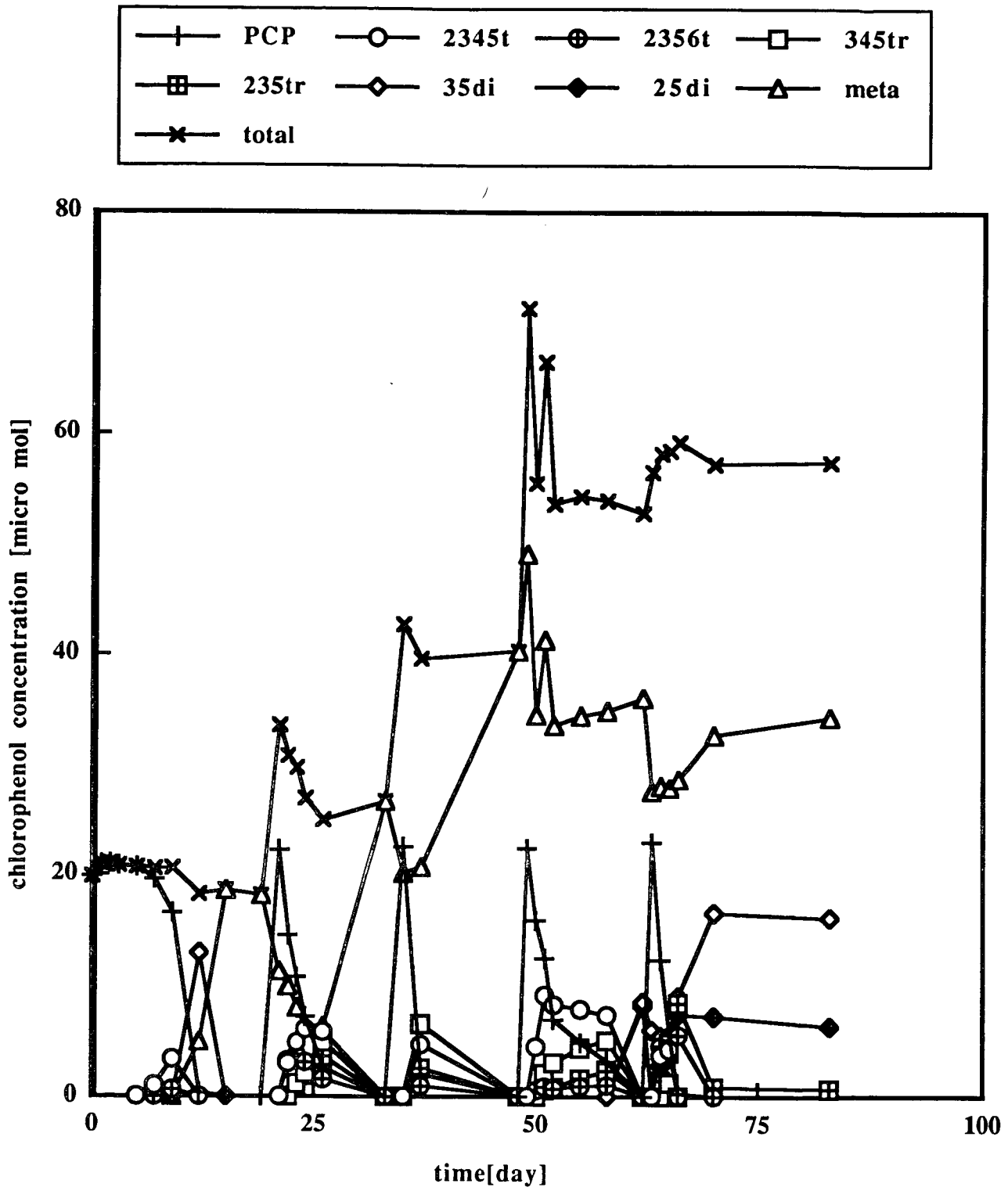


Fig.9 Effect of repeated addition of PCP to the acclimated anaerobic sludge.

MLVSS: 2,500mg/l, volume: 25ml, PCP: 20micromol/l, methanol: 25 micro l, temp: 35C

DEVELOPMENT OF MEMBRANE REMEDIATION SYSTEM FOR REMOVAL OF VOLATILE ORGANIC CONTAMINANTS FROM GROUNDWATER

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ABSTRACT

A new *in situ* remediation system based on pervaporation membrane process has been developed to clean up groundwater and soil contaminated by volatile organic solvents. The study includes the following subjects; 1) application of a simple two-dimensional groundwater flow model to system design, 2) improvement of pervaporation membranes by fluorocarbon plasma, 3) development and evaluation of membrane modules under various flow conditions, 4) trial constitution of the cleanup system operated by solar battery.

Since geological condition around a contaminated site might have a variety of influence upon performance of a remediation system in quite complex ways, the system should have enough flexibility to meet them. For the membrane system, it is realized by a number of membrane modules installed as surrounding the contamination plume. Each pumping unit for supplying purge air of pervaporation may be allocated to take care of a group of membrane modules. It should be also noted that each membrane module has effective region in which contamination can be removed. The region is mainly determined by flow conditions of water as well as membrane separation capability. By plasma surface treatment, permeabilities of silicone rubber membrane for various chlorinated solvents were improved, at least, three times better than untreated one. The separation mechanism, in which hydrophobic interaction between solvent molecules in aqueous media and membrane plays a major role to form solvent-concentrated boundary layer at the interface, has been proposed to explain the surface treatment effect.

KEYWORDS

Groundwater remediation, Volatile organic compounds, Membrane separation, Pervaporation, Fluorocarbon plasma treatment, Chlorinated hydrocarbons

INTRODUCTION

The cleanup of groundwater and soil contaminated, particularly, by volatile organic solvents is a unique problem for the environmental process engineers. Technology must consider geological problems, such as, groundwater flow and soil characteristics. Although many practical approaches have been made for removal of compounds from water, the manner of application will have to be altered due to such conditions. So the system has to be highly dependent upon these conditions as well as contaminants.

Some of the treatment systems by existing technologies are air sparging, bioremediation, phytoremediation, in-well vapour stripping, treatment wells, surfactant extraction, and advanced UV oxidation. These are categorized into two main groups, i.e., *in situ* and *ex situ* treatments. Each method is also divided into two categories, biological and physicochemical processes. **Figure 1** is showing examples of current cleanup technologies [1]. Our pervaporation (PV) membrane system may be suitable for *in situ* treatment method. The recent trend of technology development can be considered to be *in situ* methods with less environmental disturbance [2].

Membrane separation is often referred as one of such methods, and, also, as energy saving process, if membrane material with high separability and durability could be obtained. Recently, in the field of waste water treatment, membrane filtration processes have been getting more popular. That may be attributed to the appearance of high performance membranes [3].

Among the membrane processes, the PV method is relatively new, compared with filtration. The unique characteristics may be permeate vaporization occurring at one side of a membrane. And, for most cases studied so far, it has been mentioned that PV separation realized by two mechanisms, i.e., difference of permeability of each permeating compounds through membrane in addition to volatility difference at membrane surface under vacuum.

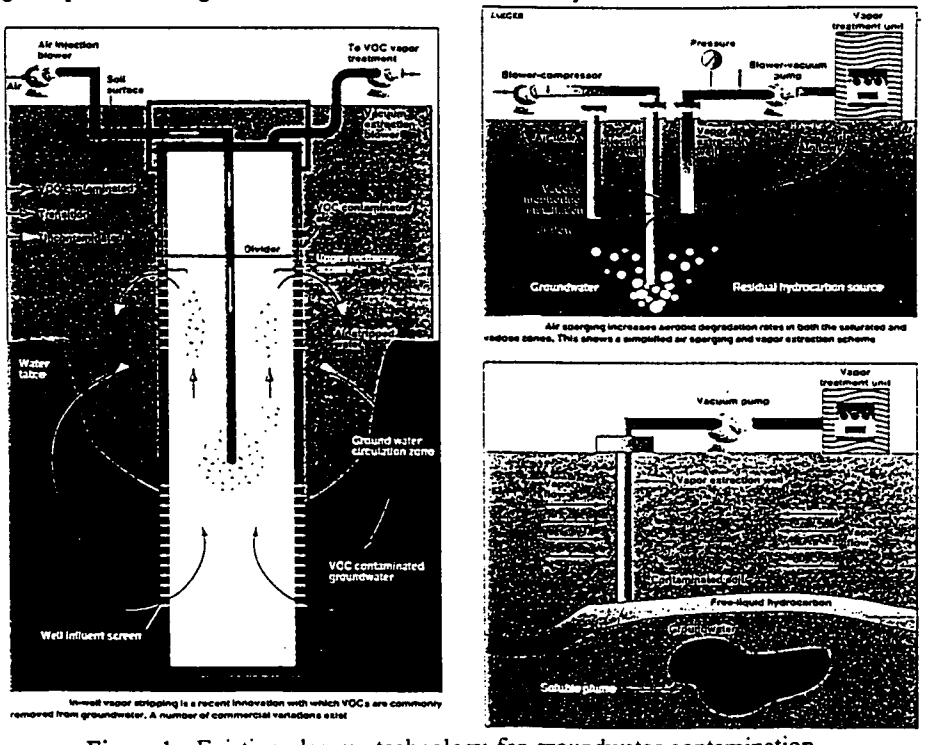


Figure 1 Existing cleanup technology for groundwater contamination
(Left) In-well vapour strippint; (Upper right) Air sparging / vapour extraction;
(Lower right) *In situ* soil venting

GENERAL SYSTEM CONCEPT

Figure 2 shows general scheme of our groundwater remediation system of PV process [2),3)]. PV process is relatively new membrane separation method as already mentioned. In the process, liquid phase of mixture, in this case, water and spilt solvent contaminants, contacts with one side of a membrane and gaseous phase of permeate, which is kept at lower pressure by continuous evacuation in most cases investigated so far, appears on the other side of the membrane. Namely, membrane separate groundwater and vapour phase of permeate in our system.

The PV modules made of a bundle of tubular membranes should be small enough to be fit in a wells for cleanup and can be installed as many to cover the contaminated region. If flow direction of groundwater could be found, the modules should be distributed for surrounding the region to prevent contamination from further expansion. The membrane modules contain a bundle of tubular or hollow fiber membranes. However, membrane should strong enough to stand against outer pressure from water or soil, although it may not be so important for shallow wells. A pump and control unit on the ground surface can occasionally supply air to purge inner space of membrane modules.

Purge gas entrains contaminant vapour removed from groundwater. In our trial system for field investigation, a small diaphragm pump could be used successfully. Collected contamination could be decomposed by heated catalytic bed, by UV oxidation vessel or, simply removed by adsorption with activated carbon. The whole system tested was so small that it might be operated by solar energy.

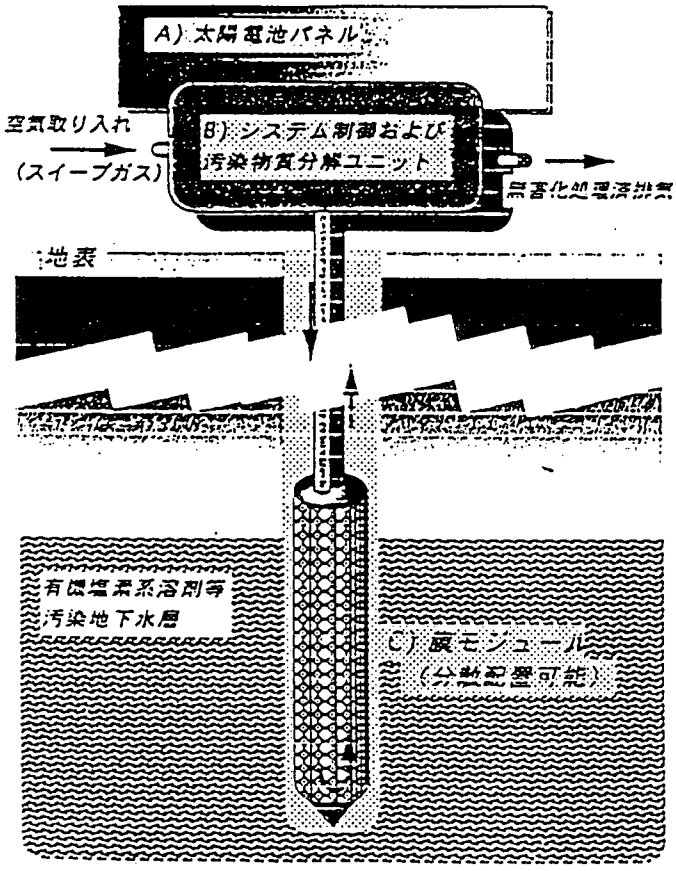


Figure 2 Air-purge type pervaporation system newly proposed in this study
(A) Solar battery ; (B) Control and pumping unit; (C) Membrane module

MEMBRANE MODIFICATION BY LOW TEMPERATURE PLASMA

To improve membrane performance, i.e. separation coefficient and permeability, many kinds of membrane materials have been investigated. There are chemical and physical factors determining membrane performance, such as, porous structure for filtrating specific size of particles and molecules, or functional groups for bearing selective affinity to specific molecules to be separated. For PV membranes, both surface and bulk characteristics could have much influence on the performance according to the solution-diffusion theory which could originally explain membrane gas separation. We tried to modify membrane surface by using low temperature plasma of fluorocarbons.

Fluorocarbon plasma can generate fluorine containing active species to make surface exposed hydrophobic. Such hydrophobicity could work for adsorbing solvent as a result of specific interaction between the surface and the hydrophobic molecules [4), 5), 6)].

Recent studies have revealed that hydrophobic surface force in an aqueous media may work as unexpectedly long distance and strong interaction. In membrane phenomena, particularly, on alcohol concentration from dilute aqueous solutions, we have also pointed out the importance of hydrophobic surface force(Figure 3). A similar mechanism, so called, the preferential sorption model, proposed by Sourirajan et al, is well known, having given a good working hypothesis for researchers of reverse osmotic membranes for desalting. In this mechanism, separation takes place by repulsive force of static charge between charged membrane surface and ions. And it should be also noted that our finding on PV was only on porous membranes coated with hydrophobic thin films prepared by fluorocarbon plasmas.

In this study, we used tetrafluoroethylene (TFE) plasma to modify substrate membranes of silicone rubber. Although the membranes were non-porous, we predicted the same separation mechanism could work [7), 8)]. We also tested other polymer substrate, such as, polysulfone and polypropylene. However, these membranes were not durable enough against chlorinated solvents or even resolved by concentrated permeate during separation. So we concluded that silicone, among tested polymers, is most substrate for supporting plasma-modified layer on the surface.

The optimal conditions for plasma treatment has been elucidated for alcohol separation, i.e. substrate exposure to plasma at lower (wattage/flow rate) ratios, though it gives slower rate of film deposition. Under such a condition, coated film tends to hold more fluorine-carbon bonds which is more hydrophobic. Under such a typical condition of TFE plasma, we investigated on effect of treatment time on membrane performance for chloroform-water (1000 ppm) by using substrates with various thickness (Figure 4). And separation coefficients for various chlorinated solvents are also shown in Figure 5. It is clearly demonstrated that TFE-plasma-treated silicone exhibited improved separations for all the solvents examined, which were separation coefficients and permeabilities three times higher than those of untreated. It is interesting to note that permeability of water did not decrease in contrast to solvent permeabilities, as shown in Figure 4, even though thickness of plasma-polymerized film increased with time, at 60 min, to be about 50 nm.

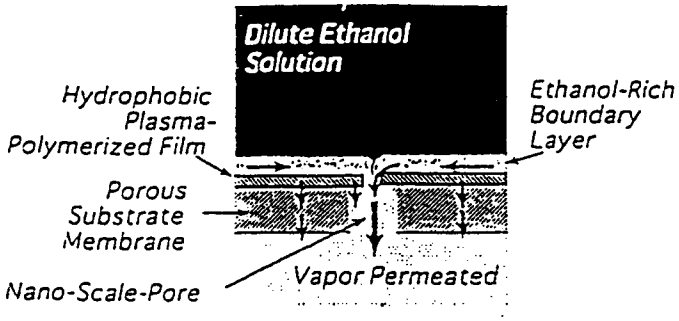


Figure 3 New separation scheme for pervaporation based on hydrophobic interaction between solvent (alcohol or chlorinated solvents) and hydrophobic membrane surface

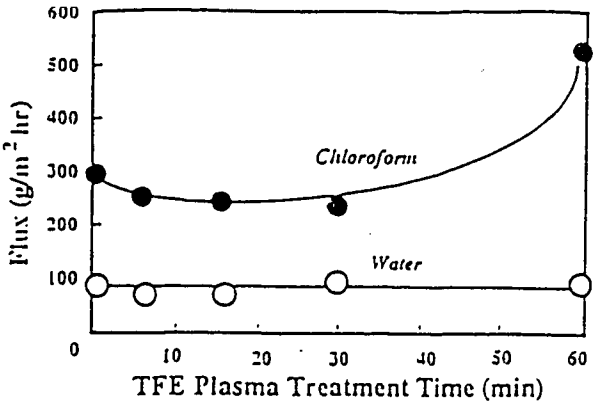


Figure 4 Dependence of permeabilities of chloroform and water on TFE plasma treatment time (Silicone rubber)

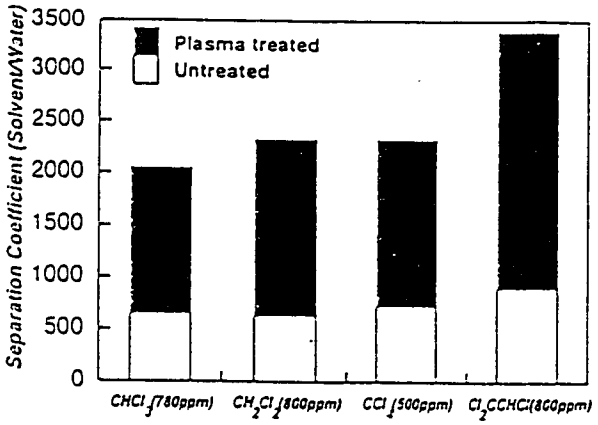


Figure 5 Separation coefficients for various chlorinated solvents (silicone rubber)

EVALUATION OF MEMBRANE MODULE

A numerical calculation based on a simple two dimensional flow model was carried out to obtain design criteria of membrane module, assuming that groundwater flow rate, 1 m/day, concentration of contamination, 20 ppm [9].

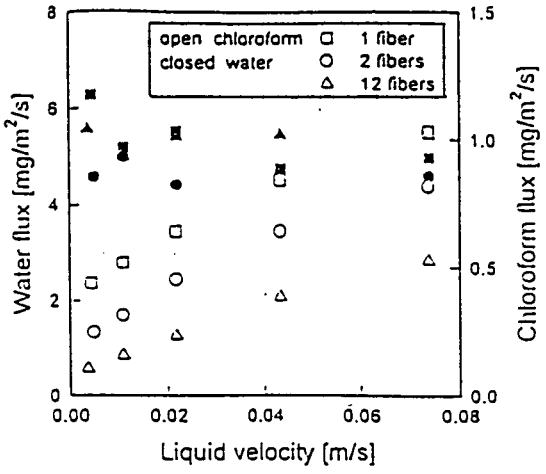
The effective region of module was defined as the range where contamination might be lower than 1 ppm, if the concentration at membrane surface could be 0 ppm. The results can be summarized as follows.

a) The effective region tends to expand at down stream, if the capability of a module is reinforced.

b) Installation of multiple modules is necessary, if dispersion coefficient of a soil layer is larger.

c) However, the effective region of a module tends to expand with the capability in such a soil layer.

On the other hand, test modules bearing a number of hollow fibers which is 170 micron-I.D., and 80 micron-thickness, were manufactured. In Figure 6 and 7, the results of evaluation under various groundwater and purge gas (nitrogen) flow rates are displayed. These results clearly indicates that main resistance for mass transport exists in the boundary layer at membrane-water interface, so that acceleration mechanism for water flow should be necessary to obtain higher rate of contamination removal. And dense packing of membranes could also lower the module capability due to stagnant region of water between membranes [10]



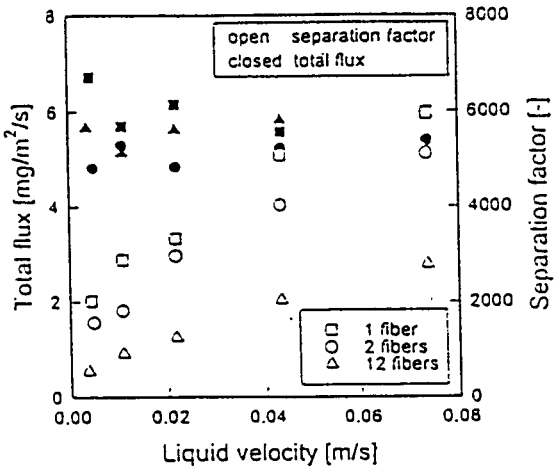
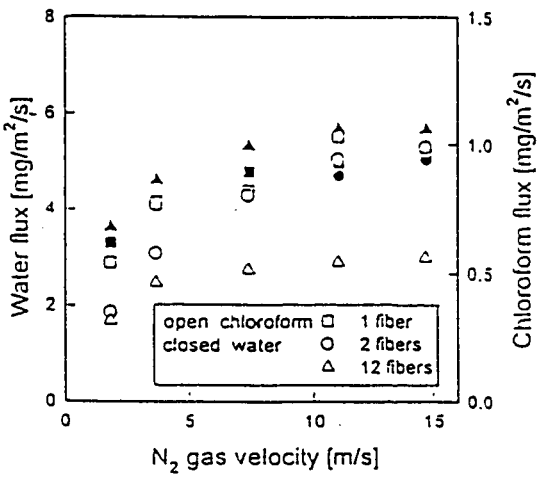


Figure 6 Dependence of module flux and separation factor on water (liquid) velocity



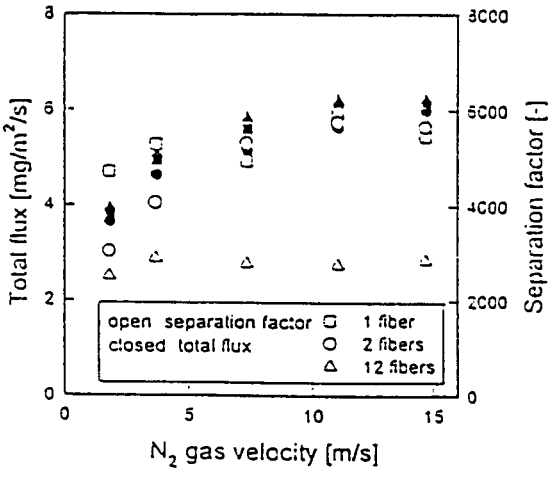


Figure 7 Dependence of module flux and separation factor on purge gas (nitrogen) velocity

FIELD TEST OF THE PV SYSTEM

The field test of trial constitution of the PV system was carried out by using contamination monitoring wells in Kimitsu-city, Chiba prefecture. Pictures in Figure 8 show the PV system made for trial and the module installed in the well. The wells were located close to a factory, contaminated by trichloroethylene. The following conclusions could be made through the test [2].

a) Membrane should be mechanically strong enough to be durable against friction with soil, or pressure applied by air pumping. Actually, the hollow fiber investigated above should be protected by net, or stronger tubular membrane should be used.

b) The modules and pipe lines from surface pumping unit should be light, for convenience of module installation.

c) Contamination was successfully removed.

d) The laboratory test demonstrated that the plasma-treated membrane was unchanged by longer period of contact with water.

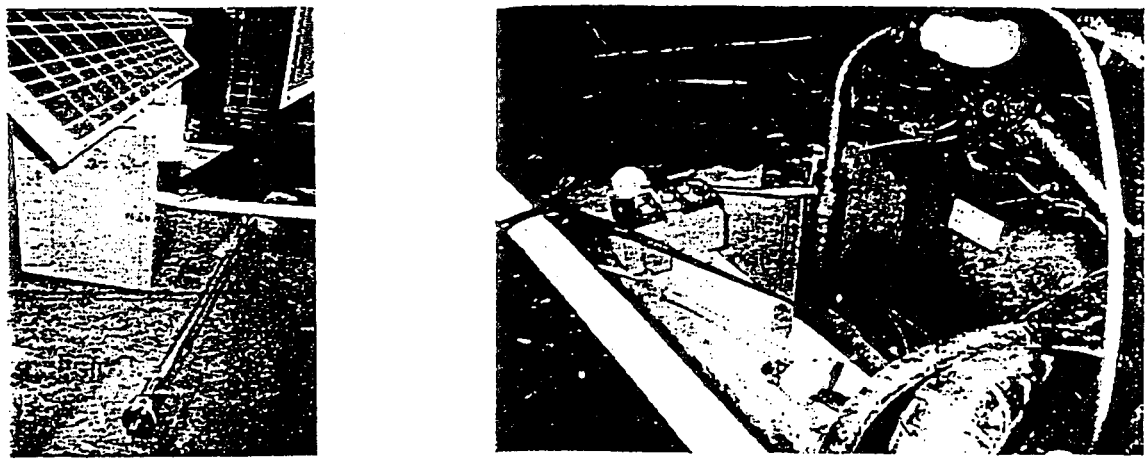


Figure 8 Trial constitution system (right) and module in test well

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Session 6

Reuse of Wastewater Resources

"Energy Recovery from Municipal Solid Waste and Waste Water"
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ENERGY RECOVERY FROM MUNICIPAL SOLID WASTE AND WASTE WATER

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ABSTRACT

Methane production from sewage is not so effective because of its low concentration. If municipal solid waste (MSW) such as kitchen garbage, paper and plastics which consists of organic substances became the raw material of methane fermentation, methane recovery rate will be remarkably improved.

The purpose of this investigation is to develop new system that recovers water and methane from sewage and solid waste by using physicochemical solubilization and methane fermentation.

Sewage is sent to a treatment plant after having been mixed with kitchen garbage that was crushed by disposers. SS is separated from sewage and concentrated. Paper and plastics among solid wastes that are currently incinerated and/or dumped at garbage pits are transported and crushed. The concentrated SS and crushed MSW are solubilized in a biological or physicochemical reactor and then the effluent is treated in a methane fermentation reactor.

Methane was produced effectively from the solubilized liquid similarly as high concentration waste water of food industry.

KEYWORD

Energy recovery, Methane fermentation, Solid waste, Waste water treatment, Physicochemical solubilization, Catalytic wet oxidation, Biological solubilization

INTRODUCTION

As a large amount of MSW is discharged from household, the treatment and disposal of it became a big problem in Japan. Most MSW is incinerated, and the incineration generates carbon dioxide and dioxine which are notorious contaminants in air pollution.

The kitchen garbage which easily putrefied must be transported frequently to avoid bad odor and by the reason of hygiene. But in this new system, kitchen garbage is transported through sewage pipe, only dry solid waste such as paper and plastics needs to use garbage trucks. So it decreases the frequency of the truck transportation and is effective against traffic congestion.

Development of new MSW treatment process is expected to dissolved some social problems and to recover energy resources.

TREATMENT PROCESS

In a treatment plant, sewage is pretreated by a polyethylene sponge filter. SS and crushed garbage that can be decomposed by microorganisms are separated from sewage and concentrated, and then they are biologically solubilized.

Paper and plastics are decomposed with the physicochemical solubilization reactor that applies the catalytic wet oxdation treatment at high temperature and high pressure conditions after sui-

tably crushing them. Methane is produced by pouring both solubilization liquid mainly comprised of organic acid into the methane fermentation reactor. Besides the methane, heat can be also recovered from the physicochemical solubilization reactor. A ratio of organic matter in the MSW is very high, and the system converts them into energy resources.

Filtration of the sewage at the pretreatment removes about 80% of SS, filtrate has low BOD and is easy to treat. Advanced treatment process is installed for water reuse. Conceptual flow of this system is shown in Figure 1.

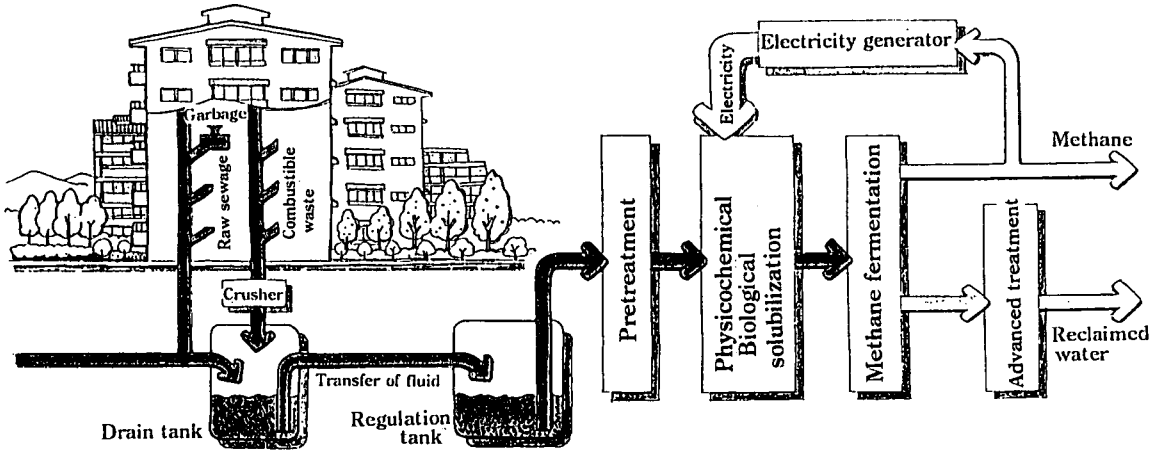


Figure 1 Methane production system for municipal solid waste

The wet oxidation process oxidizes and solubilizes organic substances that are dissolved or suspending as solids in raw wastewater under high temperature (150-250℃) and high pressure conditions(40-70 atm).

In the ordinary wet oxidation method, all organic matter are oxidized, since the necessary quantity of oxygen is supplied. But when oxygen supply is limited, some part of the organic substances is not oxidized and remain in the treated water as organic acid and others.

The test plant is shown in Figure 2. The MSW is solubilized at a no catalyst solubilization reactor at first. Catalysts are charged in the second reactor to promote the decomposition of solubilized organic substances. The effluent containing high concentration organic acids is sent to methane fermentation reactors.

Biologcal solubilization is performed to treat slurry separated from sewage in a mixing type reactor with 3 days retention time. At an alternative system flow, the slurry was solubilized in the physicochemical plant together with MSW.

Two types reactor were selected for methane fermentation, membrane combined reactors and UASB type reactors. Membrane combined type can hold methanogenic bacteria and SS in the reactor for a long time independently of hydraulic retention time, and makes better the quality of the treated water. UASB type reactor can maintain high concentration microbe as granule. So it usually has high treatment ability, but it is not suitable to treat waste water of high SS concentration. When biological solubilization is used, the effluent has high SS concentration, UASB reactor can not be chosen.

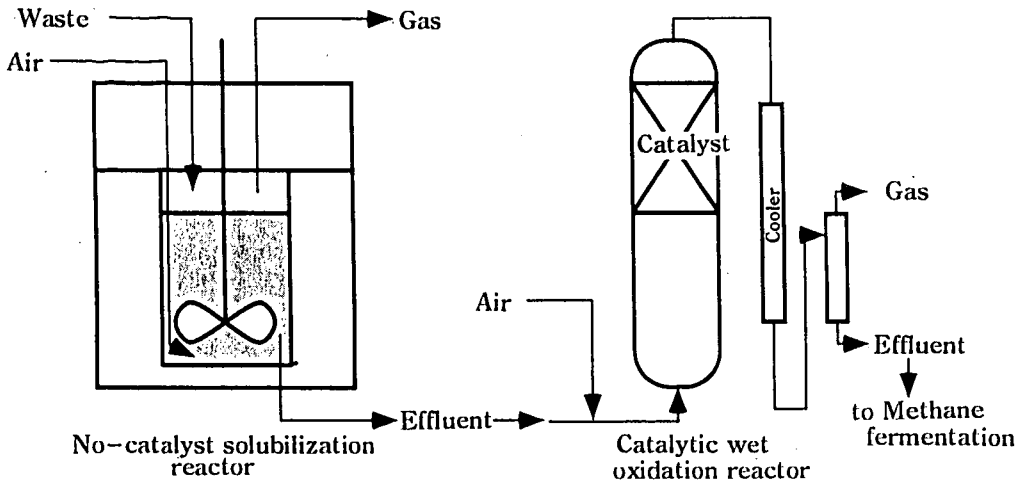


Figure 2 Physicochemical solubilization test plant

RESULTS

No-catalyst solubilization

The operating conditions of the first step physicochemical solubilization using a batch reactor is shown in Figure 3 and Table 1. The composition of solid waste used in this test is shown in Table 2.

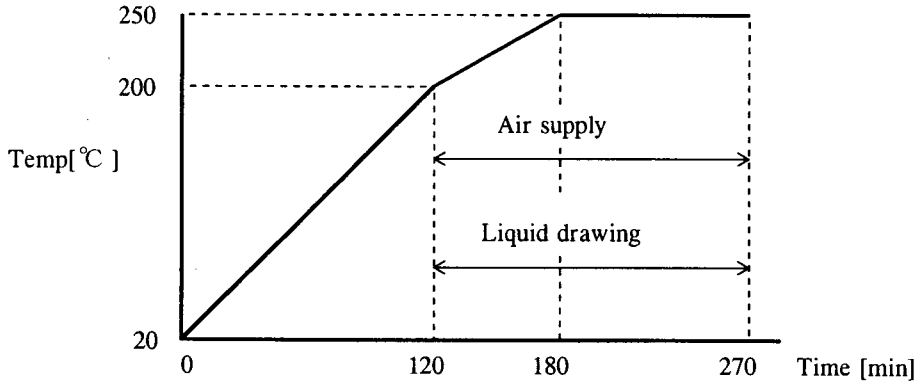


Figure 3 Operating method of no-catalyst solubilization

When the raw materials were treated altogether, SS solubilization rate and TOC recovery rate in the treated water were not satisfactory. Then the raw materials were separated two groups and optimum conditions were selected for each group. As shown in Table 1, about 32 % of TOC remained in the treated water.

Table 1 Optimum conditions and results of no-catalyst solubilization

Condition \ Raw material		Whole material	Plastics	Paper & garbage
Max temperature	[℃]	250	250	250
Reaction time at max temp.	[min]	230	90	90
Agitation	[rpm]	150	450	450
Liquid drawing	[L/h]	5	0	5
Air supply	[L/min]	10	40	0
NaOH addition	[g/100g]	–	20	5
SS solubilization rate	[%]	62	90	70
TOC recovery rate	[%]	17	31	33

Table 2 Composition of wastes

Raw material	Weight [g/d] (Wet)	(Dry)
Sewage sludge	(75+)	75
Kitchen garbage	370	74
Plastics	120	120
Paper	316	300
Others	110	110
Total	991+	679

(Plastics)

Polyethylene	40%
Polystylene	20%
Polypropylene	20%
Polyvinyl chloride	20%

Catalytic wet oxidation (CWO)

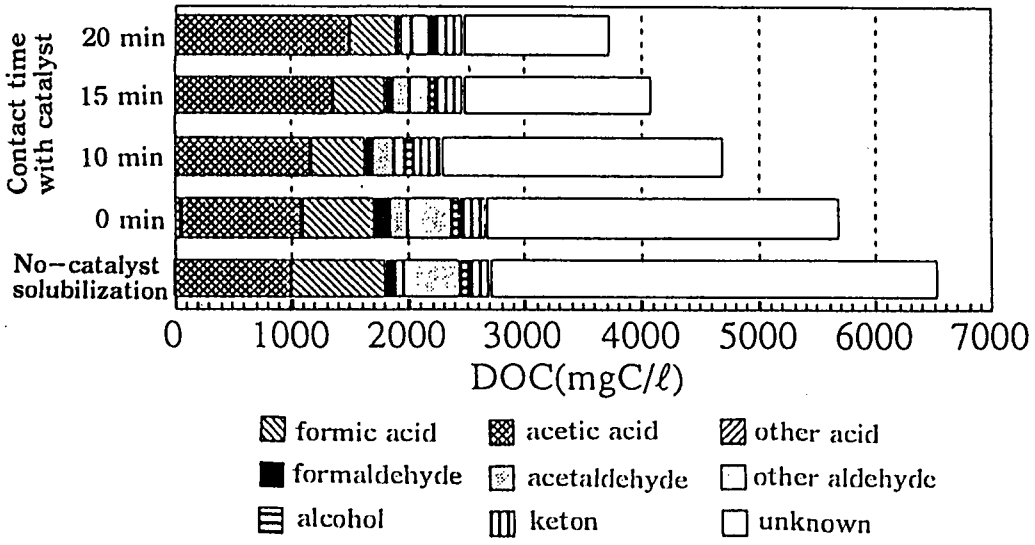


Figure 4 An example of organic substances decomposition by catalytic wet oxidation

No-catalyst solubilization effluent from a batch reactor is treated at the catalytic wet oxidation reactor continuously. Organic substances dissolved in the liquid are decomposed and become lower molecules which are suitable for methane fermentation as shown in Figure 4.

At the condition of 200 ℃ , 45atm and retention time in the catalyst zone 15 minutes, 70-80 % of TOC from the batch reactor remained in the CWO effluent. And its concentration was TOC 6,000mg/L, BOD 10,000mg/L.

Biological solubilization

The sludge contained in sewage and kitchen garbage crushed by disposers were mixed and solubilized biologicaly before methane fermentation. After 3 days reaction, high concentration effluent of TOC 11,000 mg/L was steadily produced.

Methane fermentation

Methane fermentation using the solubilized liquor from the CWO and biological solubilization process was conducted by a membrane combined mixing type and UASB type bioreactors. The result of gas production from a membrane bioreactor is shown in Table 3.

Table 3 Gas production from each solubilized liquor

	Inflluent TOC [mg/L]	Gas production [L/gTOC]	[L/L]
Catalytic solubilization	10,800	0.6	6.5
Biological solubilization	10,800	1.1	11.9
Mixture of both liquor	10,800	0.85	9.2

Treatment cost

Table 4 Cost estimation

	Case 1	Case 2	Conventional
Construction cost [M¥]	8156	9918	6350
Depreciation [M¥/y]	1154	1372	855
Running cost [M¥/y]	635	694	766
Pre treatment	57	57	—
PC solubilization	45	45	—
Methane fermentation	34	97	—
Post treatment	46	46	111
Others	453	449	655
Total Cost [M¥/y]	1789	2066	1621

Case 1 : PC solubilization → UASB
Case 2 : Bio. & PC solu. → Mem. Bioreactor
Quantity of MSW : 18,600kgDS/d, for 28,000 persons

Cost estimation of the total system showed that the construction cost will be higher but running cost will be less than conventional system.

CONCLUSION

Methane recovery rate from MSW is summarized in Table 5 on comparison with some waste water. Almost same volume of methane is produced from MSW as from high concentration industrial waste water and moreover this new system has a special characteristics not to produce dioxine.

So this system is supposed to be useful and promising to solve some problems on the MSW treatment.

Table 5 Methane production from each waste water

Waste water	Influent [mg/L] SS	BOD	TOC	BOD load [kg/m³d]	Methane production [m³/m³] *1	[L/d] *2
Wheat starch	3,650	12,700	6,400	15	5	—
Alcohol	2,190	58,000	64,300	4	29	—
Pulp & paper	—	17,800	5,400	35	6	—
Soybean protein	470	830	540	2	0.4	—
Sewage	200	150	80	0.9	0.001	0.4
Sludge in sewage	12,600	4,500	4,900	1.5	3 (0.05)	14
Sludge+garbage	18,400	29,100	15,300	10	12 (0.10)	31
Waste { Case 1 }	0	12,200	9,500	6	5 (0.14)	42
Waste { Case 2 }	10,000	17,100	11,300	6	8 (0.24)	71

*1 : Methane production volume[m³] per 1m³ waste water which is flow into a bioreactor. The value per 1m³ raw sewage is shown in the parenthesis( ).

*2 : Methane production volume[L] per person(300L sewage) in a day.

This investigation was carried out based on the commission from the New Energy and Industrial Technology Development Organization (NEDO).

Treated Wastewater Reuse in Fukuoka City

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ABSTRACT

Fukuoka City, as a geographic location, is not blessed with water resources. The Fukuoka Municipal Government has recognized this limit in water resources since the severe drought of 1978. Since then the City has struggled to supply water stably for residents and commercial activities in order to become a "Water Conservation Conscious City." As one of the water conservation measures, since 1980 the municipal government has made positive efforts to reuse treated wastewater. The "Treated Wastewater Reuse Project" covers 7.7 km^2 in service area and, based on which the treated wastewater is reused for flushing toilets in large buildings and for watering trees on streets and parks. There are 143 buildings receiving treated wastewater and the current reclamation facilities have a capacity of 4,500 m^3/day. In this project, treated wastewater has been recognized as one of the stable water resources in the urban area. Considering the shortage of water resources in the future, it is indispensable to promote "Reuse of Treated Wastewater." And there are needs to expand it for more diversified applications. For instance, it can be used for artificial landscapes in urban areas, artificial brooklets and for fountains in parks, and for stream restoration in rivers.

KEYWORD

drought, water reuse, treated wastewater, reclaimed water, sandfiltration, ozonation, chlorination, Treated Wastewater Reuse Project, reclamation facilities

INTRODUCTION

Fukuoka City is in the northern part of Kyushu island, in southwestern Japan. Urban districts are found in the Fukuoka Plain which were created by the many small and medium size rivers flowing into Hakata Bay, which faces the Sea of Genkai, the Korean Peninsula, and the Asian Continent in the north and is surrounded by mountain ranges in the other three directions. Fukuoka City is rich in beautiful natural scenery, which includes Genkai National Park. The climate is moderate and similar to that of central and eastern Europe. The annual average temperature is 16.5 ℃, the maximum temperature, 35.8 ℃, and the minimum temperature, −1.2 ℃.

Because of its geographical proximity to the Korean Peninsula and the Asian Continent, the Fukuoka area has a history, as an international trading city, of over 2,000 years. Fukuoka City is the center of administration, economics and culture in Kyushu, and performs many key functions. Fukuoka City is approximately 340 km^2 in area with a population of 1,300,000. It is the biggest city in Kyushu and the eighth largest in Japan. The wholesale business in Fukuoka City has the fourth highest sales in Japan after Tokyo, Osaka, and Nagoya. According to 1994 statistics, Fukuoka City accounted for 45% of the wholesale value and the largest share of the retail value in Kyushu.

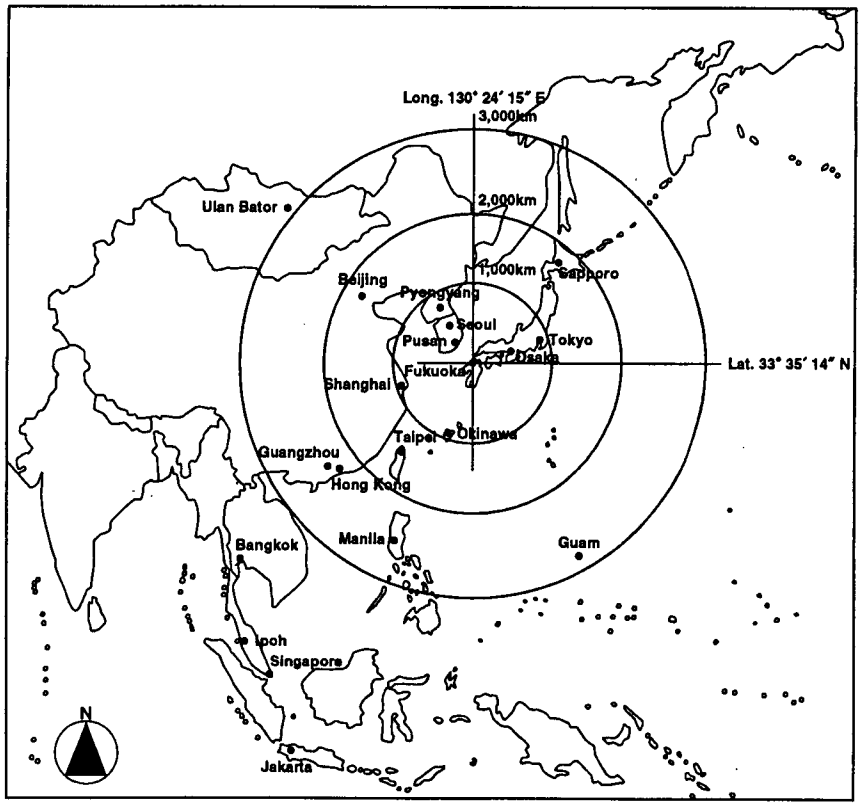


Figure-1 Location of Fukuoka

Fukuoka City also offers excellent transportation access to all of Kyushu, so here feels free to make quick trips throughout Fukuoka Prefecture and the islands from a base in Fukuoka. While you attend a convention, your accompanying family members can also enjoy a

rewarding experience. Fukuoka City is as close to major Asian cities such as Pusan, Seoul, Shanghai, and Taipei as it is to the major Japanese cities of Tokyo, Osaka, and Sapporo. Because of its geographical proximity, there are many international air routes to Asian-Pacific regions from the Fukuoka International Airport. Now Fukuoka City is progressing toward becoming a focal Asian interchange city closely tied to the sea and the rest of Asia.

In 1930, the Fukuoka Municipal Government launched its first sewerage project following other major cities. This was a combined sewer system to drain stormwater and domestic wastewater. Since the first Five-year Program for Sewer Construction of the Fukuoka Municipal Government was drawn up in 1963, we have made efforts to expand the sewered population and to construct wastewater treatment plants. In 1966, the first large scale sewage treatment plant called "Chubu Treatment Center" started operation and Wajiro, Tobu, Seibu and Saitozaki plants started in order. The ratio of the sewered population is 97.9 % as of March, 1997, and there are five wastewater treatment plants capable of treating approximately 420,000 m^3/day.

BACKGROUND OF REUSE OF TREATED WASTEWATER

Water demand is increasing in urban areas due to increases in population and other activities, and due to changes such as the introduction of the flush toilet. Now the maximum daily potable water supply of Fukuoka City is approximately 450,000 m^3/day. Water resources are obtained mainly from the following three kinds of places:

① Small and medium rivers in the urban area

② Seven reservoirs; and

③ The Chikugo River, the longest in Kyushu, outside the Fukuoka urban area

The daily average for each supply is almost the same ratio. Although the average precipitation of the Fukuoka area is 1,600 mm per year, it is hard to take water from the urban rivers because of sharply changing flow rate by rainfall. Because of this, the Waterworks Bureau of the Fukuoka Municipal Government has researched ways to increase its water resources by the construction of reservoirs, by the desalination of sea water, and through reusing treated wastewater.

Fukuoka City suffered a severe drought and had to restrict the supply of potable water from May 1978 to March 1979 for 287 days, when the maximum water suspension was for 20 hours a day. As a result, citizens were forced to consider the problem of water resources by themselves. After this water crisis, the municipal government enforced the "Fukuoka City Water Conservation Plan" to stably supply water for residents and commercial activities. The administration, citizens and entrepreneurs cooperated in making a water conserving city. Since then the municipal government has promoted the following water conservation plans to create the "Water Conservation Conscious City."

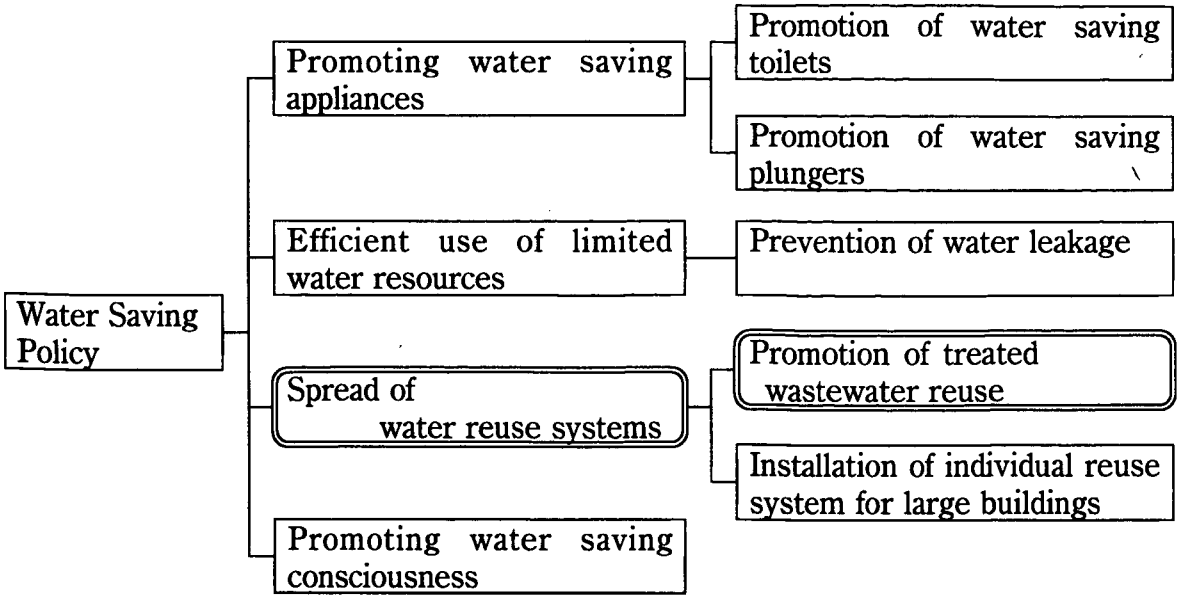


Figure-2 Water conservation plans

THE CIRCUMSTANCES OF THE TREATED WASTEWATER REUSE PROJECT

As one of the water conservation plans, the municipal government has promoted the reuse of treated wastewater. Treated wastewater has been recognized as one of the stable water resources in the Fukuoka urban area. In June 1980, the Sewage Works Bureau started a model project in the Chubu sewage treatment plant by using sandfiltration, ozonation and chlorination for commercial use in the Tenjin area, which was the first case of water reuse project in Japan. We have limited use only for flushing toilets in three public buildings, the Chuo Ward Office, the Hamanomachi pumping station, and the Chuo citizens' Center. The reclamation facility was 400 m^3/day in capacity at the beginning stage.

Following the success of this project, we have extended the supply pipe line and the area. Since March 1989, the guideline for using treated wastewater has been extended to large buildings with 5,000 m^2 or wider in floor area, or with water-supply pipe with a diameter of 50 mm or larger for both public and private buildings in the Tenjin-Watanabe Avenue area, the Seaside Momochi area, and to housing complexes in the Seaside Momochi area. The reclamation facilities were 2,000 m^3/day in capacity at the second stage.

In 1994, this model project was in operation on a commercial basis and called the "Treated Wastewater Reuse Project." In addition, in order to promote the effective reuse of treated wastewater, the area was extended to the Hakata Station area and the Water Front area and increased up to a capacity of 4,500m^3/day in August 1995.

As of March 1997, the area is 7.7 km^2, including the Tenjin-Watanabe Avenue area, the Seaside Momochi area, the Hakata Station area and the Water Front area. The number of buildings receiving treated wastewater is 143 throughout that area including, for example, the Fukuoka City Museum, the Fukuoka Tower, the Fukuoka Dome, and the JR Hakata Station.

The average daily supply is 2,500 m^3/day. The maximum is 3,600 m^3/day.

Figure-3 and Table-1 show the changes in the treated wastewater supply and the sewage installation ratio in proportion to population and daily potable water supply from fiscal 1977 to fiscal 1996.

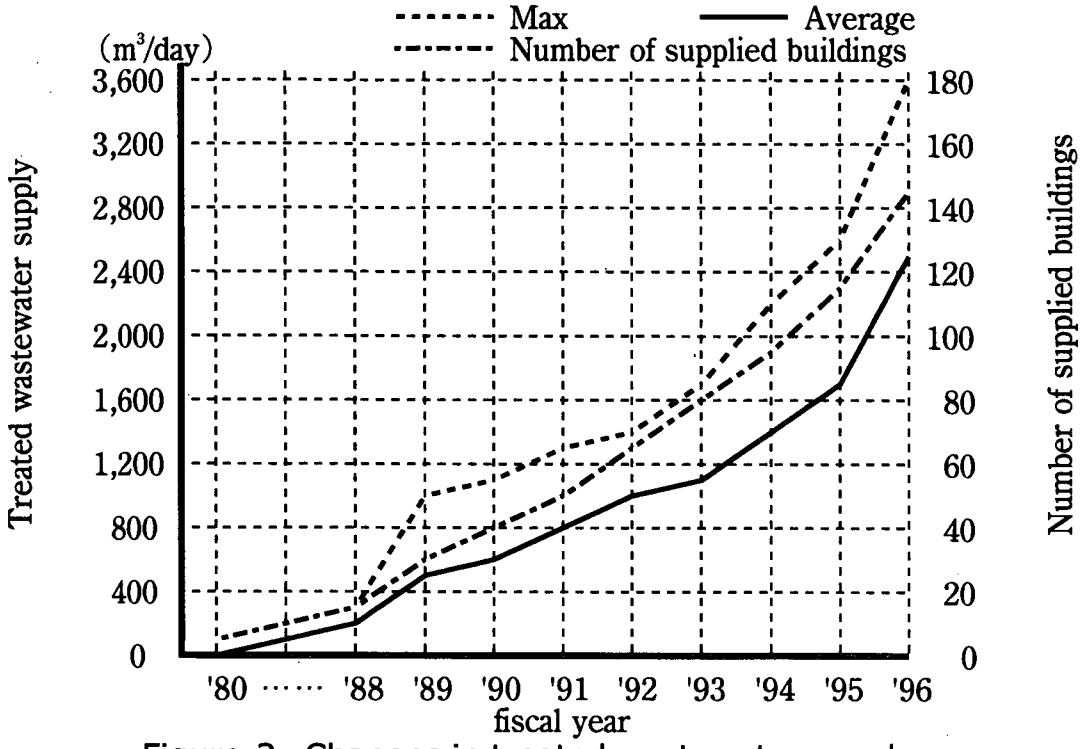


Figure-3 Changes in treated wastewater supply

Table-1 Sewered population and daily water supply

fiscal year	Population (thousand)	Percent of Sewered Population	Number of supplied buildings	Daily potable water supply per person (liters)	Remarks
1977	1,037	36.1	–	363	
1978	1,053	37.3	–	277	Water shortage
1979	1,070	40.1	–	320	
1980	1,085	42.6	3	319	Model project
1981	1,100	46.4	7	326	
1982	1,115	50.7	12	314	
1983	1,130	54.9	12	320	
1984	1,143	59.5	12	317	
1985	1,159	65.6	12	314	
1986	1,175	70.4	12	310	
1987	1,191	74.9	12	314	
1988	1,205	79.0	12	320	
1989	1,221	83.6	32	331	
1990	1,233	87.3	41	334	
1991	1,246	90.3	47	335	
1992	1,257	93.2	63	335	
1993	1,265	94.7	81	330	
1994	1,271	96.3	94	296	Water shortage
1995	1,280	97.3	115	303	
1996	1,294	97.9	143	313	

AN OUTLINE OF THE TREATED WASTEWATER REUSE PROJECT

Treatment Method

Part of the treated wastewater at the Chubu sewage treatment plant is used as raw water for the reclamation facilities. It is further treated with the sandfiltration, ozonation and chlorination processes, and then pumped to the customers as shown in Figure-4. Sandfiltration is used to remove suspended solids, ozonation to eliminate smell and color, and chlorination to disinfect bacteria and viruses.

Quality of supplied water

Table-2 shows the water quality changes from the influent to the Chubu sewage treatment plant to the reclaimed water and the Water Quality Standards for flush toilets. The quality of the reclaimed water meets the Water Quality Standards in the "Report on Survey Concerning the Recycling Use of Treated Wastewater, etc." (Ministry of Construction and Japan Sewage Works Association, March, 1991)

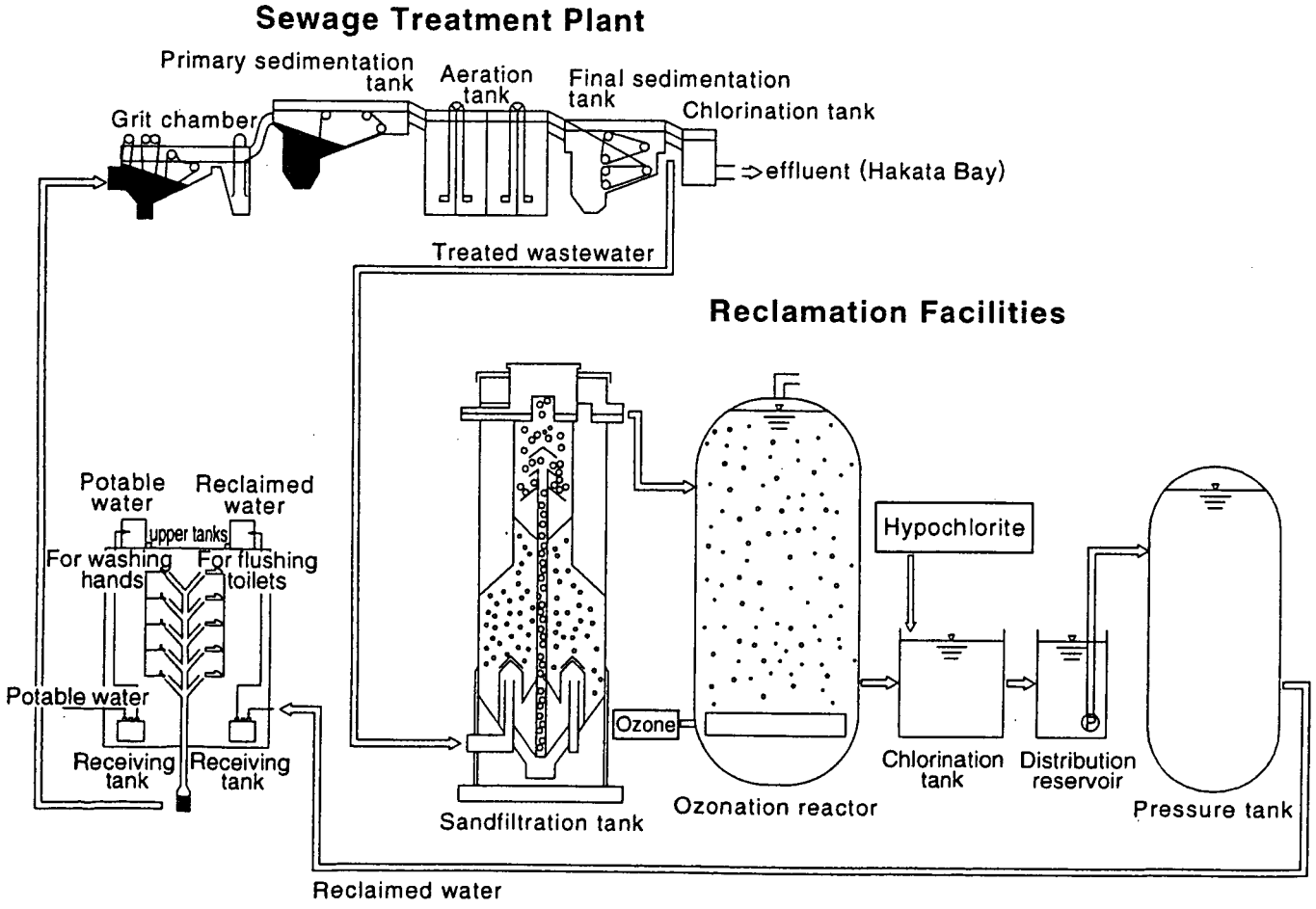


Figure-4 Flow diagram of the Treated Wastewater Reuse Project

Table-2 Water quality changes

	Influent	Secondary treated wastewater	Sand-filtration effluent	Ozonation effluent	Disinfection effluent (Reclaimed water)	Water quality at distribution point (City Hall)	Water Quality Standards for flush toilets
pH	7.1	7.3	7.1	7.5	7.5	7.5	5.8–8.6
Odor	-	-	-	-	Not	Not	Not unpleasant
Color(degree)	-	11	-	4	4	4	Not unpleasant
Turbidity(degree)	-	5	2	-	1	<1	Not unpleasant
COD_{Mn}(mg/l)	71	8.2	7.3	6.2	7.1	7	·
BOD(mg/l)	180	3.1	2.0	2.7	2.6	2.5	less than 20
Number of Coliform group (cells/100ml)	-	-	-	-	<100	<100	less than 1,000
Residual Chlorine(mg/l)	-	-	-	-	3.1	1.2	To be retained
Total nitrogen(mg/l)	35.5	19.1	-	-	20.1	19.1	
Total phosphorus(mg/l)	4.40	0.86	-	-	0.97	0.91	

Water Quality Standards : "Report on Survey Concerning the Recycling Use of Treated Wastewater, etc."

(Ministry of Construction and Japan Sewage Works Association, March, 1991)

Outline of the water reuse project

As of March 1997, the service area for the project was 7.7 km^2, including the Tenjin-Watanabe Avenue area, the Seaside Momochi area, the Hakata Station area and the Water Front area. Figure-5 shows the area.

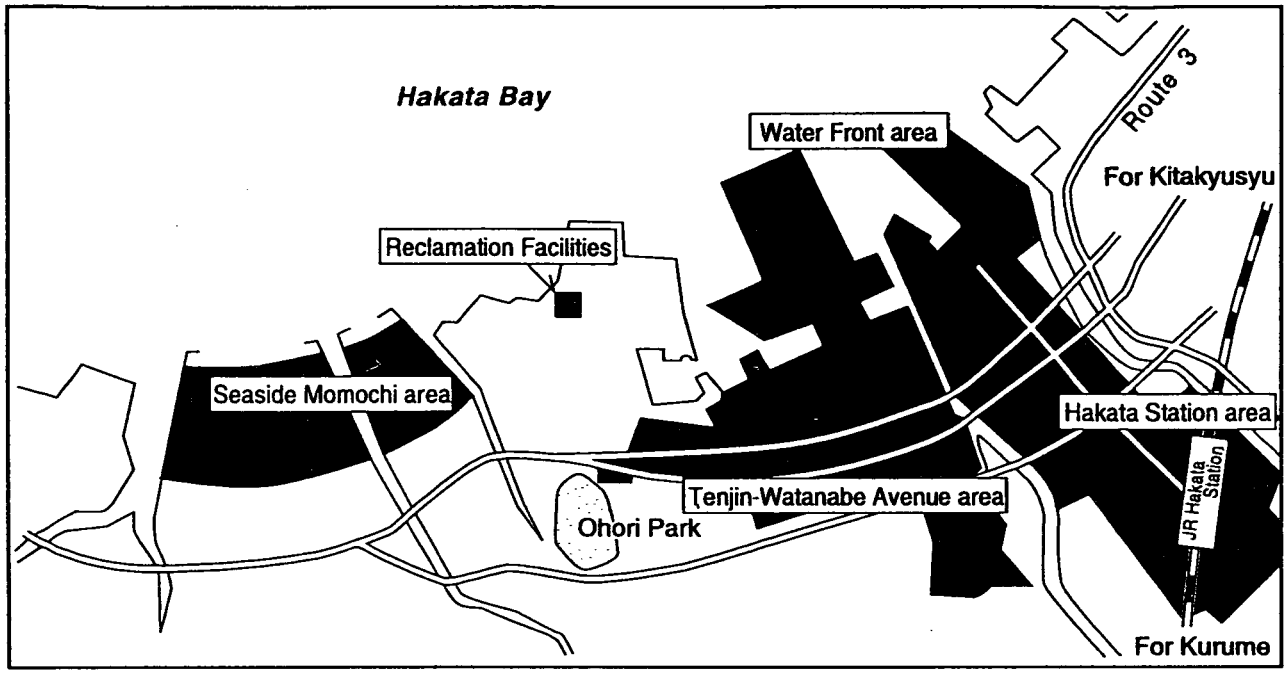


Figure-5 The service area

In the area, the supplies of the reclaimed water are flushing toilets in large buildings with 5,000 m^2 or wider in floor area, or with water-supply pipe with a diameter of 50 mm or larger, and watering trees on streets and parks.

Table-3 Outline of the water reuse

Service Area	Tenjin–Watanabe Avenue area	199 ha
	Seaside Momochi area	138 ha
	Hakata Station area	267 ha
	Water Front area	166 ha
	total	770 ha
Supplies	Flush toilets, Irrigation water in parks and streets	
Service initiation	June 1, 1980	
Process	Secondary treated wastewater ⇒ Sandfiltration ⇒ Ozonation ⇒ Chlorination ⇒ Reclaimed water	
Capacity	8,000 m^3/day (current 4,500 m^3/day)	
Distribution pipe length (March 1997)	Tenjin–Watanabe Avenue area	17.2 km (ϕ 75 ~ 200)
	Seaside Momochi area	9.5 km (ϕ 75 ~ 200)
	Hakata Station area	18.7 km (ϕ 150 ~ 300)
	Water Front area	2.3 km (ϕ 75 ~ 200)
	total	47.7 km

MANAGEMENT

Financial conditions

At the first stage, the reclaimed water rate for substitution was the same as the potable water rate. Later, although the potable water rate was raised, the reclaimed water rate was kept as it was, because the profit from it was more than the expense, owing to the increase in the treated water supply by the redevelopment projects. At present, the reclaimed water rate is about 80% of the potable water rate.

Table-4 Cost

Cost (Expense) (fiscal 1995, not included tax)

	cost per year (thousand yen)	cost per $1m^3$ (yen)
Operation & Maintainance Cost	81,496	136
Depreciation	38,120	64
Interest	68,818	115
Total	188,434	315

Total supply of reclaimed water in fiscal 1995 : 598,590 m^3/year

Promotion of water reuse

An applicant who plans to construct a new large building with 5,000 m^2 or wider in flow area, or with water-supply pipe with a diameter of 50 mm or larger should submit a water saving plan including that for water reuse and efficient water use for the new building before construction. When any applicant has a construction plan in the reclaimed water service area, it is positively encouraged to install a water reuse system due to the water reuse plan by the municipal government. For the introduction of the system, the Sewage Works Bureau gives guidance on the formalities from application to initiation notification.

Prevention of pipe misconnection

In enforcing the project, what is most concerned about is an accident caused by misconnecting pipes for potable water or gas. Therefore the pipes of reclaimed water under the ground are painted yellow, covered with a yellow polyethylene sleeve, and have yellow indication tapes are attached to them. In addition, the pipes in street should be buried with a yellow tape printed "WARNING! Reclaimed water pipe is laid here." The valves for the pipes under ground should be engraved with the mark of "Reclaimed water." The reclaimed water pipes inside the buildings are indicated by one of two methods: painting the pipes green or attaching green indication tapes. In order to prevent confusing them with others, before starting the supply to the buildings, the Sewage Works Bureau inspects all toilets by putting an artificial color into head tanks in cooperation with other bureaus concerned. Due to these preventive measures, no accident on misconnection has occurred yet.

Maintenance of the reclaimed water pipes

The Sewage Works Bureau has maintained the reclaimed water pipes by repairing and exchanging flowmeters. But as for the maintenance of the underground pipes, the Sewage Works Bureau has made a contract with the Water Works Bureau and the Water Service Center which have the know-how to repair and construct reclaimed pipes in case of emergency, because it is as necessary to the maintenance of reclaimed water pipes as it is for that of the portable water pipes.

CHALLENGES TOWARD FUTURE

The "Treated Wastewater Reuse Project" is going well with citizens' understanding and cooperation, and from this treated wastewater has been recognized as one of the stable water resources in the Fukuoka urban area. But for securing water resources in the future, it is indispensable to promote reclaimed water utilization. In the current reclaimed water service area, the Fukuoka Municipal Government is promoting expansion of both the service area and the capacity due to increasing demands of water, and has a plan to introduce the water reuse system to the Eastern and Western areas where it will be redeveloped. The range of the utilization is limited only to flushing toilets and watering trees on streets. As there are needs for expanding it for more diversified applications, the Fukuoka Municipal Government has researched other applications, for instance, for artificial landscapes in the urban area, and for resources for artificial brooklets and fountains in parks, and for stream restoration in rivers.

Session 7

Environment Preservation

"Eutrophication Control through Food Web Management in Estuarine Lagoons -A Case Study of Lake Shinji and Lake Nakaumi-"

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"Control of Anthropogenic N_2O – A Greenhouse Gas – Emission from Several Man-related Fields"

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EUTROPHICATION CONTROL THROUGH FOOD WEB MANAGEMENT IN ESTUARINE LAGOONS - A CASE STUDY OF LAKE SHINJI AND LAKE NAKAUMI -

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ABSTRACT

This study quantified the role of filter-feeding bivalves, aquatic birds, and macrophytes on nutrient budget in eutrophic estuarine lagoons, Lake Shinji and Lake Nakaumi, Japan. In L. Shinji, growth of the commercial bivalve, *Corbicula japonica*, deserves 15 % of nitrogen loading to the lagoon in summer. This amount of nitrogen is removed through fisheries in this lagoon without the expense for water quality control. In L. Nakaumi, grazing on biofouling mussels by the wintering diving ducks reduces the further input of nitrogen and phosphorus from the dead flesh of mussels in summer. Possible amounts of nitrogen and phosphorus removed through fisheries of edible algae, *Gracilaria verrucosa*, from L. Nakaumi were estimated to be 17 t and 1.2 t. These amounts are equivalent to 1.3 % and 0.82 % of present annual loads of nitrogen and phosphorus into L. Nakaumi and L. Shinji.

KEY WORD

ecosystem function, aquatic bird, filter-feeding bivalve, fisheries, macrophyte

INTRODUCTION

Seventy percent of the world's human population lives on coastal plains and another large fraction on major river systems, which can be regarded as extensions of coastal plains up to the river fall lines. Intensive human occupation of coastal plains, together with the materials transported to the seas by rivers, makes coastal zones the depositories of human waste through both deliberate dumping and unintended action (river and ground

water pollution). Eutrophication of the coastal zone, through altered land use and waste disposal practices of man, affects the productivity and structure of coastal ecosystems as a result of absolute or relative changes in the abundances of nutrients (phosphorus and nitrogen). Growing use of coastal regions and riverine basins for habitation and development may be contributing to an increase in frequency and spatial extent of nuisance blooms.

Until recently, ecosystem goods (such as food) and functions (such as waste assimilation) have not to be captured in commercial markets or quantified in terms of economic values. In the report that estimated values for ecosystem services (Costanza et al. 1997; Table 1), coastal biomes of easy access for mankind (i.e. estuaries, tidal march, swamps, floodplains, wetlands) are characterized as high values in "waste treatment (the recovery of mobile nutrients and removal or breakdown of excess nutrients)" and "food production (the portion of gross primary production extractable as food)".

These evaluations seem reasonable, because rivers have served as natural conduits in transporting materials including nutrients to the seas from long before the habitation of mankind. Biomes in coastal plains should have developed their ecological function to sustain themselves under eutrophic conditions. For example, nuisance blooms of phytoplankton, which

Table 1 Summary of average global value of annual ecosystem servises (unit: 1994 US$ ha^{-1} yr^{-1}). Open cells indicate lack of available information. From Costanza et al. (1997).

Biome	Waste treatment	Food production
Open ocean		15
Shelf		68
Coastal		93
Coral reefs	58	220
Estuaries		521
Tidal marsh / mangroves	6,696	466
Swamps / floodplains	1,659	47
Wetlands	4,177	256
Lakes / rivers	665	41
Forest	87	43
Grass / rangelands	87	67
Cropland		54

may alter the stability of aquatic ecosystem, could not occur under the heavy grazing by secondary producers (Fig. 1). If the primary producers and/or secondary producers in the biomes are edible for mankind, eutrophic coastal biomes can be a farm with natural and free fertilizer supplier.

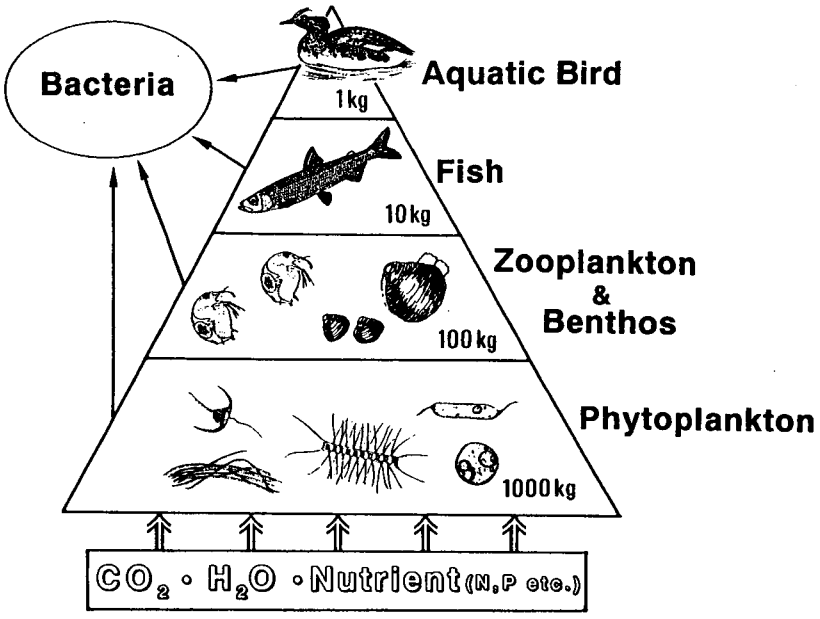


Fig.1 Schematic figure of food-web in an aquatic ecosystem

GSJ is running a research project, "Eutrophication control through food web management in estuarine lagoons (1994-1999)", to develop restoration methodologies for eutrophication which utilize the food-webs in aquatic ecosystems including shells, fishes, macrophytes and birds. The research field is coastal estuarine lagoons, Lake Shinji and Lake Nakaumi (Fig. 2).

The aim of the project consists of various interdisciplinary themes such as

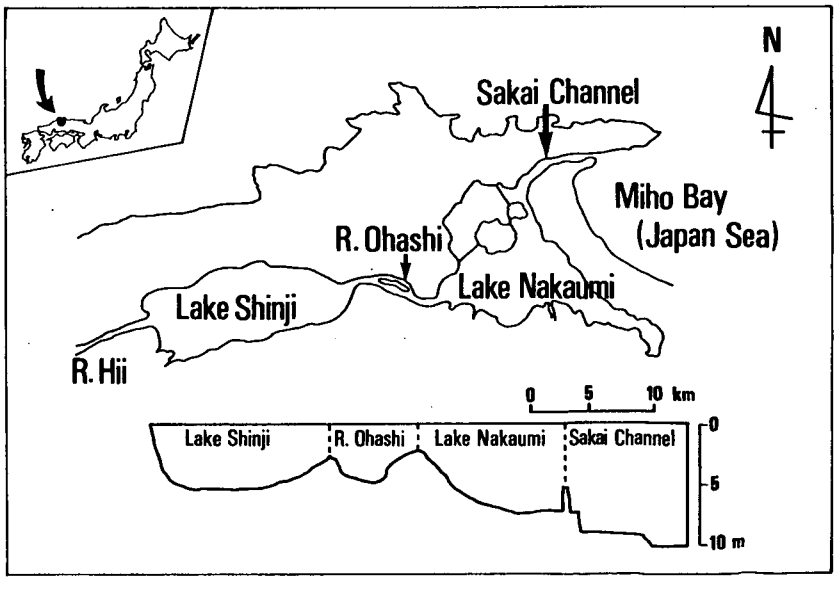


Fig. 2 Location of L. Shinji and L. Nakaumi

habitat structure, ecological function, sediment processes, nutrient dynamics, and physical restoration techniques. Some results concerning the role of filter-feeding bivalves, aquatic birds, and macrophytes on nutrient cycling in the eutrophic lagoons are introduced in the following sections.

FILTER-FEEDING BIVALVES

Lake Shinji (Fig. 2) is an oligohaline eutrophic lagoon where commercial filter-feeding bivalve, *Corbicula japonica*, densely inhabits. Fisheries yield of *C. japonica* is more than $23 million per year.

Fisheries of clams are not only important for economic reason but also relieving estuarine ecosystem from hypertrophication. In L. Shinji, growth of *C. japonica* in terms of nitrogen deserves 15 % of nitrogen loading to the lagoon in summer (Fig. 3). This amount of nitrogen is removed through fisheries in this lagoon without the expense of water quality control.

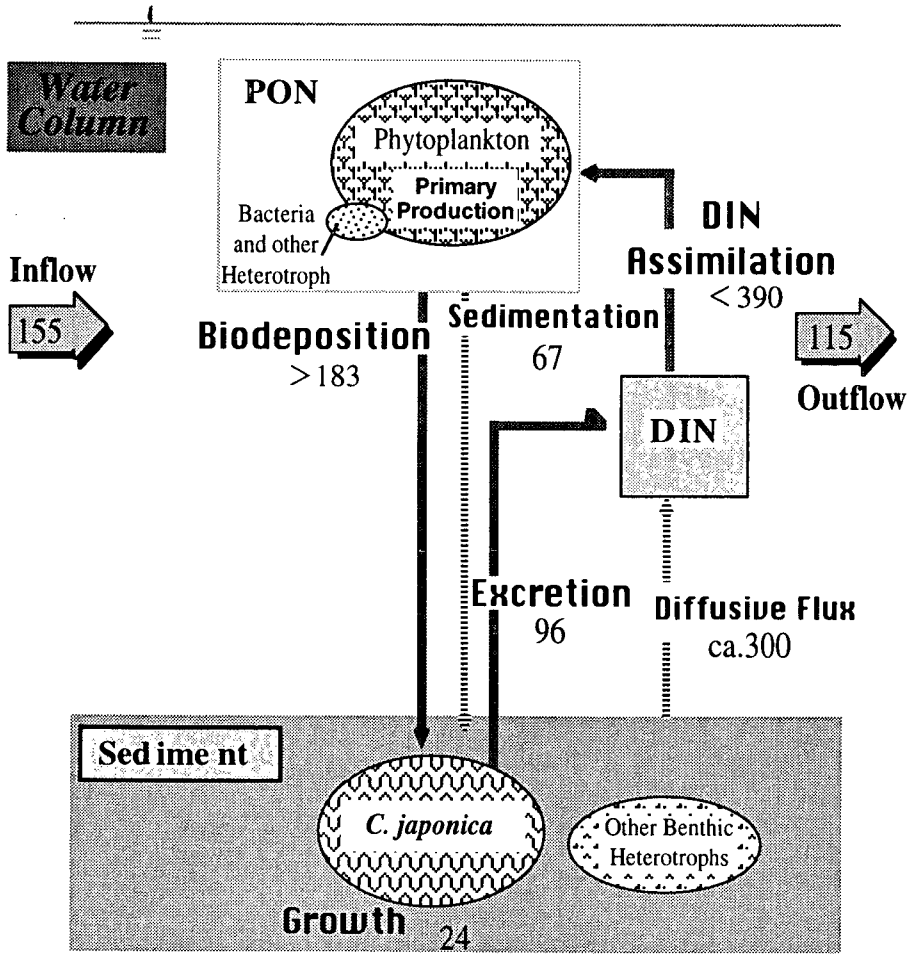


Fig. 3 Possible nitrogen cycling in Lake Shinji in summer based on Yamamuro & Koike (1993, 1994). Unit: kg atom N d^{-1}

Removal of nutrient through fisheries should work most efficiently when the target is a filter-feeding bivalve in shallow estuarine environment. When the target of fisheries is secondary producers like *C. japonica*, 10% of organic materials produced by phytoplankton is assimilated (Fig. 1). When the target of fisheries is the animal of higher trophic level than the secondary producer, i.e., fishes which feed on the secondary producers, production of such fishes would be only 1% of the primary production. Thus, the fisheries yield from the lake where the target is fishes should be less than the amount from L. Shinji.

Above hypothesis is examined with comparing the fisheries yield in three eutrophic lakes in Japan (Table 2). Nevertheless the gross productions of phytoplankton are almost equal among the lakes, the fisheries yield per unit area is much bigger in L. Shinji than two other lakes where the targets of fisheries are mostly fishes.

Table 2 Fisheries yield and gross production in three eutrohpoc lakes in Japan.

Lakes	Fisheries yield ($t\ yr^{-1}$)	Area (km^2)	Maximum depth (m)	Fisheries yield per unit area ($t\ km^{-2}\ yr^{-1}$)	Annual gross production ($g\ C\ m^{-2}\ yr^{-1}$)
L. Suwa	167	12.9	7.6	12.9	770
L. Kasumigaura	4,331	167.6	7.3	25.8	750
L. Shinji	10,165	79.2	6.0	128	730～1,100

Hydrodynamic condition which enables bivalves to obtain phytoplankton growing in surface water is indispensable for continuous growth of bivalve. The sedimentary environment of sand in lagoon is usually under various flows; channel flow, waves, tides, and ocean current. Waters over the sandy sediments are mixed both horizontally and vertically. In such well-mixing environment, animals which settle at the sediment to wait for foods lose less energy during the collection of foods than the animals which swim against flows to obtain foods (Fig. 4). Therefore, shallow sandy environment is a good candidate for the natural eutrophication control through the fisheries of filter-feeding bivalves.

AQUATIC BIRDS

When the dominant bivalve in the water area is not edible, protection of the predator of the bivalve is necessary to control water quality through the removal of bivalves. Small biofouling mussel, *Musculus senhousia*, inhabits

the shore of Lake Nakaumi (Fig. 2). L. Nakaumi is a polyhaline lagoon, and it is as eutrophic as L. Shinji. *M. senhousia* comprises 56% of macrobenthic biomass in L. Nakaumi.

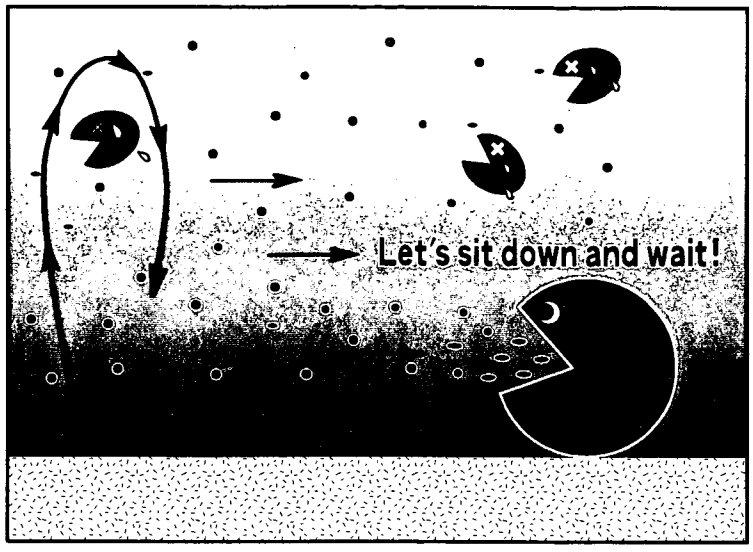


Fig. 4 Conceptional figure on the merit of sessile filter-feeding in well mixed water

Three species of diving ducks, *Aythya fuligula* (tufted duck), *Aythya ferina* (pochard), and *Aythya marila* (scaup) winter in L. Nakaumi. Our estimation suggests that averaged wintering population of *Aythya* spp. in L.

Table 3. Effect on nutrient budget by *Aythya* spp. through their feeding on non-commercial bivalve, *Musculista senhousia* (Yamamuro et al. submitted).

	Carbon	Nitrogen	Phosphorus
Amount of CNP per individual of *Musculista senhousia* in March	11 mg	2.1 mg	0.16 mg
Number of *M. senhousia* fed by ducks during winter		2.8×10^{10}	
Amount of CNP in 2.8×10^{10} *M. senhousia* in March...(A)	310 t	59 t	4.5 t
Amount of oxygen used to decompose 310 t C when RQ is 0.85 and carbon is totally used for respiration	970 t O_2		
Monthly nutrient loads to L. Nakaumi and L. Shinji...(B)		253 t	23.7 t
(A)/(B)		23%	19%

Nakaumi (50,276 individuals) eats 2.8×10^{10} individuals of *M. senhousia* during their stay from Oct. 15 to March 15 (Table 3). Since 2.8×10^{10} individuals of *M. senhousia* contains 310 t of organic carbon, 59 t of nitrogen (N) and 4.5 t of phosphorus (P) in flesh in March, the death of the same amount of *M. senhousia* in summer would at least induce the same amount of NP input and 970 t of oxygen consumption assuming that the respiratory quotient is 0.85 and the carbon is totally used for respiration by decomposing bacteria. NP input from the dead flesh of *M. senhousia* in certain month in summer would increase the loads to L. Shinji and L. Nakaumi by ca. 23 and 19 % of N and P, respectively (Table 3). Nutrient efflux from the sediment induced by oxygen depletion would further increase the NP loads. Therefore, predation of bivalves by the diving ducks are preventing further deterioration of water quality caused by the NP inputs in summer.

The population of *Aythya* spp. has increased in L. Nakaumi while it has been relatively constant in L. Shinji where dominant bivalve is a target of fisheries. Meanwhile, the nearby wintering place for the diving ducks in Nakdong River Estuary, Korea, was lost during the 1980's because of the barrage and reclamation projects (Doornbos et al. 1986, Kim and Won 1994). The diving ducks' population has also declined in the United States due to human impact (Erwin 1996). In L. Nakaumi, the mass of biofouling mussels enable diving ducks to increase their wintering population, which is one of the key factors that control the water quality in the lagoon.

Plants

To estimate the role of macrophytes fisheries in controlling water quality in eutrophic lagoons, nitrogen and phosphorus contents of macroalgae in L. Nakaumi were analyzed (Yamamuro, 1997). Nitrogen and phosphorus contents of edible algae, *Gracilaria verrucosa*, were 3.1 and 0.21 % dry w, respectively. The amounts of removed nitrogen and phosphorus from L. Nakaumi through fisheries of 551 t dry w of *G. verrucosa* in 1960 were therefore estimated to be 17 and 1.2 t. These amounts were equivalent to 1.3 and 0.82 % of present annual loads of nitrogen and phosphorus into L. Nakaumi and L. Shinji. Increase of the fisheries of *G. verrucosa* up to 5 times of the yield in 1960, would deserve removal of 6.5 and 4.1 % of nitrogen and phosphorus loads to the lagoons. This may be possible because the fisheries yield of *G. verrucosa* in 1960 was 13% of estimated annual growth.

Until chemical fertilizers became commonly used, farmers utilized

macrophytes both in fresh and saline waters as fertilizer. At that time, farmers discarded waste to waters very cautiously.

Farmers in the coast of Lake Biwa, the biggest freshwater lake in Japan, used *Hydrilla verticillata* and *Vallisneria denseserrulata* in summer as fertilizer for vegetables. They covered the foot of the plants with the wet plants. As fertilizer, these macrophytes are not rich in nitrogen and phosphorus (2.4 and 0.8 % dry w), but concentration of potassium(4 to 6 % dry w) was assumed to be effective (Hasegawa 1939). It is notable that macrophytes were not only effective as fertilizer but also effective as water supply and weeding killer in summer.

Not only macrophytes but also sludge and small fishes had been used as fertilizer by the farmers living near lakes and lagoons. Removal of these organic materials from lakes and lagoons should have prevented the water from eutrophication.

ECONOMIC VALUE OF EUTROPHICATION CONTROL THROUGH FOOD WEB MANAGEMENT

Since prehistoric era, mankind has preferred inhabiting in coastal zones where lands are rich in nutrient and animal proteins are easy to obtain even for children and women. At present, most citizens do not obtain foods from waters. Farmers neither use macrophytes, sludge and small fishes as fertilizer. These changes may have accelerated the eutrophication of waters in coastal zones in Japan.

In Lake Kasumigaura, one of the most eutrophic lakes in Japan, more than 1 million dollars are annually spent for eutrophication control such as dredge of the sludge, plantation of reeds, and removal of blue-greens.

In L. Shinji, the annual removal of nitrogen (N) and phosphorus (P) through the fisheries of commercial bivalve, *Corbicula japonica*, is 69 t and 5.8 t, respectively (Shimane Prefectural Fisheries Experimental Station 1984). Since the sludge of L. Shinji contains 0.11 % of N, 0.045 % of P, and the wet/dry weight ratio is ca. 2.4 (Yamamuro unpubl.), 31,000 - 151,000 t of sludge should be dredged annually for the same amount of NP removal through fisheries. It is obvious that the removal of nutrients through fisheries is more costless and useful than dredge of the sludge.

Eutrophication control with the aid of ecosystem may not be quantitatively remarkable in removal of nutrients. However, it would not require the maintenance budget after the establishment of the suitable ecosystem. It would also make the water area closer to citizens who are not engaged in primary industry. Children harvesting shell/fish by

themselves for their dinner may become aware of our dependence on the natural resources in this planet earth, and that the pollution of biomes means the pollution of ourselves.

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CONTROL OF ANTHROPOGENIC N_2O-A GREENHOUSE GAS-EMISSION FROM SEVERAL MAN-RELATED FIELDS

温室効果ガスN_2Oの人為起源由来の発生制御

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ABSTRACT

To control the emission of non-CO_2 greenhouse gases, a three-year project titled *Study on Development and Assessment of Strategy and Technology for Control Greenhouse Gases CH_4 and N_2O* is under going, which is granted by the Japan Environment Agency and involved in 14 institutions of four countries--Japan, China, Korea and Thailand. The project covers the following fields: wastewater treatment, automobile, cultivated soil for both farming and grazing, treatment and disposal of excess sludge and solid waste, and ruminants. From the past one-and-half-year work, Some N_2O evolution pathways were put forth concerning microbial activities and automobile. Optimum operational conditions for low N_2O emission were obtained and advantageous processes with low N_2O emission were recommended in various sub-projects. Several new or modified processes were developed with low N_2O discharge. Strategies and measures about the management of ruminants breeding, plant cultivation, fertilizing and irrigation, were also put forward for mitigating N_2O emission.

Keywords: N_2O control, automobile, cultivated soil, greenhouse gas, industrial combustion, ruminant, solid waste treatment and disposal, wastewater treatment.

INTRODUCTION

As the global warming is becoming serious, control of greenhouse gases emission has caused world-wide attention. Compared with the work concerning CO_2, less efforts has been made on CH_4 and N_2O. However, since the greenhouse effects of N_2O and CH_4 are 200-300 and 20-30 times of that of CO_2, and since N_2O has much longer life in the nature, N_2O and CH_4 may play more and more important roles in global warming in the near future (Inamori, *et al.*, 1991). Therefore, the knowledge of their evolution should be of great importance and necessity to control their emission and to mitigate global warming. As an important developed country in Asia-Pacific region, Japan has important

contributions to regional greenhouse emission (Nityuke and Arai, 1995). Moreover, due to its economic and technological situation, Japan is expected to do more to control greenhouse gases emission. A Global Environment Research Fund granted by the Japan Environment Agency has thus been put in action since 1992. It is now entering the second tenure of the fund which is from April, 1995 to March, 1998.

A project titled *Study on Development and Assessment of Strategy and Technology for Control of Greenhouse Gases CH_4 and N_2O*, is also granted by the Fund, which Dr. Yuhei Inamori is in charge of. With the two-step objectives--to control CH_4 and N_2O emission and to reduce their concentrations in the atmosphere, the project is involved with 9 institutions of 6 ministries in Japan and 5 foreign institutions, and is composed of 9 sub-projects and 15 sub-sub-projects (Table 1). According to the research fields concerned, the sub-projects can be classified into five groups, they are, those concerning wastewater treatment (sub-project 1, 2, 9), automobile (sub-project 8), cultivated soil for both farming and grazing (sub-project 5, 6), treatment and disposal of excess sludge and solid waste

Tab. 1 Different themes of the project entitled *Development and Assessment of Strategy and Technology for Control Greenhouse Gases CH_4 and N_2O*

Person in charge: Yuhei Inamori

No.	Sub project	Institution	Person in charge	Cooperating country
1	Strategy and technology for controlling CH_4 and N_2O emission from bio, eco-technological domestic wastewater treatment systems	National Institute for Environmental Studies, EA	Yuhei Inamori	
2	Strategy and technology for controlling greenhouse emission from sewage treatment systems	Public Works Research Institute, MC	Eiichi Nakamura	
3	Technology for controlling CH_4 and N_2O emission from solid waste disposal and treatment	The Institute of Public Health, MHW	Masaru Tanaka	Korea
4	Strategy and technology for controlling trace gases emission from combustion	National Institute of Resource and Environment, MITI	Yoshizo Suzuki	
5	Study on controlling CH_4 and N_2O emission from farmland	Japan International Research Center for Agricultural Sciences	Katsuyuki Minami	Thailand; China
		National Institute of Agro-Environmental Science, MAFF	Haruo Tsuruta	
6	Study on trace greenhouse emission from meadow and their controlling technologies	National Grassland Research Institute, MAFF	Katsumi Yamamoto	
7	Study on CH_4 and N_2O emission from ruminants	National Institute of Animal Industry, MAFF	Mitsunori Kurihara	
8	Study on control CH_4 and N_2O emission from automobile	Traffic Safety and Nuisance Institute, MT	Matsuo Odaka	
9	Development of sludge and wastewater treatment technologies applicable to North-east Asia	National Institute for Environmental Studies, EA	Xiao-Lei Wu Hai-Nan Kong Hyun-Geoun Park	China; Korea

Note: EA, MC, MHW, MITI, MAFF and MT are the abbreviations of Environment Agency, Ministry of Construction, The Ministry of Health and Welfare, The Ministry of International Trade and Industry, Ministry of Agriculture, Forestry and Fisheries and Ministry of Transportation, respectively.

(sub-project 2, 3, 4, 9) and that concerning ruminants (sub-project 7). Different themes of the Project

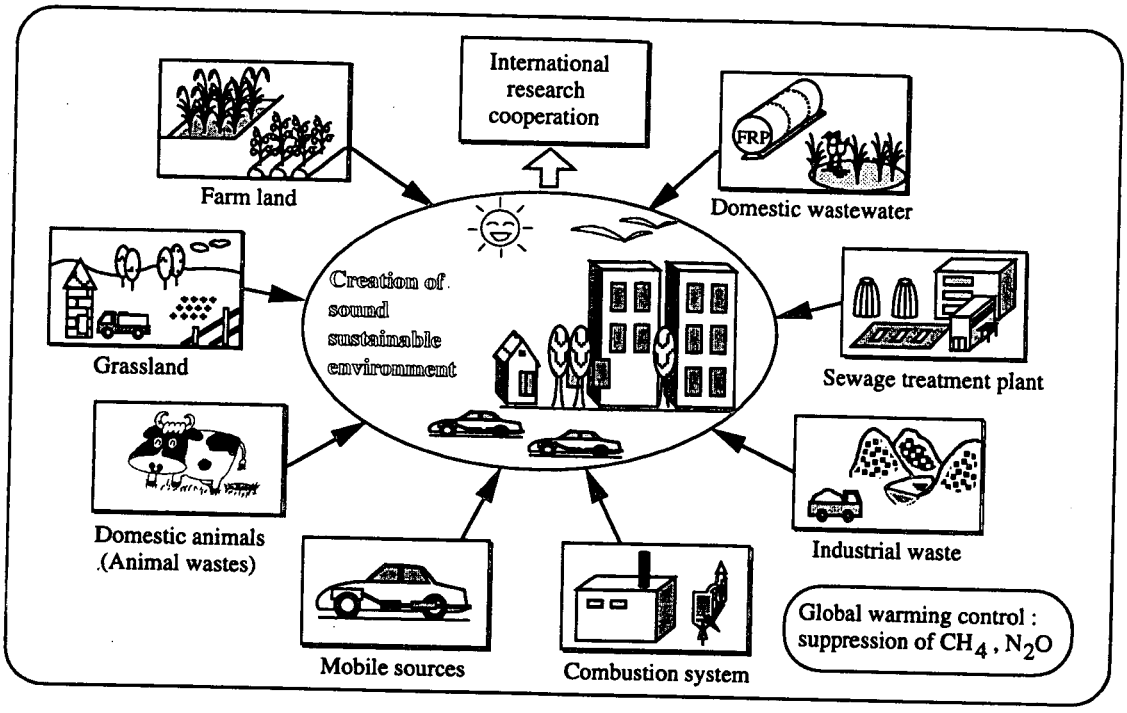


Figure 1 Association of the Sub-projects

is also illustrated in Figure 1. It can be seen that the Project focuses its attentions on anthropogenic CH_4 and N_2O. As characteristics of the project, ecological ideas, cleaner production and sustainable development are emphasized. In addition, under the guidance that no boundary exists for environmental problem, the project puts the international cooperation at a very important place. Five institutions of three foreign countries are also involved with. Exchange of researchers and information, technological support and feed back have made the project of international importance. From the past one-and-half-year investigation, results concerning N_2O were stated in the following.

RESULTS AND DISCUSSIONS

Control of N_2O Emission from Wastewater Treatment

Emphases of the three sub-projects involved in this field are different. Sub-project 1 lays its emphasis on comparing N_2O producing capabilities of the existing wastewater treatment processes, and on modifying the existing and/or developing some new wastewater treatment processes for mitigating N_2O emission. Sub-project 2 focuses its attentions on how to reduce N_2O emission through the maintenance of sewage treatment stations/plants. The main work of sub-project 9 is to develop some technologies with high cost-effectiveness adaptable to Northeast Asian countries, including China and Korea.

In Sub-project 1, by comparisons of N_2O emission from several wastewater treatment processes, including conventional activated sludge process, trickling biofilter and RBC, intermittent aeration process was proved to be an optimum process with low N_2O emission (as well as with high nitrogen removal capability). As an example, N_2O emission from intermittent aeration process was approximately 3 times less than that from conventional activated sludge process (Figure 2). In order to get some ideas on N_2O emission from the intermittent aeration process, influences of aeration time in

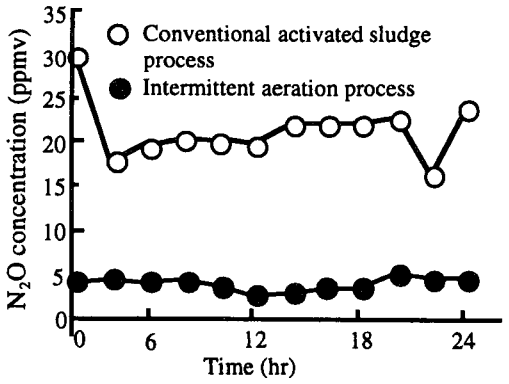


Figure 2 N_2O emission from different wastewater treatment processes

an aeration/stirring cycle (20/60 minutes, 30/60 minutes and 60/60 minutes) and HRT (4, 6 8, 12 hours) were tested. Results showed when influent BOD concentration was 200 $mg \cdot l^{-1}$, and total nitrogen concentration was 50 $mg \cdot l^{-1}$ (including 25 $mg \cdot l^{-1}$ of NH_4-N), longer HRT and aeration time of 30 minutes led to the less N_2O emission and higher total nitrogen removal. Investigations into the behaviors of intermittent aeration process with pH controlled and $FeSO_4$ dosed (The experimental

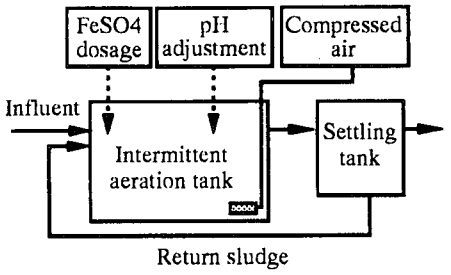


Figure 3 Scheme of intermittent aeration process with pH controlled and coagulant dosed

set-up is shown in Figure 3) showed that optimal constant pH value in the reactor was helpful to reduce N_2O emission and upgrade nitrogen removal. Moreover, addition of the coagulant was beneficial for both suppressing N_2O release and upgrading phosphorus and nitrogen removal.

Moreover, experiments were also conducted for comparing the contributions of aerobic and anoxic conditions to N_2O emission in the intermittent aeration process. Results showed that N_2O concentrations in the exhaust were much higher under aerobic conditions than under anoxic conditions (Figure 4). However, the concentrations of N_2O dissolved in the reactors were higher under aerobic conditions than under anoxic conditions (Figure 5). The phenomena suggested that it was the aeration that stripping N_2O generated under anoxic conditions out of the reactor under aerobic conditions. Dissolved N_2O could thus not ignorable while considering the N_2O producing capability of a wastewater treatment process.

On the other hand, in Sub-project 9, microbial behaviors toward N_2O emission were studied. N_2O producing abilities of *Alcaligenes faecalis* (a typical heterotrophic nitrifier), *Nitrosomonas europaea* (a typical autotrophic ammonia oxidizer which can conduct nitrite reduction) and *Nitrobacter winogradskyi* (a typical nitrite oxidizer) (Wu *et al.*, 1995) were compared under aerobic conditions. Unit *N. europaea* was proved to produce the most N_2O, which was 283～542 times of that of unit *N. winogradskyi* and 19～54 times of that of unit *A. faecalis*. However, owing to it heterotrophic living style and possible high population, *A. faecalis* was suggested to have the potential to play important roles in N_2O evolution (Inamori *et al.*, 1996).

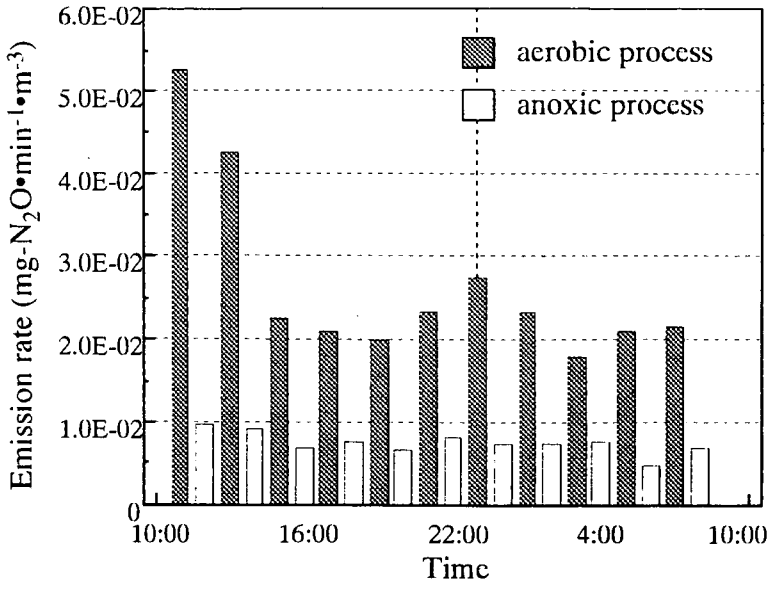


Figure 4 Variation of N_2O production rate in the exhaust

Then *A. faecalis* was introduced into activated sludge and became a predominant genus in the activated sludge ecosystem. When influent BOD and total nitrogen concentrations were about 200 $mg \cdot l^{-1}$ and about 60 $mg \cdot l^{-1}$, respectively, different levels of DO concentration (5, 2, 0.5 $mg \cdot l^{-1}$), pH value (5.5, 7, 8.5) and *A. faecalis* amount (10^{10}, 10^9, 10^8 $CFU \cdot l^{-1}$) were kept to test their influences on N_2O emission under aerobic conditions. Results showed that the systems with introduced *A. faecalis* produced N_2O 5 times less than the system without *A. faecalis* addition in most cases. Moreover, total nitrogen removal efficiencies of the former systems were over 10% higher than that of the latter system. It is obvious that introduction of *A. faecalis* was useful for reducing N_2O emission and helpful for upgrading nitrogen removal as well (Figure 6, Figure 7) (Wu *et al.*, 1997a). Results also showed

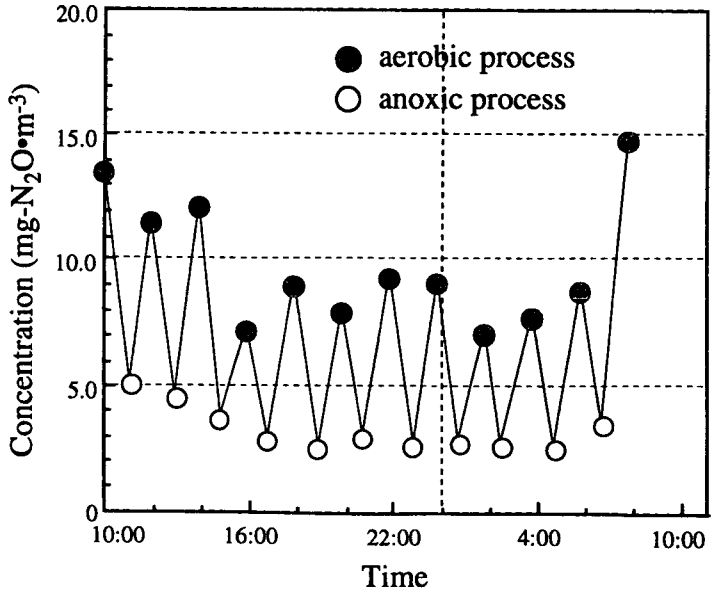


Figure 5 Change of dissolved N_2O concentration

that higher and quicker total nitrogen removal corresponded to less N_2O production.

Several possible N_2O evolution pathways were put forth on some hypotheses (Figure 8) (Wu *et al.*, 1997b). The relative amount of the autotrophic nitrifying bacteria with nitrite reduction functions and the heterotrophic nitrifying denitrifying bacteria was urged to determine the influence of DO on N_2O emission and the behavior of N_2O generation in an activated sludge system. It was suggested that

N_2O emission may be controlled through manipulating the amounts and activities of the two kinds of microorganisms.

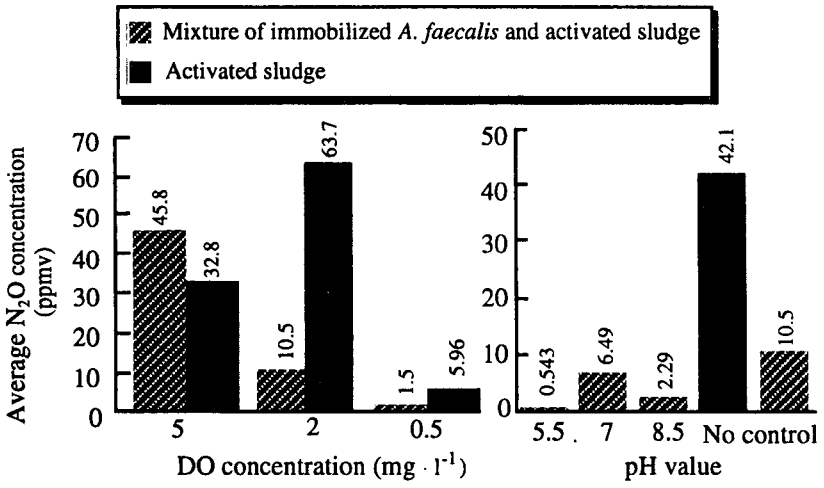


Figure 6 Average N_2O concentration of different conditions (Sub-project 9)

The results from maintenance of the sewage treatment stations/plants (Sub-project 2) suggested that keeping the treatment facilities covered to prevent the wastewater from dilution in rain season and keeping high temperature of the wastewater in winter were helpful to reduce N_2O emission. Low COD/TN (total nitrogen) ratio (lower than 2) was concluded to be beneficial for N_2O evolution, and optimum COD/TN ratio was thus suggested to reduce N_2O emission.

Control of N_2O Emission from Treatment and Disposal of Excess Sludge and Solid Waste

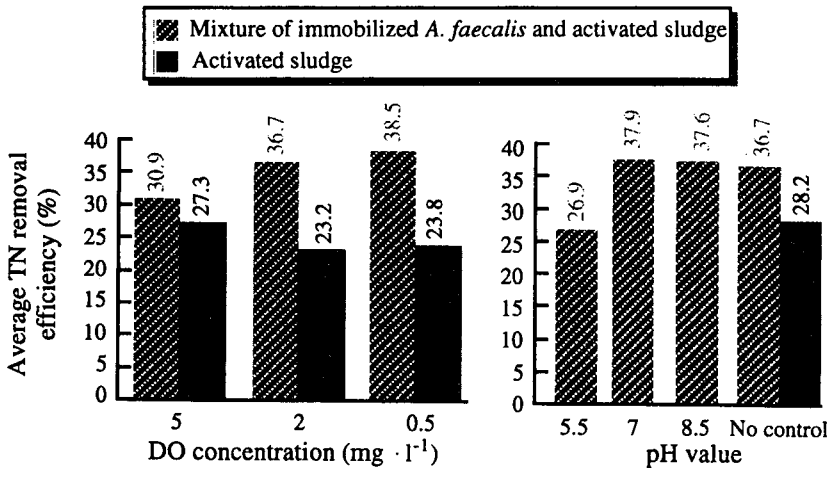


Figure 7 Average efficiencies of total nitrogen removal under different conditions (Sub-project 9)

Combustion is thought to be one of the main processes for treating of excess sludge and solid waste. Two kinds of combustors were employed to treat excess sewage sludge from wastewater treatment plants. They were bench-scale circulating fluidized bed combustor (CFBC) (Sub-project 4,)(Suzuki, 1996) and full-scale fluidized combustor (FC) (Sub-project 2) (Makamura, 1996). In both cases, N_2O evolution behaviors and the conditions for low N_2O emission were studied.

In the case of CFBC (high temperature was kept by electrically heating), the higher the combustion temperature was, the lower the N_2O emitted from the combustor. on the other hand, oxygen concentration of 3% (to the total gas) led to peak N_2O concentration in the exhaust. It was clear that N_2O was mostly from the volatile nitrogen compounds of the sludge, and the ratio of N_2O-N

produced to total nitrogen in the sludge was about half of the ratio in case of coal. Similar results were obtained from experiments concerning the FC where high temperature was kept by oil combustion. Higher free board temperature led to less N_2O emission, and consequently resulted in lower total global warming potential (GWP) of the exhaust, although higher temperature also resulted in more CO_2. For an instance, when the free board temperature increased from 846℃ to 874℃, N_2O emission reduced by 3/4, and total GWP decreased by 20%. However, combustion cost rose because of the increase of needed to maintain the higher temperature.

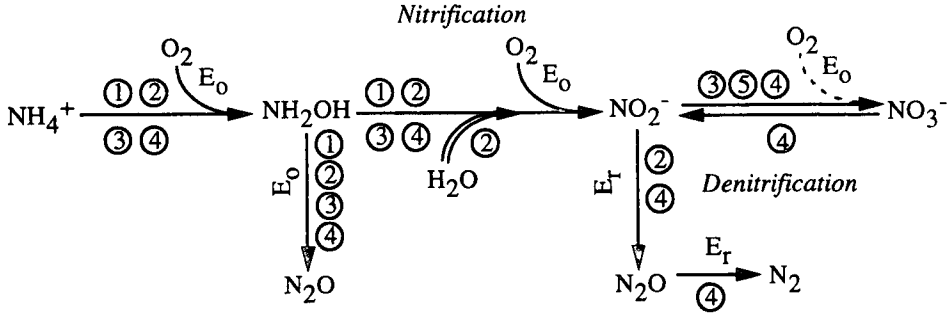


Figure 8 Possible ways of N_2O evolution from activated sludge under aerobic conditions.

①②③④⑤ stand for autotrophic ammonia oxidizers without nitrite reduction functions, autotrophic ammonia oxidizers with nitrite reduction functions like *Nitrosomonas europaea*, heterotrophic nitrifiers without aerobic denitrification functions, heterotrophic nitrifiers with aerobic denitrification functions like *Alcaligenes faecalis* and nitrite oxidizers, respectively. E_o, E_r represent oxidase and reductase. The two-line arrow shows that H_2O can be a oxygen source of NO_2^- for *N. europaea*.

On the other hand, removal of ammonia from solid waste was proved to be beneficial for reducing N_2O emission from the solid waste combustion and from its landfill disposal (Sub-project 3). High temperature aerobic sludge digestion was proved to be cost-effective in both mitigating N_2O emission and reducing the operational cost (Sub-project 9).

Control of N_2O Emission from Automobile

Automotive exhaust is regarded as one of the main causes of the greenhouse gases. By now, how to reduce CO_2 emission has caused much attention. Some measures have been taken to reduce CO_2 emission, including the popularization of the compressed natural gas fueled vehicles. On the other hand, less researches have been made on N_2O emission from automobile, comparatively. Based on the last-tenure investigations into the N_2O emission co-efficient of automobiles, Sub-project 8 was arranged with the purpose of clarifying the mechanisms of N_2O evolution in vehicles in the present tenure.

The experiments were conducted with non dispersive infrared analyzer (NDIR) and Folie transforming infrared analyzer (FTIR) used to analyze the gas samples (Otaka, 1996). Characteristics of N_2O emission from three kinds of gasoline fueled vehicles (with no catalyst, with oxidation catalyst and with three way catalyst) were compared. Driving mode patterns and catalyst temperature of the gasoline fueled vehicle with three way catalyst were changed to test their influences on N_2O evolution in the vehicles.

Results showed that, the vehicles with three way catalyst discharged more N_2O than the other two kinds of vehicles. In the vehicles with three way catalyst, when the catalyst temperature increased to near 100℃, N_2O emission increased shiftily. After 230℃, N_2O tended to decrease. Peak values of N_2O emission generally corresponded to the increase and decrease of the vehicle's moving speed. In the course of acceleration, there were a great deal of NO_x and CO in the gas reaching the entrance to the

catalyst, N_2O was thus thought to derive from the reduction of NO_x, as commonly regarded. However, when the speed decreased, there was almost no NO_x in the gas at the entrance to the catalyst. In addition, oxygen concentration was at high level in the gas. Therefore, the N_2O emitted in this case should not result from the reduction of NO_x. Another interesting experimental phenomenon was that when the catalyst temperature increased to 180℃, NH_3 started to emit. After 180℃, NH_3 emission kept the trend of increasing in the experimental period. Moreover, peak NH_3 concentration appeared in the deceleration course.

To explain the phenomena, experiments were made, in which NH_3 gas diluted by the air was arranged to pass through three catalyst units, including a platinum unit, a palladium unit, and a three way catalyst unit. N_2O was detected in all the three catalyst units. When the temperature of the three way catalyst was 250℃, about 1/3 of the influent NH_3 was transformed into N_2O. Therefore, N_2O generated in the case of the speed decreasing could be thought to result from the oxidation of NH_3 which was adsorbed by the catalyst. The peak N_2O concentration was lower when the catalyst temperature was higher, which was in harmony with the results that oxidation of NH_3 was inhibited by the high temperature (higher than the 250℃).

In general, N_2O emission from the vehicles with three way catalyst was attributed to two processes, reduction of NOx in the case of acceleration and the oxidation of NH_3 in the case of deceleration. Therefore, to reduce NH_3 should be considered of importance to control N_2O emission, as well as to modify the catalyst composition and to control the ratio of air to fuel.

Control of N_2O Emission from Cultivated Soil and Ruminants

Cultivated soil is referred to as a huge anthropogenic N_2O source. N_2O emitted from soil is thought to derive mostly from nitrification and denitrification processes carried out by soil microorganisms. N_2O emission from soil is therefore affected by the type and amount of nitrogen sources (NH_4-N, NO_3-N, NO_2-N and etc.), the aerobic and anoxic conditions, the soil temperature, the soil pH and so on.

In the Sub-project 5 (Tsuruta, 1996) and 6 (Yamamoto, 1996), four kinds of commonly-used fertilizer were used to tested their contributions to N_2O emission, they were: urea, meister, CDU and nitrogen-free fertilizer. Results showed that the order of N_2O production from the four fertilizers was urea> CDU> meister>nitrogen-free fertilizer. On the other hand, fertilizer should be fertilized according to the soil temperature, the rain fall and the properties of the soil. For example, CDU and LP70 could be used in the case of high soil temperature and heavy rain fall, which could keep the grass production and reduce N_2O emission. In addition, introduction of nitrification inhibitors into fertilizer was proved to be helpful to reduce N_2O emission. Generally, it is beneficial to mitigate N_2O emission to modify fertilizer composition, to arrange the fertilization according to the climate, irrigation and the weather.

It was clear that N_2O concentrations inside the cow stomach and outside the cow were almost the same, suggesting that not like the CH_4, almost no N_2O was produced in the cow stomach.

Ongoing Work and Proposed Researches in the Near Future

In the period left in the tenure, new measures and strategies are expected to be put forth. As an example, the behaviors of various vehicles with different catalysts to N_2O emission will be tested in real moving modes. The performance of some new catalysts will be determined and the feasibility will be assessed. Strategies for management of the grassland, farmland and ruminants are expected to be put forth for control CH_4 and N_2O emission. Some modified and/or new technologies are expected to be developed and the cost-effective assessment to them will also be carried out. For an instance, aimed at reducing N_2O emission and upgrading wastewater treatment, modification of the intermittent

aeration process will be made through introducing some effective microorganisms into the reactors. Full scale experiments will be made to testify the results obtained from fundamental experiments.

CONCLUSIONS

Almost no N_2O generated in the cow stomach. Fertilizing slow-release fertilizer, and introducing nitrification inhibitors into the fertilizer could reduce N_2O emission from cultivated soil. Higher combustion temperature, optimal oxygen concentration could reduce N_2O emission from excess sludge and solid waste combustion. To remove ammonia from solid waste was thought effective to mitigate N_2O release from solid waste combustion and its landfill plants. Relative amounts of different microorganisms in activated sludge affected the behaviors of N_2O emission in the activated sludge system, and determined the effects of DO conditions on N_2O evolution. Controlling their amounts and activities could thus be helpful to reduce N_2O emission from activated sludge wastewater treatment processes. Intermittent aeration process was proved to be a suitable process to control N_2O emission as well as to removal nitrogen. N_2O could derive from ammonia oxidation when the vehicles with three-way catalyst decelerated.

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Session 8

CSO Control

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"Measures against Combined Sewer Overflow in Osaka City"
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MEASURES AGAINST COMBINED SEWER OVERFLOWS BY STORAGE SEWER

Hideo Suzuki

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ABSTRACT

As of April, 1997, the percent of sewered population in Kyoto City has reached 98.7%, with sewer pipes servicing an area of 14,761 ha. Of this area, 6,019 ha situated in the central part of the city are serviced by a combined sewer system. The increasing rainwater and wastewater runoff in this area, however, has created an insufficiency in the capacity of the running sewers of the combined sewer system. As a result, damage due to floods in certain areas during periods of heavy rainfall, and problems of overflow from the overflow chambers during periods of light rainfall have occurred, and the need for improvement measures has been indicated. Due to the fact that the water in the lower course of the Yodo River is used as drinking water for nearly 11 million people, and in answer to the increasing demands of the citizens for a pleasant waterside environment, Kyoto City is actively engaged in the enforcement of advanced wastewater treatment in the wastewater treatment plants and improvements of the combined sewer system.

In this report, the sewerage works of Kyoto City are briefly summarized, and the current status of improvement measures for the combined sewer system are described. Furthermore, at present research concerning the effectiveness of improvement plans are being carried out in the Kisshoin treatment district, and the results of measurements concerning water quality in wet weather are also reported.

KEYWORDS

Urban Wet Weather, Combined Sewer Overflows (CSOs), CSO Control, Flood Control, Storage Sewer, First Flush

INTRODUCTION

The sewage works of Kyoto City have been carried out as one of the most important projects of the city. As of April, 1997, 98.7% of the population of the city is serviced by the sewer system. As a result, the water quality of the rivers within the city, which previously were suffering from pollution is steadily improving year by year, and sportsmen fishing for the Japanese *'ayu'* trout can now be seen on the Kamo River, which runs through the center of the city.

However, due to the fact that Kyoto City is located in the middle course of the Yodo River, the water of which is used as the drinking water for nearly 11 million people downstream, and in answer to the increasing demands of the citizens for a pleasant waterside environment, it is necessary to improve water quality still more. To these ends, Kyoto City is actively engaged in the enforcement of advanced wastewater treatment in the wastewater treatment plants and improvements of the combined sewer system.

In this report, improvement plans for the combined sewer system in Kyoto City are briefly summarized, and research concerning the evaluation of the effectiveness of improvement plans in the Kisshoin treatment district, where improved facilities are already in use, is described.

COMBINED SEWER SYSTEM IMPROVEMENTS

Present Situation and Problems

Until about 1970,the sewer system of Kyoto City was constructed with the combined sewer system. As a result, as of April 1997, of the 14,761 ha which comprises the entire sewered area of the city, 6,019 ha located primarily in the central parts of the city are serviced by combined sewers. The portions of the city which are serviced by the combined sewers are characterized by increasing storm water runoff due to the expansion of impervious areas connected with urban development and wastewater due to changes in the life styles of the residents, and the capacity of existing running sewers has become insufficient. As a result, there is an increasing danger of floods occurring during periods of heavy rainfall, and there are areas which suffer damage from floods. Moreover, while one advantage of the combined sewer system is that the pollutants from the roads and other surfaces which are washed in during the early stages of wet weather can be treated simultaneously with the rainwater, if the rainwater influent exceeds a certain level a portion of the wastewater

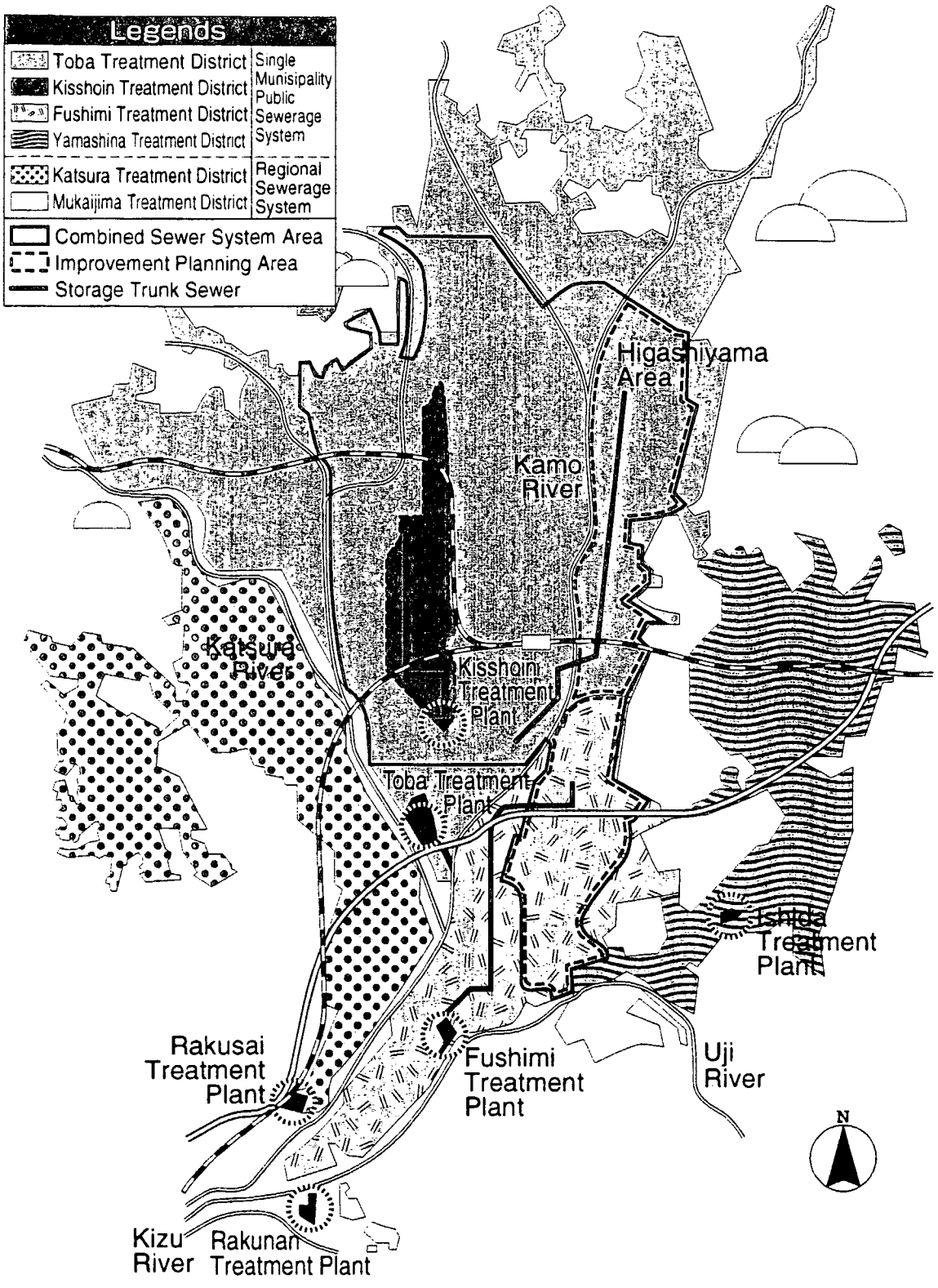


Figure 1 Planning of Public Sewerage System in Kyoto City

is discharged from the overflow chambers into the rivers. Demands have also been made for improvement measures to control water pollution.

Purposes and Measures

In an effort to alleviate these problems, Kyoto City has drawn up and instituted improvement plans for the combined sewer system to function as flood control and combined sewer overflow (CSO) control.

The measures described below have been employed for CSO control. These measures have resulted in the achievement of a reduction in the total pollutant loads from the treatment plants and overflow chambers to the same levels as with the separate sewer system.

(1) Increasing the intercepting capacity of the overflow chambers

Through the construction of separating chambers for the new trunk sewer and reconstruction of the overflow chambers, the intercepting ratio at the overflow chambers will increase to more than three or five times. Furthermore, by decreasing the frequency, and volume of overflows from the overflow chambers the CSO loading will diminish.

(2) Temporary storage and treatment of CSOs

Wastewater which exceeds the maximum hourly wastewater flow is continuously taken into the new trunk sewer, where it is temporarily stored. The wastewater that has been stored in the trunk sewer is sent to the wastewater treatment plant after the wet weather has ended, thus diminishing the CSO loading.

As a measure for flood control, a new trunk sewer has been laid to supplement the capacity insufficiency of the running sewers. The trunk sewer enables both the rapid discharge and storage of storm water, and has been designed with the objective of preventing floods even during wet weather as severe as 62 mm/hr, which occurs as infrequently as only once every ten years.

Summary of Improvement Plans

At present, operations for combined sewer improvements throughout Kyoto City are planned to center around those areas serviced by older facilities, and as shown in Figure 1, are being carried out in the Kisshoin district, the Higashiyama area and the Fushimi district. A summary of each of the three plans is shown in Table 1. The next stage of operations will be comprised of plans for improvements to be carried out in the Toba treatment district excluding the Higashiyama area, an improvement area of approximately 3,670 ha.

Table 1 Outline of Improvement Planning

District name			Kisshoin	Higashiyama	Fushimi
Purpose			Flood Control and CSO Control		
Area (ha)			474	1,253	1,195
Trunk Sewer	Name		Kisshoin	Higashiouji	Fushimi
	Diameter	(mm)	ϕ800～ϕ2,800	ϕ1,350～ϕ4,500	ϕ6,000
	Length	(m)	4,900	8,110	7,170
	Storage Volume	(m^3)	13,000	67,000	171,000
Other Facilities					Storage Tank 25,000m^3
Pollutant Loading Reduction(%)	CSOs(BOD)		90	70	60
	Overall(BOD)		20	25	15
Present Status			running	under construction	under construction

A major characteristic of the improvement plans of Kyoto City is the construction of a new trunk sewer in an arrangement which makes efficient use of the terrain of the city, gradually sloping from north to south. The trunk sewer can be used as storage pipe during periods of light rainfall, and as bypass pipe during periods of heavy rain storms. Furthermore, in order to predict the effectiveness of these improvement operations, the Modified Road Research Laboratory Method (M.R.R.L. Method) was used as the simulation model for rain water runoff analysis and the Public Works Research Institute Model (P.W.R.I. Model) was used as the simulation model for pollutant load runoff analysis.

IMPROVEMENT PLANS FOR THE KISSHOIN TREATMENT DISTRICT

Characteristics of the Kisshoin Treatment District

The Kisshoin treatment district is a long, narrow area measuring approximately 1.5 km from east to west, and approximately 7 km from north to south. The JR Kyoto Line divides the district across the center, with the Shujaku line servicing the upper area (north side, 456 ha) and the Karahashi line servicing the lower area (south side, 128 ha). The problems that each of the two areas faced were different. The Shujaku line, servicing the upper area, faced problems of CSOs to the Takase River from four overflow chambers and localized flooding. The area serviced by the Karahashi line was plagued with problems of floods over the entire area. Improvement plans were drawn up to simultaneously alleviate the problems of both areas, and construction was started in 1986. Operation commenced in 1994.

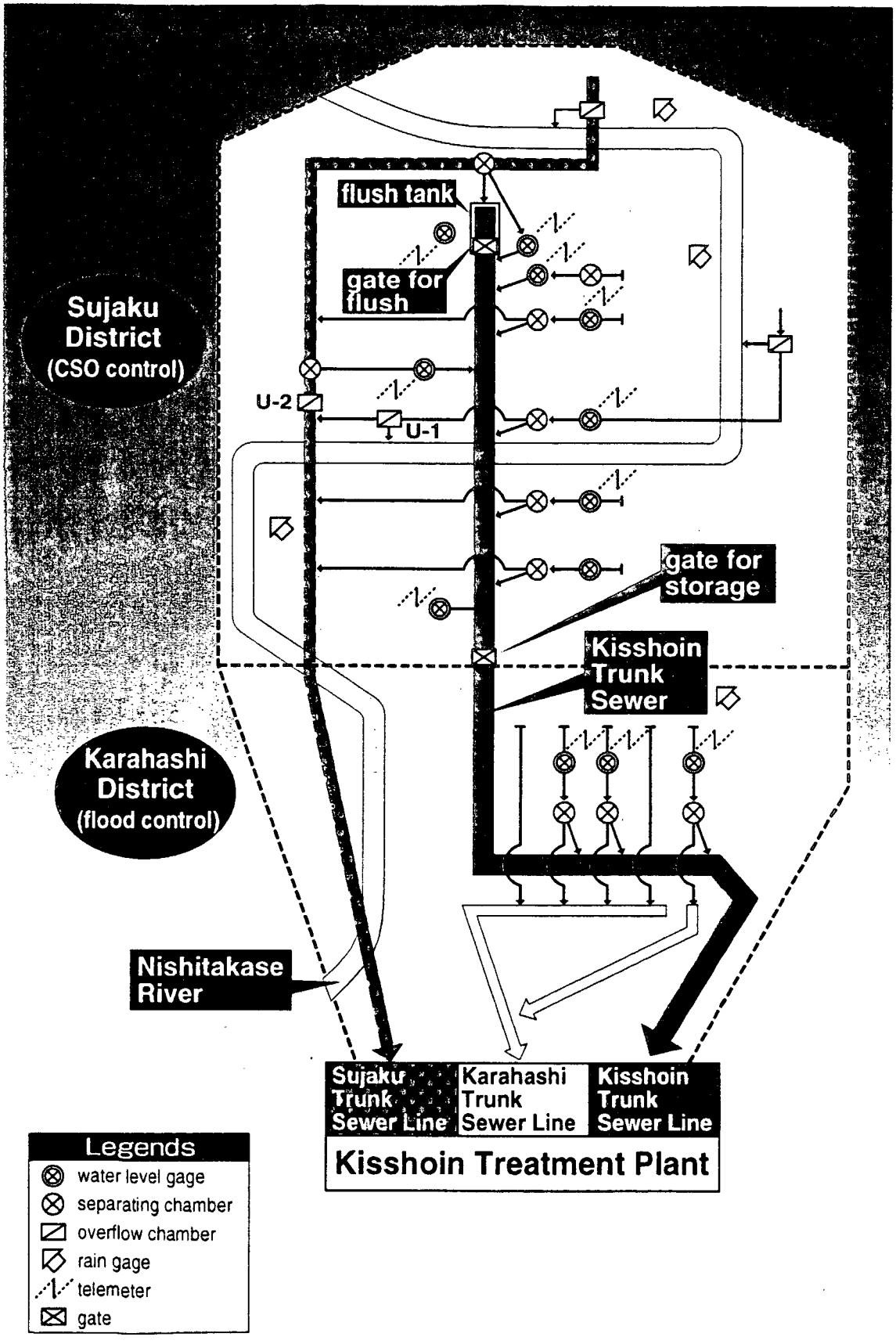


Figure 2 Improvement Planning for the Kisshoin Treatment District

Planned Facilities

Planned facilities are shown in Figure 2. A new trunk sewer (Kisshoin Trunk Sewer) was laid down the center portion of the treatment district. As shown in Figure 3, the trunk sewer was laid in an arrangement to make use of gravity flow to the wastewater treatment plant at the southern end of the district, and a gate for storage was placed in the center portion. The upper portion of the trunk sewer functions as storage, contributing mainly to CSO control for the Shujaku line during wet weather. In addition, the lower section of the trunk sewer functions as bypass pipe, and together with the pumping facilities in the wastewater treatment plant, serves as flood control for the Karahashi line.

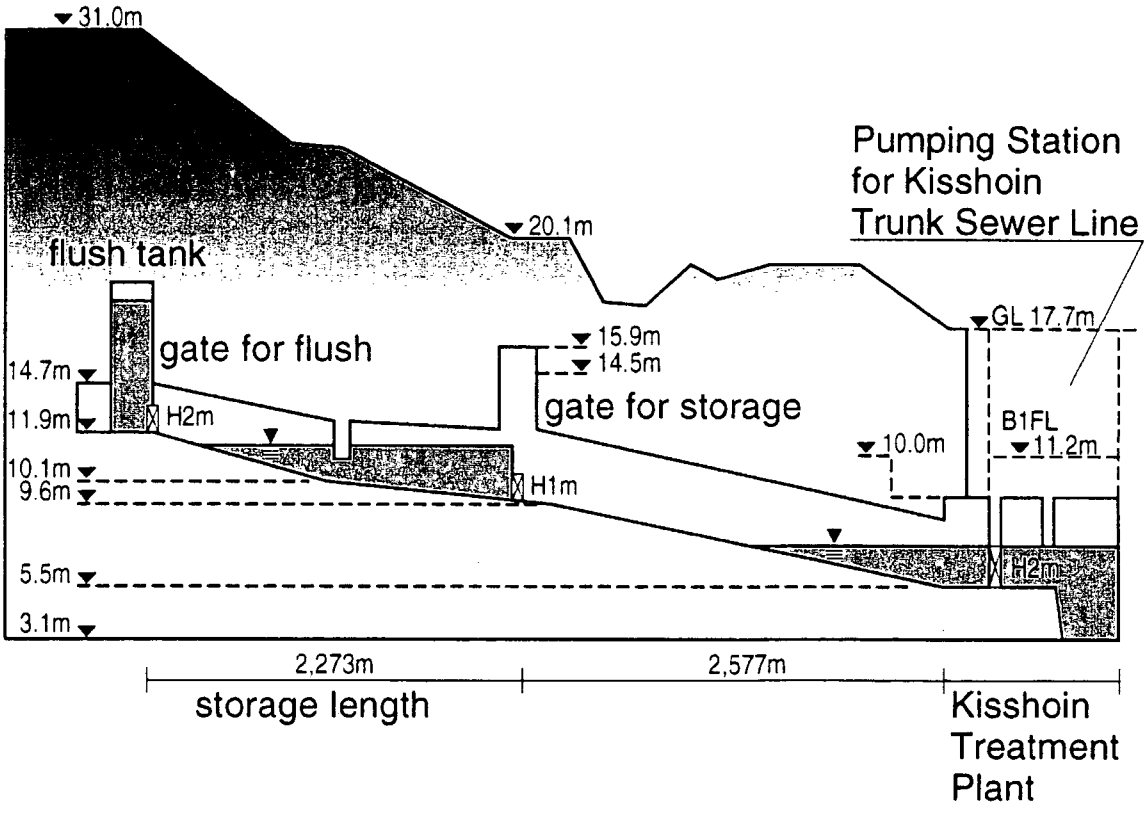


Figure 3 Longitudinal Section of the Kisshoin Trunk Sewer

The storage capacity used for CSO control is approximately 13,000 m^3. An area of 346 ha is covered for CSO control, and the trunk sewer can store approximately 5 mm of rainfall (for a runoff coefficient of 0.7). When the influent of rainwater exceeds the storage capacity, the system is designed so that the overflows spill over the gate and run down to the lower area. Three separating chambers for flood control have been installed in the lower flow area, and one in the upper flow area. When the rainwater rises above the levels of the fixed weirs, it overflows and is received by separating sewers. As shown in Figure 4, separating

chambers for CSO control are installed in six locations, consisting of a fixed weir and orifice.

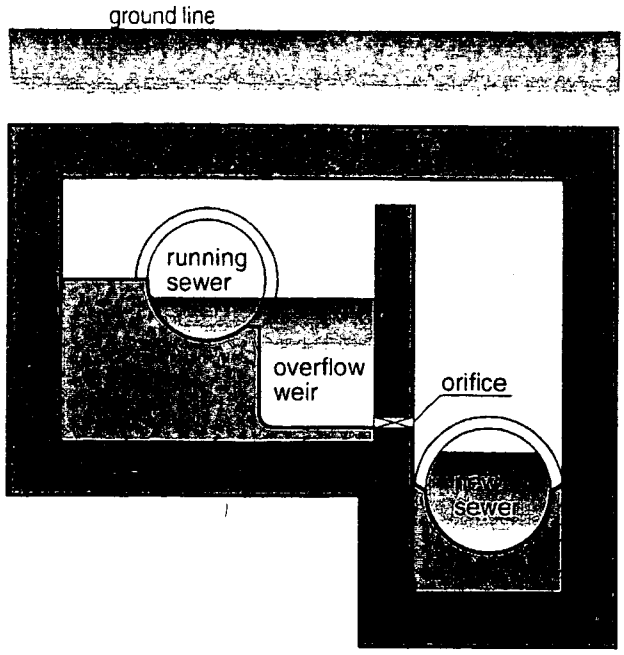


Figure 4 Structure of Separating Chamber

RESEARCH OF IMPROVEMENT EFFECTIVENESS

Summary and Purpose of Research

Research was commenced in 1996, and at present is still in progress. The purpose of the research is to evaluate the effectiveness of flood control and CSO control. Figure 5 shows a flow diagram of the research.

Research of flood control consists of carrying out simulations with actual rainfall to ascertain the application of a hydrodynamic model and set parameters. Model analysis will then be carried out with design storm water to evaluate the flood control effectiveness of the Kisshoin trunk sewer.

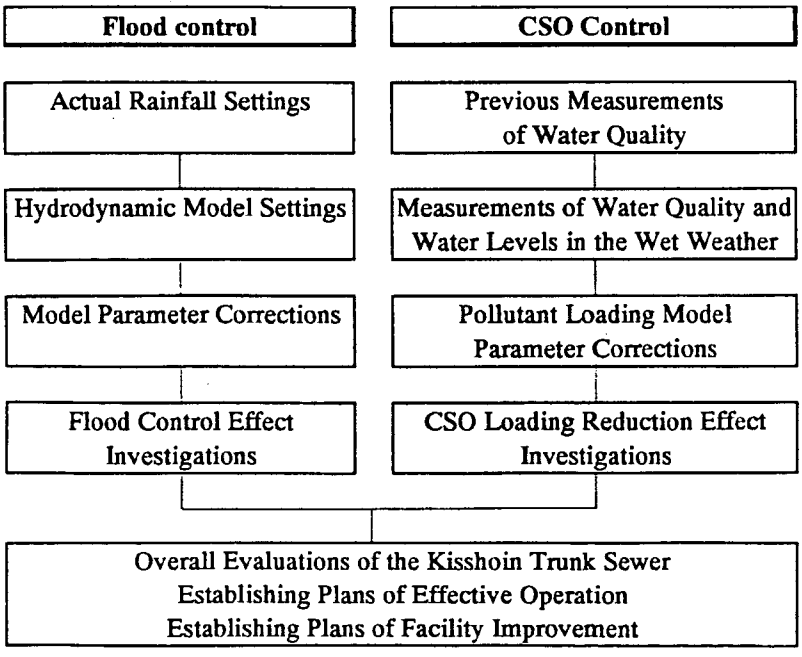


Figure 5 Flow Diagram of Research in the Kisshoin Treatment District

The research of CSO control consists of measuring changes in the quality of the wastewater in wet weather and the quality of the wastewater in the storage sewer. Afterward, pollutant load runoff model parameters are examined and set, based on the results of the water quality measurements. Evaluation of the pollutant load reduction effects for an annual representative rainfall will then be carried out.

Following is a report of one example of the results which were achieved in the water quality measurements carried out in wet weather, and in the examination of the pollutant loading reduction at the separating chambers.

Methods of Water Quality Measurements

Measurements were carried out in the sewers near the overflow chambers in two locations (indicated by U-1 and U-2 in Figure 2). Water quality samples were continuously collected during wet weather, and water quality analyses were made. These measurements were carried out seven times between June and October of 1997.

Automatic water samplers and rain gauges were placed at each sampling location. When a specified rainfall occurred (more than 1.5 mm per 30 minutes), the automatic water samplers were set to go into operation. Water quality samples were collected at 10 minute intervals for the first hour, after which they were collected at 30 minute intervals until 24 samples were obtained. Water quality analyses were made for SS, BOD, and COD. At the same time, water level gauges were placed inside the sewers at four points (before and after each water sampling location) to measure the changes of water level during wet weather.

Water quality measurements were also carried out on the wastewater stored in the Kisshoin trunk sewer. When the gates for storage were opened after rainfall had ended, samples of the stored wastewater were collected at 30 minute intervals at the Kisshoin Wastewater Treatment Plant, which is positioned at the lowest point of the Kisshoin trunk sewer. Water quality analyses were made for SS, BOD, and COD.

Results of Water Quality Measurements in Wet Weather

The rainfall conditions during measurements are shown in Table 2. Following is a report of one example of the results which were achieved using the measurement data (No. 2) taken from the U-2 overflow chamber on July 17, 1997.

Table 2 Rainfall Conditions for Research Period

No.	Date	Rainfall Time Period			Actual Raining Time	Total Rainfall Volume	Rainfall Intensity		Dry Weather Duration before Rainfall
							5min,max	1hour,max	
					min	mm	mm/5min	mm/hr	day
1	Jul. 7	11:40	~	11:50	10	4.0	2.00	4.00	4.9
2-①	Jul.17	3:40	~	(11:30)	170	7.5	0.50	2.50	3.6
2-②	Jul.17	(16:30)	~	19:10	160	13.0	0.75	7.00	-
3	Jul.26	3:40	~	20:50	820	40.5	1.00	7.00	8.3
4	Jul.27-28	17:20	~	7/28 18:50	810	34.0	1.00	6.25	0.3
5	Sep.16-17	23:50	~	9/17 6:00	370	67.5	2.80	22.00	8.7
6	Sep.23	5:25	~	10:00	160	3.5	0.30	1.50	6.0
7	Sep.25-26	17:30	~	9/26 9:20	880	76.0	1.50	14.50	2.3

(1) Rainfall conditions and changes in water quality

Figure 6 shows the rainfall conditions for July 17, 1977, the variations in water quality for SS, BOD, and COD, and the variations in water level inside the sewer pipes. Light rainfall started about 4:20 am at a rate of between 1–3 mm/hr, and continued to 8:20 am, when the rain temporarily stopped. At approximately

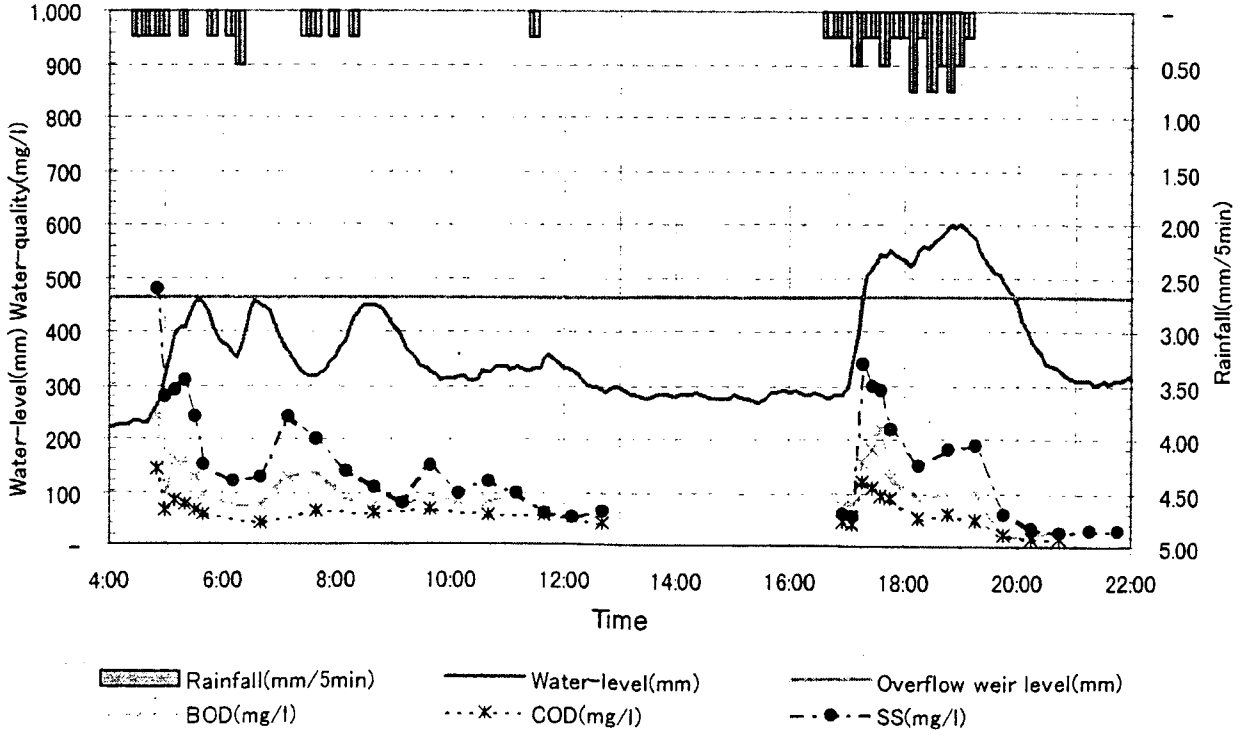


Figure 6 Time Series for Rainfall, Water-level and Water-quality (July 17,1997)

4:30 pm the rain began to fall once again at a rate of between 4–6 mm/hr, and continued until about 7:15 pm. The total rainfall was 7 mm in the morning, and 13 mm in the evening.

Variations in SS, BOD, and COD all showed the same tendencies, and the ratio of each concentration showed almost no change. Furthermore, the peak value for water quality concentration might not be obtained during the morning rainfall. Even so, when compared with the water quality concentration during dry weather, the water quality concentration at the early rainfall was 12–13 times higher for SS, approximately 4 times higher for BOD, and approximately 3 times higher for COD. Moreover, even though the data for the evening rainfall was taken only about 8 hours after the morning rainfall stopped, a peak was observed in the water quality concentration which is thought to be influenced by rainfall.

Furthermore, these changes in water quality are frequently supported by the results of other measurements. The same tendencies (first flush) can be observed in 7 cases out of 8 for

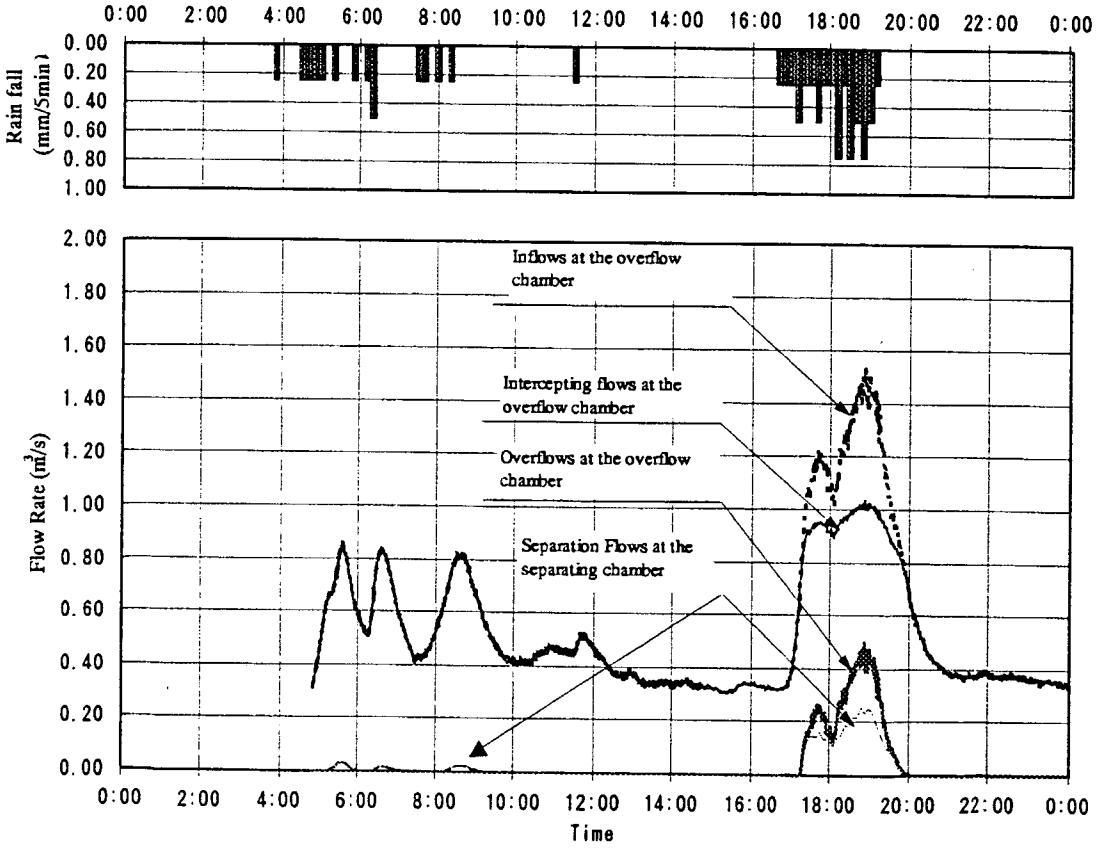


Figure 7 Time Series for Flow Rate of Separation and Overflow (July 17,1997)

the U-2 overflow chamber, and in 4 cases out of 6 for the U-1 overflow chamber. Compared with the water quality data during dry weather, the maximum data during wet weather were approximately 25 times higher for SS, 10 times higher for BOD, and 9 times higher for COD.

(2) Water separation and overflow conditions

Figure 7 shows the time series for the flow rate from the separating chambers and the overflow chambers for July 17. During the morning rainfall, wastewater was intercepted at the separating chambers for 170 minutes, but wastewater overflowed from the overflow chambers. During the evening rainfall, wastewater was intercepted for 180 minutes, and wastewater overflowed for 160 minutes. The overflow volume from the overflow chambers was 2,293 m^3, occurring only during the evening rainfall. The separation flow from the separating chambers was 125 m^3 for the morning rainfall, and 1,414 m^3 for the evening rainfall.

(3) Examination of pollutant loading reduction

Table 3 shows the results of CSO loading reduction from the overflow chambers, calculated from the water quality and water volume data described above. Since there was no overflow from the overflow chambers during the morning rainfall, the reduction ratio for SS, BOD, and COD were all 100%. The reduction ratio during the evening rainfall was 38% for all three values.

Table 3 CSO Loading Reduction (No.2)

No.			2-①	2-②	
Rainfall Conditions	Total Rainfall volume	mm	7.50	13.00	R
	Actual Raining Duration	min	170	160	T
	Average Rainfall Intensity	mm/hr	2.65	4.88	R/T×60
BOD	CSO Loadings	kg	0	246	A
	Separation Loadings	kg	12	153	B
	Total Loadings	kg	12	399	A+B
	CSO loading Reduction	%	100.0	38.3	B/(A+B)
COD	CSO Loadings	kg	0	143	A
	Separation Loadings	kg	7	89	B
	Total Loadings	kg	7	232	A+B
	CSO loading Reduction	%	100.0	38.4	B/(A+B)
SS	CSO Loadings	kg	0	430	A
	Separation Loadings	kg	19	265	B
	Total Loadings	kg	19	695	A+B
	CSO loading Reduction	%	100.0	38.1	B/(A+B)

Calculating the CSO loading reduction from other measurement data, the pollutant load reduction ratio from the overflow chambers

was between approximately 25–70% for SS, BOD, and COD. These changes in the values were caused by the characteristics of the rainfall, but it can be assumed that CSOs can almost be prevented during periods of light rainfall.

CONCLUSIONS

In this report, a summary of the sewage works in Kyoto City was first provided, and the present conditions of combined sewer improvements were explained. Next, an example of the results of measurements carried out on water quality during wet weather used to evaluate the effectiveness of combined sewer improvements in the Kisshoin Treatment District was also reported.

Kyoto City has plans to continue working on combined sewer improvement operations as one of its most important projects. In the areas where improvement operations have already commenced, these works are industriously being carried out. The development of improvement plans and the commencement of construction and operations in other areas is also an important goal of the city.

Overall evaluation of the Kisshoin trunk sewer will be carried out continuously, based on the results of the measurements described in this report. We will achieve more effective improvements in both facilities and operating methods.

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New Strategies for Combined Sewer Overflow

Dipl.Ing. Paul Schaad, Abwasserverband Obere Iller, Sonthofen/Bavarian

1.1. General remarks

Through the research project **02WA09374**, supported by the Federal Ministry of Education, Science, Research and Technology, the decentralised storm water basins of the canal network are managed by means of rainfall run-off prognosis and optimisation modules. Through run-off control and canal network management

- **the water load in mixed water discharge is minimised**
- **the intake to the sewage treatment plant is evened out**
- **the basin volume as well as the investment costs are reduced**
- **the running costs are reduced through remote control technology and process control engineering**

The cost saving amounts to approx. 30 - 35 % of the planned investment costs.

1.2. Rainfall prognosis

1.2.1 Introduction

A rainfall run-off simulation based on the continuously accumulating rainfall and water level measurement data of the network in the operation phase **is to result in a projection of the expected operating state of the network.**
For this purpose, by rain weather **the distribution as well as the intensity of the rainfall** in the whole Authority area **must be measured and transmitted to the central station.**Suitable for this purpose are **pluviographs or a radar rainfall measuring device.** The radar rainfall measuring device records the spatial **distribution as well as the rainfall intensity on a surface with a side length of 125 x 125 m.**
In order to increase the reliability of real time canal management, the inflow load of the canal network in the event of rainfall is to be projected with the help of an online prognosis model. **A hydrodynamic simulation usually cannot, despite the higher level of exactness, meet the specific requirements of the online application in respect to computer time, storage, numerical stability, and data transfer.** Therefore simplified models should be attempted to be used.
Simplified models for canal calculation have long been used in Germany, particularly for the verification of basin dimensioning. This verification takes place with the help of hydrological simulation following a relatively set pattern. The choice of the calculation program as well as the estimation of the corresponding model parameters are set a priori by the respective state regulations. When model difficulties arise because of a particular local network configuration, a solution is worked out in co-operation with the water authority. The latter tests the validity of the simulation results

before the measures are taken over. The relation to the real drainage system is thereby of a secondary nature.
Such a procedure is not acceptable for online projection models. The output of the online simulation must be compared with **real data** before implementation. **All requirements of the optimisation module for the determination of the control strategy must be fulfilled; otherwise the danger arises that an incorrect inflow projection destroys the calculations of the control optimisation.**
So that model adjustment is possible, the following requirements must be met:

- **digital, detailed description of the drainage system**
- **digital measurement data (rain intensity, water levels in the storage units, run-off rates)**
- **possibility for numerical simulation with various models, at least one of which is a hydrodynamic model**

1.2.2. Formulation of the model segments

Online projection models must simulate at least the following processes:

- **run-off formation**
- **concentration and**
- **carriage**

Suitable mathematical descriptions have long existed. Within the context of our examination, various model segments were chosen and programmed as seen in the following overview:

- **The run-off formation considers moisture loss, infiltration loss and trough loss. The infiltration losses are calculated using the equations of HORTON or NEUMANN.**
- **The run-off concentration is calculated either on the basis of the linear concept model formation (storage analogue) or with the help of non-linear physical models on the basis of the Manning-Stickler-equation for surface run-off (compare ATV A 110, 1998).**
- **The run-off carriage in the canal can also be explicitly taken into account. In terms of model techniques, it is a simple hydraulic model on the basis of the resistance equation of PRANDTL-COLEBROOK or Manning-Stickler. Pressure run-off and backwater can also be logged.**
- **Storage facilities are described by characteristic curves as exact as desired.**

In programming, particular attention was paid to the following points:

- **Conversion of the model equations**
- **Description of the surface and the canal**
- **Control of the program sequence**
- **Control of the output**

In addition to the formulation of the model segments, the ongoing project work for the drainage area of the Obere Iller Wastewater Authority included the following tasks:

- **Description of the drainage system**
- **Design of the hydrological model**
- **Simplification of the canal description**
- **Choice of the model segments for rainfall coverage, the calculation of rain loss for the run-off concentration and carriage**

1.2.3 Model definition and adjustment

To date, surface run-off has not been taken into consideration. Most of the programs in Germany (Smusi, Kosim, Hystem, Dyna) use the linear storage cascade for the simulation of this process.
Just a few programs (among others, SWMM) favour using a non-linear physical model formation. **The structure of the area surface can hardly be reconstructed in respect to flow paths (high complexity).**
In off-line applications, the model parameters are usually calculated with the help of rough estimates, or, in the best case, with statistical regression.
The latter combines the parameter in question with more or less randomly chosen area characteristics (e.g., surface, slope). Their use may not be extrapolated outside of the equalizing area (mainly small areas < 1 ha). **Following the simplification principles presented above, it was decided to expand the standard model for run-off concentration (the linear storage cascade) to include the carriage.**

1.2.4 Conclusion and further developments

For both storm water basins in Sontofen, RÜB 1 and RÜB 2, the simplified model formation, after calibration, can supply a very high degree of realistic results.

This assumes that the activated storage capacity as well as the carriage behaviour is correctly estimated.
When the storage behaviour is also to be considered, the assumption of the constant flow restriction must be substantiated through measurement data or hydrodynamic calculations. Such results can be transferred to drainage systems which show a similar tree-type structure. Further testing is required for networks with another topology, e.g., for linear drainage systems (carriage conduits).
An investigation presently being made on the application of such models to the various main collectors in the area of the Authority shows the hydrodynamic effect to be apparently stronger.

○Research has thus concentrated on the following areas:

○The formulation of non-linear model concepts for flow description and of the corresponding calibration algorithms.

The latest studies show that non-linear concept models can be much better adjusted to hydrodynamic events than linear models. A further advantage of such models is that the area of validity extends to low load levels. This could, for example, improve the hydrological carriage calculation, which is critically influenced by sedimentation processes during dry weather. A considerable impediment to the wide-spread use of non-linear models lies in the physical interpretation of the model parameters and, accordingly, their assessment. Therefore calibration models which are based on non-linear mathematical optimization are necessary here.

The development/adjustment of (numerically stable) hydraulic models. The one emphasis concentrates on the description of the network and the other concentrates on the model formulation. The attempt is being made, for one thing, to develop programs for the automatic management of canal data with the goal of a system description which optimally corresponds to the chosen model segments. For example, the question of how exact the network description should be for the hydrodynamic calculation needs to be answered.

A main interest of model formulation is the development of alternative calculation schemes for the solution of the differential equation systems, particularly the SAINT-VENANT equation system.

○The automatic calibration of the detailed hydrodynamic model formation based on the measurement data with a control-based system.

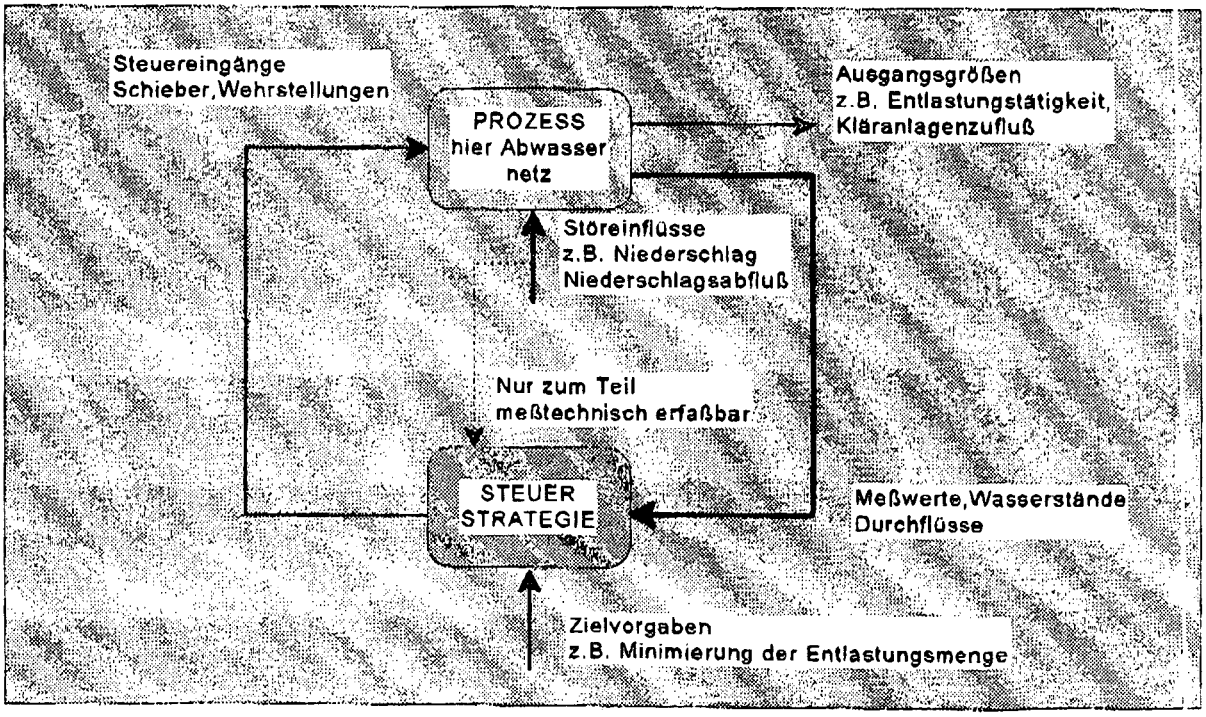
1.3 Authority control algorithms with real time optimization

1.3.1 Introduction

An important segment within the Authority control system is the strategy, i.e. **the program which calculates the control decisions on the basis of the measurement information available from the network at the time.** In this application area there have been up to the present time no generally suitable realisation concepts. First the **real time optimization program**, which was developed within the context of the BMBF project and used on the network of the Obere Iller Wastewater Authority makes such a tool available. Picture 1 shows the control circuit which results in such a canal network control system. **This control circuit is unique in that it has to do with a multi-sized control task and, that the goal is not the maintenance of a particular set value, but rather the minimisation of particular negative results, e.g. the minimisation of the rainfall discharge.**

For reasons of transparency in design and operation, for the limitation of the effects of partial system failure and for the minimisation of communication and calculation needs it is sensible to attempt a hierarchical structure and decentralisation of the control system. Smaller, interconnected network sub-systems, e.g. complete storm water units or backup canals can be equipped with a local control system. The local control system strategy takes over the task of regulating the control instruments in its area based on the local measurement values so that, e.g. the storage unit is limited to a certain discharge level.

The central control system is able to view the sub-systems in a simplified manner. The provision of a limited number of set values replaces the direct regulation of the control instruments in the network. The essential data which is needed on the central level from the sub-system is:



- **The current stored volume**
- **The current run-off from the sub-systems**
- **Inflow with the help of the rainfall run-off model with inflow projection**
- **The current measurement values of discharge**
- **Status signals for operation monitoring**

1.3.2 Choice of the realisation approach

Basically, the following well-known approaches can be considered for the realisation of an Authority control system strategy:

- **Control strategy on the basis of real time optimization procedures**
- **Linear multi-sized regulators**
- **Systematic control-based procedures (fuzzy control, experts systems, decision matrixes)**
- **Decision regulations (heuristics) suitable for free programming**

Every conceivable realisation must, of course, take the particular network givens (network topology, number, size and position of the storm water units, control system possibilities, etc.) into account.

Both of the first two approaches revert to a mathematical (or hydrodynamic) network model for this. **The design of the control system strategy follows in a systematic, computer aided and easily generalised form.**

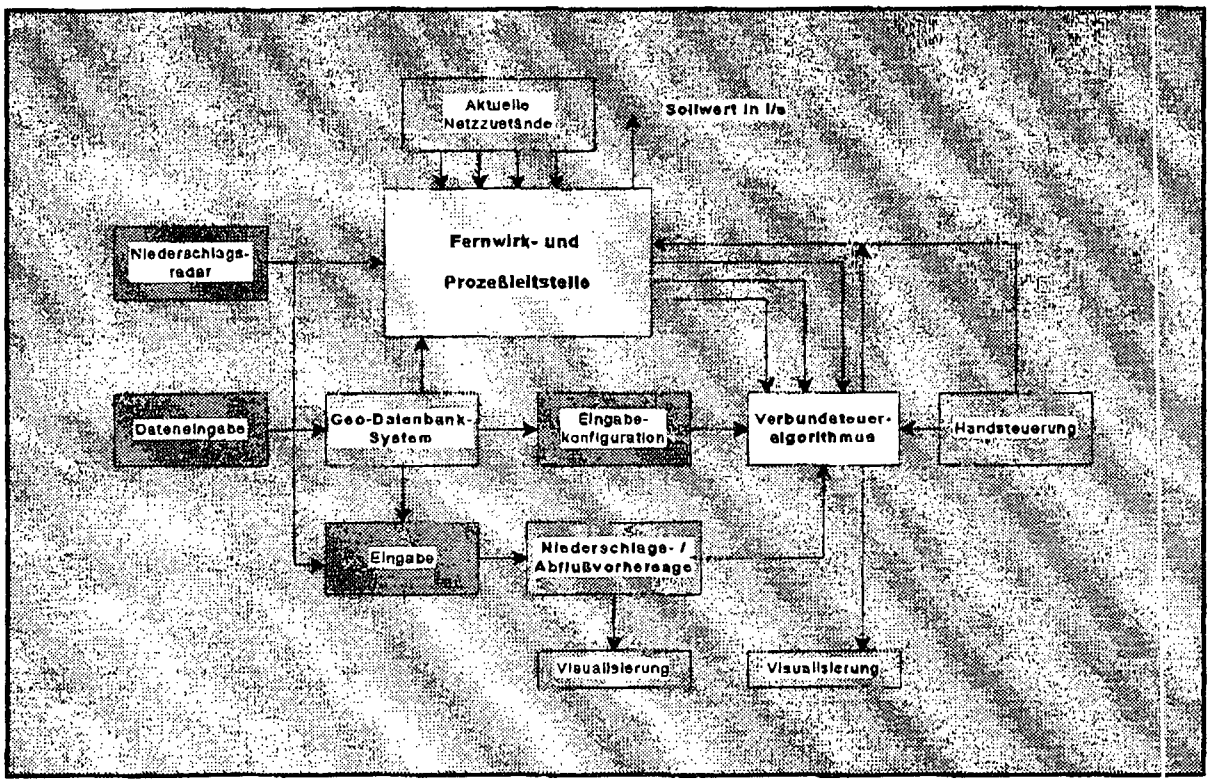
In control based procedures as well as in free programming, suitable decision making regulations and appropriate parameters must be found. This is, finally, always a matter of the developer's intuition. In complex networks and/or with later extensions, this type of procedure quickly reaches its limits. A systematic utilisation of the maximally possible control potential is not guaranteed, which does not, admittedly, eliminate the possibility that practically, through constant improvement and extension of the control base, and with the corresponding expenditure of energy, a satisfactory operation can be attained.

Control strategies on the basis of real time optimization exhibit high effectiveness (individual treatment of each single load event), flexibility in respect to the modification of single sub-system goals and their order of priorities, the possibility of expansion in the case of later connection of further network sub-systems and a general suitability for transfer to different network structures. With the proper program technique design, a real

time optimization can react to short-notice changes in the network situation, e.g. the failure of individual control instruments. It is thereby possible to take all conceivable failure situations into account.

1.3.3 Practical applications in the Obere Iller Wastewater Authority

Picture 2 shows schematically the core network in which a first application of the Authority control strategy described above has already been accomplished. It is now planned that the application will be successively extended to further network sub-systems of the Obere Iller Wastewater Authority.



When completed, the final stage will include approx. 30 storage units (storm water basins and backup canals). A step-wise preparation of all requirements such as calibrated N-A-models, verified measurement values and verified network descriptions is necessary.

Based on the current data, such as **water level in the canal network, storm water basin, discharge from the individual basins (instantaneous discharge in the body of water as well as discharge to the sewage treatment plant) inflow to the sewage treatment plant, as well as data from the rainfall run-off model, a simulation of the network processes with a corresponding optimization algorithm results.**

1.4. Result:

In all, **40 storm water basins were planned** at a **total cost volume amounting to approx. DM 53m.** Through the reduction of the basin volume and the reduction of the total number of storm water basins, a total cost of **DM 39m** is expected. A comparison of the investment costs for non-controlled basins and an Authority control system shows an investment costs savings in the amount of approx. **DM 10.8m.** In addition, the planned Ostrach collector brings a savings in the amount of DM 3.5 m, so that **the total savings pays off at DM 14.3m .**

1.5 Operation costs:

Non-controlled, non-electronically monitored system mechanisms cause operation costs to the amount of **approx. DM 445,000.** If, on the other hand, system mechanisms such as storm water basins, pumps, etc. are electronically monitored, the running operation costs for personnel and/or telephone fees amount to approx. DM 57,000. Storm water basins which are electronically controlled and monitored as well as the various pumps and measurement stations result in operation costs to the amount of DM 56,000.

1.6 What can be reached through a centralized Authority control system:

* **Reduction of overflow frequency, overflow amount and overflow time in the body of water**
* **Reduction of contaminant entry in the body of water**
* **Exploitation of back-up space**
* **Maximal mixed water treatment in the Authority sewage treatment plants**
* **Reduction of the investment costs through decreasing basin volume**
* **Reduction of running operation costs**

1.7 Rainfall treatment in the future:

The above research project is given a very high priority by the Federal Ministry of Research. **According to a statement by the Federal Ministry of Research, this project makes an important contribution to rainfall management and treatment, which to a particular degree is of considerable importance to the new federal states.** Approval of the project for the development of a centralized control system for the management of regional storm water units and storm water basins was given by the Federal Ministry of Research and Technology in a letter of 27.7.1993. The costs falling under grant applications amount to **DM 6,370,900.00.** The grant rate is 50%

so that the Obere Iller Wastewater Authority bears the amount of **DM 3,185,450.00**. In the letter of 27.7.1993, Dr. Paul Krüger, the Federal Minister of Research and Technology, characterized the research project as **innovative and directive for the enlargement of drainage systems. According to a conservative estimate by Prof. Dr. Ing. Göttle in 1993, future rainfall treatment in the Federal Republic will require investments of approx. DM 15b. Assuming that through a run-off control system and detailed data calculation approx. 35-40 % of the investment costs can be saved, the savings in the Federal Republic, despite increased expenditures, amount to approx. DM 5b. In Bavaria, a savings to the amount of approx. DM 1.8b can be expected.**

MEASURES AGAINST COMBINED SEWER OVERFLOW (CSO) IN OSAKA CITY

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ABSTRUCT

A greater part of Osaka City has developed on low lands, where storm water is not drained naturally. Accordingly, efficient wastewater treatment and flood control are necessary in the City. To this end, Osaka City has developed a combined sewer system, which is more economical than a separate system.

In a combined sewer system, if the total volume of stormwater exceeds a certain limit, untreated stormwater is discharged into public water bodies. In such a case, sediment in sewers is also discharged, posing a difficult problem in water quality consecration.

Various methods have been used to purged CSO. The system cannot be improved via a single method; rather, it is necessary and effective to implement comprehensive measures, employing several methods to suit the characteristics of a particular drainage area.

Major measures for improving CSO include:

1.leading as great a volume of pollutants as possible to sewage treatment plants in dry weather, to avoid the pollutant accumulation in sewers:

2.storing first flush, which contains a large volume of pollutants, for treatment at sewage treatment plants after rainfall: and

3.treating wet weather savage directly.

Osaka City plans to employ various methods for these measures. A task related to measure 1 is the renewal of superannuated sewers: this task is important because in Osaka, where sewer system development began early, a large portion of sewers is superannuated of have inappropriate gradients. To remedy this situation, Osaka City will renew these sewers, based on the comprehensive examination of degree of sewer superannuation, the necessity of flood control, and the effect of sewer renewal for CSO. Methods used for measure 2 include temporary storage of stormwater in reservoirs; and temporary storage of stormwater in large scale floodways. Methods employed for measure 3 include sedimentation using a settling tank for stormwater treatment; removal of refuse via a fine-mesh screen; and treatment of a large volume of stormwater in wet weather via the activated sludge process.

Since the implementation of measures to improve the combined sewer system is enormously costly, Osaka City seeks to achieve such improvement economically, by effectively combining the above mentioned methods. This report discusses these methods.

KEYWORDS

Combined sewer overflow control, Storage Facility, Reduction effect of pollutant load

INTRODUCTION

Osaka City, located midpoint in the Japanese Archipelago, is the central city in western Japan. It has about 2.5 million permanent residents (Fig. 1), with another 1 million people coming in from outside the City during the day.

With its center located on low-lying land, including the delta at the lower reaches of the Yodo River, Osaka has always had problems of drainage. During construction in the 16th century, streets were arranged according to a plan and ditches were dug behind buildings to drain rain and wastewater. Advanced industrialization and subsequent population increase in the 19th century brought on the need for more efficient rain and wastewater drainage, for hygienic reasons. Accordingly, since the end of the 19th century, Osaka City has developed its sewerage system by using the drainage ditches built in the 16th century, constructing sewers of brick and employing other methods. Due to these circumstances, Osaka City has developed its sewerage mainly by adopting combined sewers. Wastewater treatment commenced in the 20th century, when the problem of river contamination, caused by released wastewater, became con-spicuous. Today, nearly the entire city area is served by the sewerage system. With the activated sludge process implemented at all of the City's 12 wastewater treatment plants, water quality in rivers in Osaka City has improved considerably.

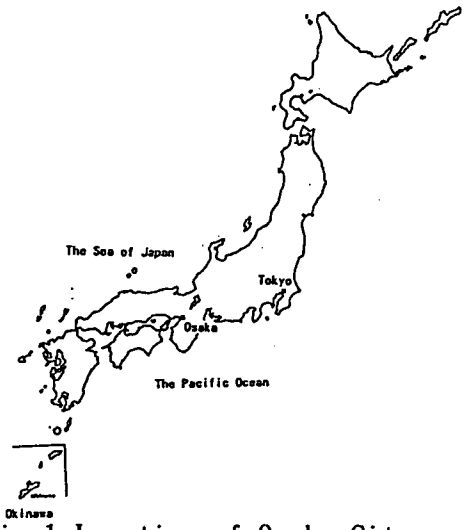


Fig. 1 Location of Osaka City

The combined sewer system, widely adopted in Osaka City, is structured in such a way that stormwater inflow exceeding a certain amount is discharged directly into public water bodies without treatment. It is believed that stormwater thus released carries with it pollutants accumulated in sewer pipes, seriously affecting the water quality in public water areas such as rivers and Osaka Bay.

Furthermore, Osaka Bay, into which Osaka City's wastewater is released, is of typical semi-closed form, with annually recurrence of red tides. Even today, despite the City's completely developed sewerage system, no sign of improvement can be seen in this regard. Red tides are believed to occur due to excessive nitrogen and phosphorus in the sea water; to dissolve red tides it is essential to reduce these substances.

Therefore, Osaka City has decided to reduce wet weather pollutant load discharge into public water bodies, and introduce an advanced wastewater treatment method capable of high-level removal of nitrogen and phosphorus.

To improve the water quality in public water bodies, Osaka City is carrying out its sewerage service with two primary objectives: the promotion of advanced wastewater treatment and CSO countermeasures. This paper introduces the CSO countermeasures and their effects.

SEWERAGE IN OSAKA CITY

In Osaka City, modern sewerage development projects commenced in 1894. In 1940, Osaka commenced the operation of wastewater treatment plants. After World War II, more wastewater treatment plants and sewers were constructed to accommodate the City's population increase accompanying urbanization. Nevertheless, drastic increases in population and industrial output resulted in water quality deterioration in rivers and so forth. At the same time, the excessive underground water pumping that accompanied industrial development resulted in ground subsidence throughout the City, the ground level subsiding by over 2 meters in some seriously affected districts. Consequently, the ground level in some districts went below sea level, thereby deterring drainage of stormwater by gravity in a large portion of the City. Against this background, Osaka City set out to develop drainage facilities, giving priority to laying sewers and building pumping stations to ensure effective stormwater drainage and improving the local environment. Today, as a result, almost the entire area of Osaka City is served by the sewerage system. Still, drastic urbanization, leading to the disappearance of farmland and natural reservoirs, resulted in increased stormwater outflow, some districts flooding even with precipitation below the design level. As a basic solution to this problem, large trunk sewers and pumping stations are currently under construction, to drain stormwater in excess of the existing facilities' drainage capacity.

Pumping stations are designed in such a way as to send sewage, at up to three times the maximum hourly volume of wastewater (3 Qsh), to a treatment plant, and to discharge stormwater above that level directly into the environment, after sand sedimentation and screening. At wastewater treatment plants in wet weather, sewage three times the maximum hourly volume of wastewater (3 Qsh) is subjected to sedimentation, followed by discharge of 2 Qsh and entry of 1 Qsh into an aeration tank. Wastewater treatment plants are also designed to release stormwater exceeding 3 Qsh directly into rivers. Fig. 2 illustrates this flow.

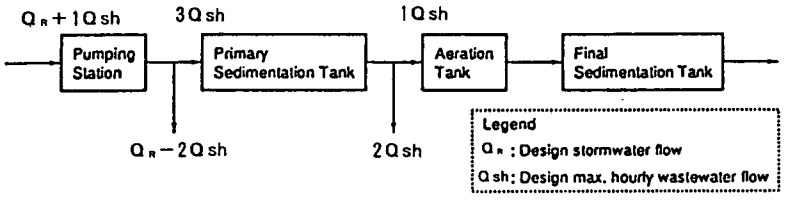


Fig. 2 Conventional Wet Weather Sewage Treatment

IMPROVEMENT MEASURES

Various methods have been used to upgrade CSO. The system cannot be improved via a single method; rather, it is necessary and effective to implement comprehensive measures, employing several methods to suit the characteristics of a particular drainage area.

Major measures for improving CSO include:

① leading as great a volume of pollutants as possible to sewage treatment plants in dry weather, to avoid the pollutant accumulation in sewers;

② storing first flush, which contains a large volume of pollutants, for treatment at sewage treatment plants after rainfall; and

③ treating wet-weather sewage directly.

Osaka City is implementing CSO countermeasures by efficiently combining the above improvement measures. The goal of these measures is to reduce the annual discharged pollutant load (comprising dry and wet weather loads) to a level equal to or lower than that of a separate sewer system. Fig. 3 details these measures.

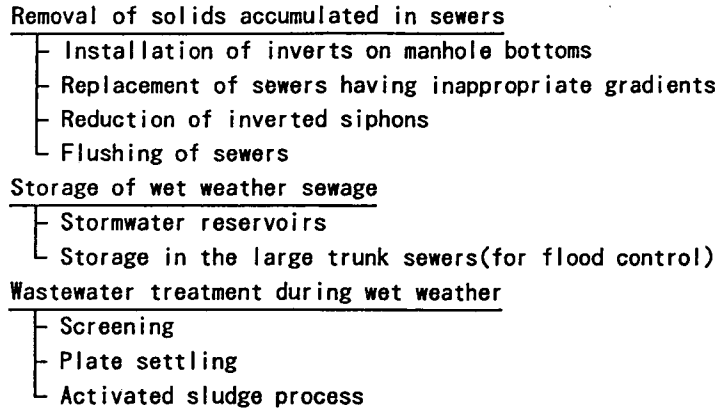


Fig. 3 Measures to Improve the Combined Sewer System in Osaka City

1) Improvement of sewer structure

A major part of Osaka City's area is located on a soft alluvial ground. Accordingly, some of the sewer pipes in the City do not have appropriate gradients. This situation has been aggravated by the influence of land subsidence, which has resulted from the use of groundwater from about 1950 to about 1970 (Osaka's industry expanded rapidly during these years). To facilitate sewer cleaning, pits are provided on manhole bottoms. Partly due to the pits, however, pollutants tend to accumulate in sewers. As a measure related to pollutant source, sewers are being improved to drain pollutants in the sewers without causing pollutant accumulation to sewage treatment plants in dry weather. There are a total of some 140,000 manhole bottom pits, which will be completely filled with concrete in the next five years. Inappropriate gradients will be corrected, partly through sewer reconstruction, starting with sewers where pollutants accumulate in large quantities.

2) Storage of wet weather wastewater

Sewage resulting from early-stage precipitation with a high pollutant concentration is stored temporarily and sent to a treatment plant for activated sludge treatment. Osaka City seeks to store a total of about 1 million m^3 of stormwater, so that about 5 mm of precipitation can be contained using two types of facilities, that is stormwater reservoirs and large trunk sewers for flood control.[1)]

At present, stormwater reservoirs are under construction at two sites. As the areas of sewage treatment plants are limited, the reservoirs are fully utilized by installing rapid sand filtration equipment on the upper part, or by constructing the reservoir in the space below facilities other than the sewage facilities. Fig. 4 illustrates one example of such efficient space use.

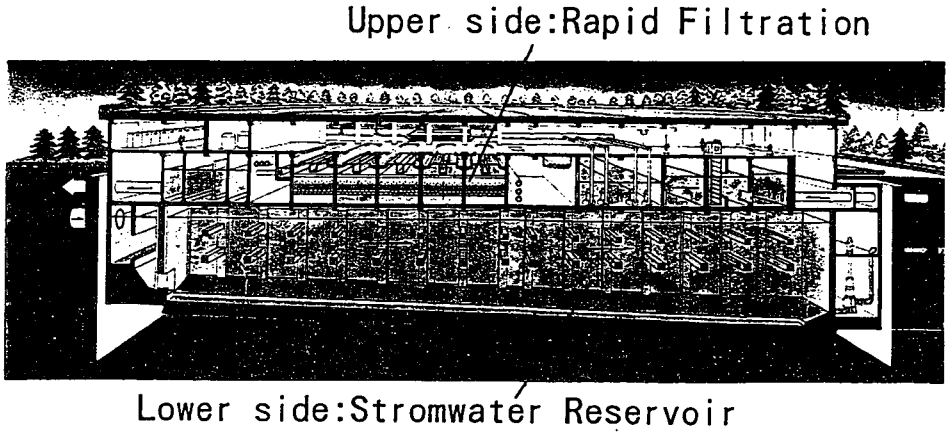


Fig. 4 Wet Weather Sawage Reservoir and Rapid Filtration

For flood control, Osaka City has large trunk sewers and pumping stations for stormwater under construction and some of them are in operation. These sewers are not only large in scale but are situated at great depth and designed for only in wet weather, with stormwater flowing in from conventional sewers. Figs. 5 and 6 show example sketches of the Naniwa Grand Floodway. In wet weather, these facilities will be used exclusively for stormwater removal, to prevent flooding; however, in a small-scale rainfall, stormwater will not be discharged but stored and sent to the wastewater treatment plant to reduce discharged pollutant load. To do this, pumping stations at the lower reaches of trunk sewers are equipped with large-diameter pumps for discharging stormwater, as well as small-diameter pumps for sending stored stormwater to the treatment plant. In trunk sewers, to remove pollutant solids that settle during storage, water feed pipes are laid inside inverts installed, as shown in Fig. 7, for maintenance and management, stored water being carried from lower to upper reaches via these pipes to flush the pipes.

Since large trunk sewers are installed for flood control, wet weather sewage storage using these sewers must be carried out in such a way as not to adversely affect their flood control effectiveness. In the future, therefore, a system will be adopted to enable the storage of as much wet weather sewage as possible, by estimating the amount of stormwater flowing into trunk sewers, using an existing radar precipitation prediction system.

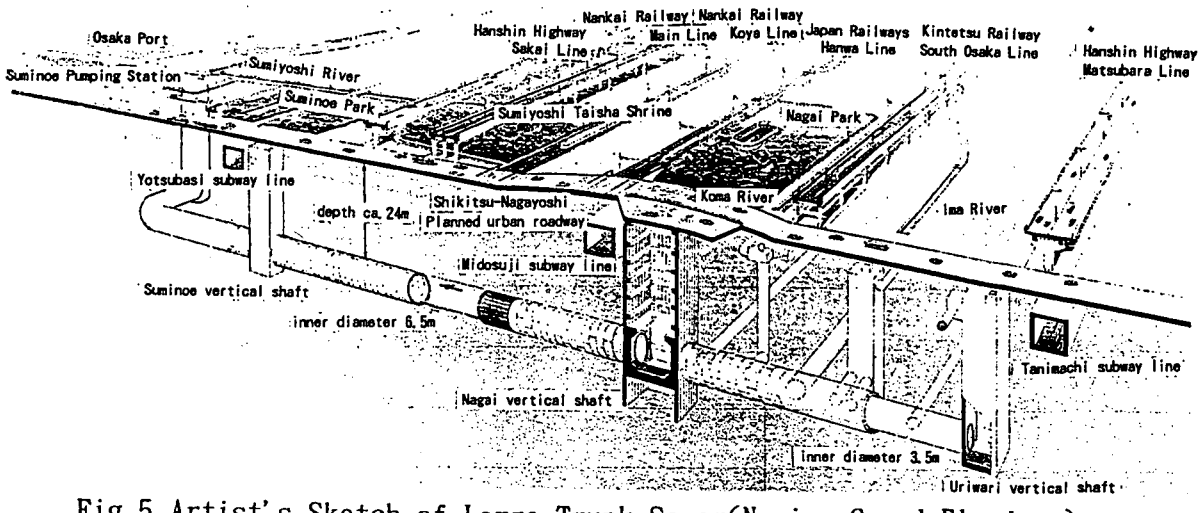


Fig. 5 Artist's Sketch of Large Trunk Sewer(Naniwa Grand Floodway)

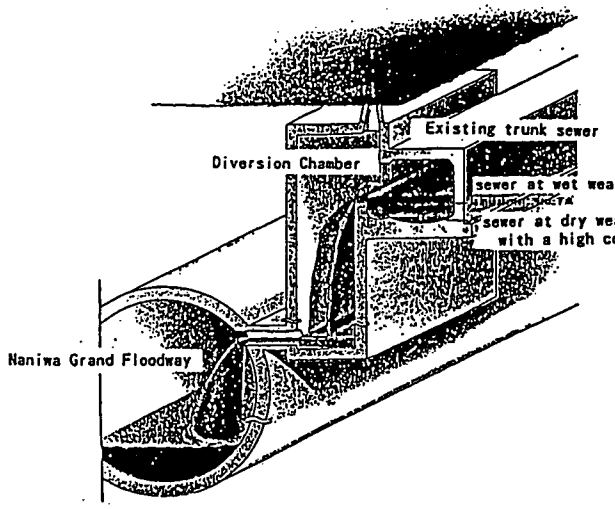


Fig. 6 Storage in Large Trunk Sewer

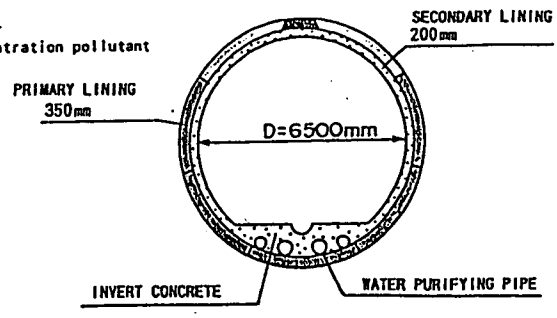


Fig. 7 Cross Section of Large Trunk Sewer

3) Wastewater treatment in wet weather

In Osaka, as mentioned earlier, pollutants easily accumulate in sewers in dry weather, due to inappropriate pipe gradients and pits in manhole bottoms. Accordingly, pollutant load increases sharply in the early phase of stormwater runoff, and decreases only gradually over a long period of time. This pollutant runoff pattern therefore does not present a general first flush. It is thought that in view of this pattern, continual treatment will prove effective in treating stormwater. Osaka City is developing a treatment method based on this view.

Osaka City's wastewater treatment facilities are located on limited premises, which are difficult to expand as the surrounding areas are already fully urbanized. Accordingly, studies have been conducted on methods of treating as much wet weather sewage as possible in this limited area.

Among such methods is the activated sludge process of a large volume of wet weather sewage, called the Wet Weather Activated Sludge Method (WWASM). In Osaka City, wastewater is treated via the activated sludge process. Treatment facilities in the City are designed for operation via both the conventional activated sludge process and the stepped aeration process.

Ordinarily, treatment facilities are operated using the conventional activated sludge process. In the event of rainfall involving an inflow of more than 1 Qsh, primary effluent is subjected to adsorption by leading a portion of the wastewater into chamber 4 at the end of the aeration tank (AT) shown in Fig. 8.

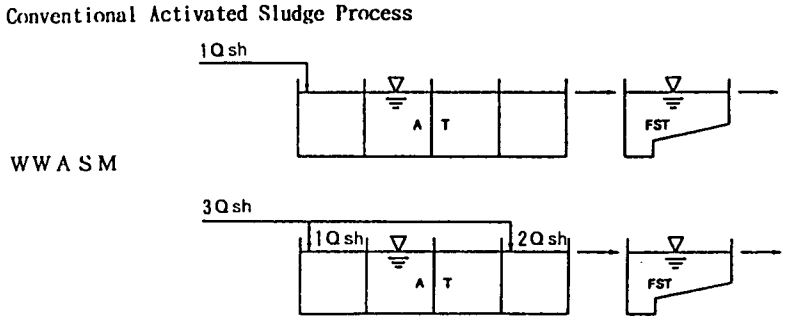


Fig. 8 Procedure for WWASM

In AT chamber 4, operated via the conventional activated sludge process, suspended and colloidal solids in primary effluent are coagulated and adsorbed. If F/M ratio is relatively low, dissolved organic matter is also adsorbed quickly by activated sludge and thus removed. Normally, wet weather influent concentration is lower than that of dry weather influent, except during the period immediately after the onset of rainfall. It is presumed, therefore, that wet weather sewage can be treated without significantly increasing the biological treatment load from the normal level.

As for solid-liquid separation in the final sedimentation tank (FST), the inflow of a large volume of primary effluent into AT chamber 1 may cause the transfer of a large volume of activated sludge in the AT into the FST, hence a rapid increase in solids load in the FST, which as a result, may become overloaded, causing a rise in FST sludge surface and the leakage of activated sludge. If a portion of primary effluent is led into AT chamber 4, however, only a portion of sludge in chamber 4 is transferred into the FST, permitting stable solid-liquid separation without significantly increasing solids load.

The MLSS concentration of influent into the FST, as well as the ratio of solids load in wet weather to that in dry weather, were estimated for the WWASM under the conditions shown in Table 1. Fig. 9 shows the time-related change of these factors. MLSS concentration becomes mostly constant 50 to 60 minutes after separate inflow. MLSS concentration in the steady state is calculated as follows: $1,500 \times (1 + 0.3) / (3 + 0.3) = 590$ g/m^3. Solids ratio instantaneously reaches a level of 2.0. At 50 to 60 minutes after separate inflow, however, the ratio decreases to a level of 1.0. This suggests that solids load in the WWASM is not significantly larger than that in dry weather.

Table 1 Conditions for Calculation

1. Initial factors
① MLSS: 1,500 g/m^3
② MLSS at chamber 4 equal to influent FST concentration
③ HRT at AT for 1 Qsh inflow: 5 hrs
④ Return ratio (for 1 Qsh): 30%
⑤ Constant return sludge concentration
⑥ MLSS increase (caused by influent) ignored
2. Variable factor
① Time required for increasing inflow into chamber 4 from 0 to 2 Qsh (min) T = 10, 20, 30 (min)

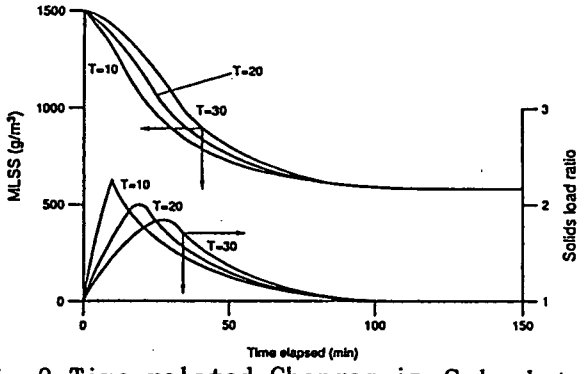


Fig. 9 Time-related Changes in Calculated MLSS and Solids Load Ratio

However, overflow rate (OFR) in FST, at 84 m^3/m^2·day(3.5 m^3/m^2·hour),is approximately 3 times that in normal dry weather at an inflow of 3 Qsh. (Osaka City's design OFR in FST in dry weather for 1 Qsh is 28 m^3/m^2·day.) For satisfactory solid-liquid separation, it is essential to ensure that the initial MLSS settling velocity must be higher than the OFR. In other words, the present treatment method proves effective if activated sludge SVI is relatively low.
The WWASM uses the biosorption process to remove dissolved organic matter; and the step aeration process to ensure uniformity of biological load in the AT and to keep solids load in the FST at a constant level.

Between 1992 and 1994, Osaka City conducted studies on the WWASM for 3 Qsh, involving experiments using actual facilities. The studies yielded satisfactory results: the treated water quality was roughly equal to, or only slightly inferior to, that in dry weather.[2)]

The WWASM can be introduced through minor modifications of existing facilities, e.g. the use of electrically operated step gates. Accordingly, the method will be introduced to all sewage treatment plants in Osaka, with the goal of treating 3 Qsh of sewage in wet weather.

As for other facilities for wet weather sewage treatment, Osaka City is constructing plate settlers, as well as fine meshed screens for removing debris in wastewater.[3] As shown in Fig. 10, a plate settler consists of inclined plates, aligned at intervals of 5-to 10 cm along the wastewater flow. The settler increases wastewater surface area, and enhance settlement efficiency by ensuring a smooth flow, facilitating the scaling-down of facilities. Treatment of stormwater by this method at an average flow velocity of 0.5-0.6 m/s, with a detention time of 10 minutes, is believed to remove over 50% of suspended solids (SS).

As shown in Fig. 11, the screening method involves letting stormwater pass through a fine (4 - 6 mm) meshed screen to remove debris in sewage, and is capable of removing about two-thirds of the debris contained in wastewater.[4] It can be used in a pre-treatment facility leading to a plate settler, and even improve the scenery in the water area into which the stormwater is released. These physical methods are introduced into wastewater treatment facilities where major restrictions are imposed with regard to discharged water quality for such reasons as fishing in water areas into which treated water is released.

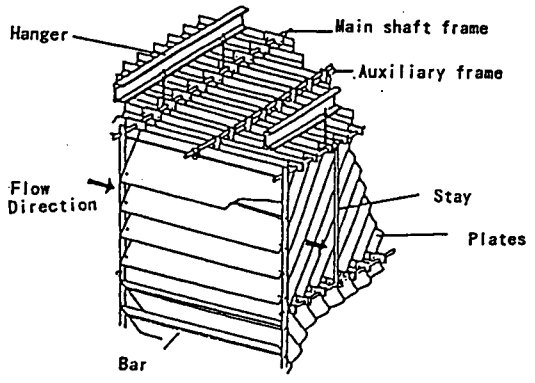


Fig. 10 Construction of Plate Settler

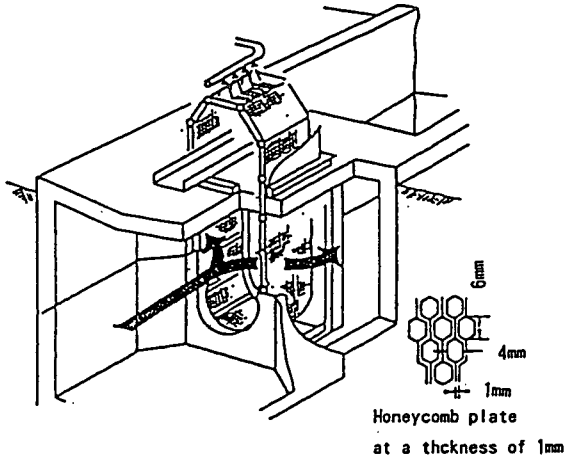


Fig. 11 Fine-mesh Screen Equipment

EFFECTIVENESS OF IMPROVEMENT MEASURES

To gauge the effectiveness of the improvement measures mentioned above, a simulation was carried out in a treatment service area of about 3,000 ha for all cases of precipitation in Osaka City in a year. For analysis, a stormwater runoff model (prepared via the modified RRL method)[5] and a pollutant load runoff model (prepared by the Institute of Civil Engineering, the Ministry of Construction)[5] were used; removal load was calculated by combining them. Figs. 12 and 13 indicate the model construction and the basin model of the treatment service area, respectively. Table 2 indicates set values showing pollutant load reductions achieved by different treatment methods. Improvement measures examined were stormwater storage in large trunk sewers, the WWASM for 3 Qsh of sewage in wet weather, and use of a stormwater reservoir. In this service area, large trunk sewers for stormwater are almost complete. The storage capacity of the sewers, which can be used for CSO countermeasures, totals about 180,000 m^3; in determining the value, care was taken to ensure safety against flood. A stormwater reservoir (capacity: 40,000 m^3) is currently under construction on the premises of a wastewater treatment plant. Table 3 shows annual flow rate allocation ratios for each wet weather treatment level, regarding different improvement methods devised through simulation.

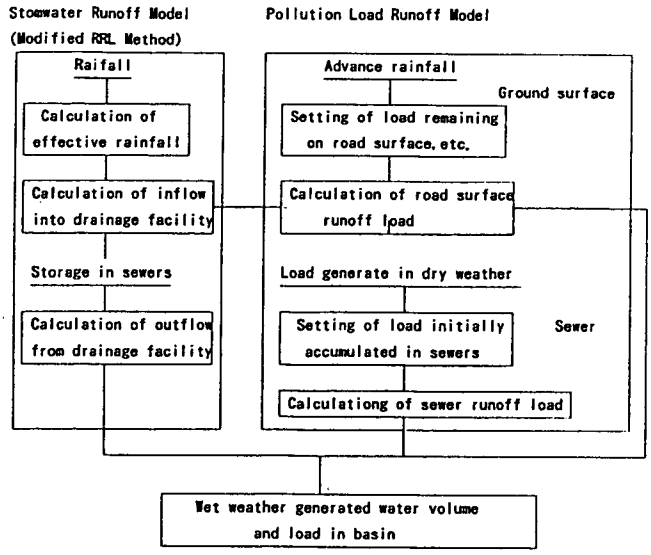


Fig. 12 Analysis Model Construction

Table. 2 Model Setting

Removal Model Setting: Settling Treatment Model

Water Quality		
Items	Inflow(mg/l)	Wet Weather
B O D	above95	BODout=7.21×BODin$^{0.881}$
	below95	BODout=BODin
S S	above43	SSout=43×(SSin/43)$^{1.94/OFR+1.5}$
	below43	SSout=SSin

OFR:Overflow Rate Inflow quality=Inflow quality at treatment plant

Removal Model Setting: Activated Sludge Treatment Model(1Qsh treatment)

Water Quality		Dry Weather	Wet Weather	
Items	Inflow(mg/l)	Effluence(mg/l)	Removal-rate(%) Effluence(mg/l)	upper limit
B O D	above56		90%	20
	5.6-56	5.6	5.6	(Technical
	below5.6		0%	standerds)
S S	above7	7.0	7.0	
	below7		0%	

Inflow=Settling Treated water quality

Removal Model Setting: Activated Sludge Treatment Model(3Qsh treatment)

Water Quality		Wet Weather	
Items	Inflow(mg/l)	Removal-rate(%) Effluence(mg/l)	upper limit
B O D	above37	85.0%	20
	5.6-37	5.6	(Technical
	below5.6	0%	standerds)
S S	above14.	14.0	
	below14	0%	

Inflow=Settling Treated water quality

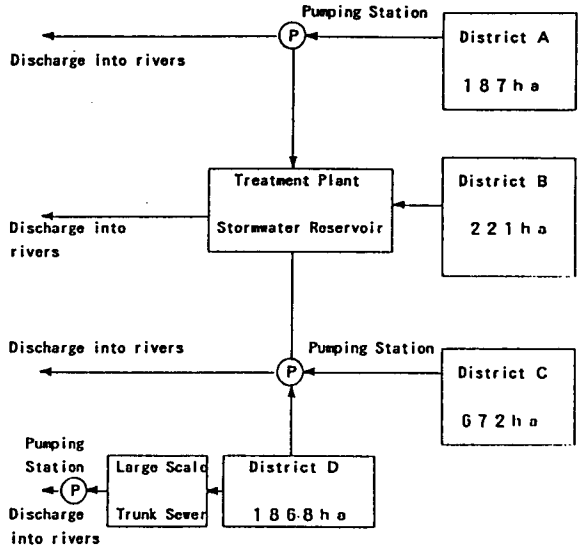


Fig. 13 Basin Model of the Treatment Service Area

Table-3 Volume Ratio in each Wet Weather Treatment
—Results of Simulation for a Model Treatment District—

	CSO Countermeasure	Present	stage 1 Storage in Large Trunk Sewer	stage 2 WWASM for 3Qsh	stage 3 Storage in Stormwater Reservoir
Volume Ratio (%)	Direct Discharge	36.6	28.0	28.0	27.1
	Settling Treatment	27.0	25.8	0.0	0.0
	A.S.T. Total	36.4	46.2	72.0	72.9
	A.S.T.	36.4	36.4	62.2	58.3
	A.S.T. (Stored Water)	0.0	9.8	9.8	14.6

A.S.T. : Treatment by Activated Sludge Process

85 rainfalls occurred in the object year. The total volume of sewage flowing into the sewer system in wet weather was 34 million m^3/year.

On the second stage, the WWASM for $3Q_{sh}$ can increase the volume of activated sludge treatment to about 62% of sewage in wet weather, compare to 36% in stage 1. On the third stage, the storage of wastewater from early stage precipitation in special reservoirs or large trunk sewers enables the activated sludge treatment of about 15% of wet weather sewage after a rainfall. In consequence, about 73% of the annual volume of sewage in wet weather can be treated by the activated sludge process.

Fig. 14, 15 show the effects of the above improvement measures in reducing the annual total discharged load, comprising dry- and wet-weather loads. On the second stage, implementing of

the WWASM can reduce both BOD and SS loads by about 400t/year. On the third stage, BOD load can be reduced by about 650t/year and SS by 950t/year, that is about 40% reduction in both BOD and SS. If the measures of stage 1 to 3 are implemented thoroughly in the object treatment district, the total annual discharged loads can be reduced to a level roughly equal to that of a separate sewer system.

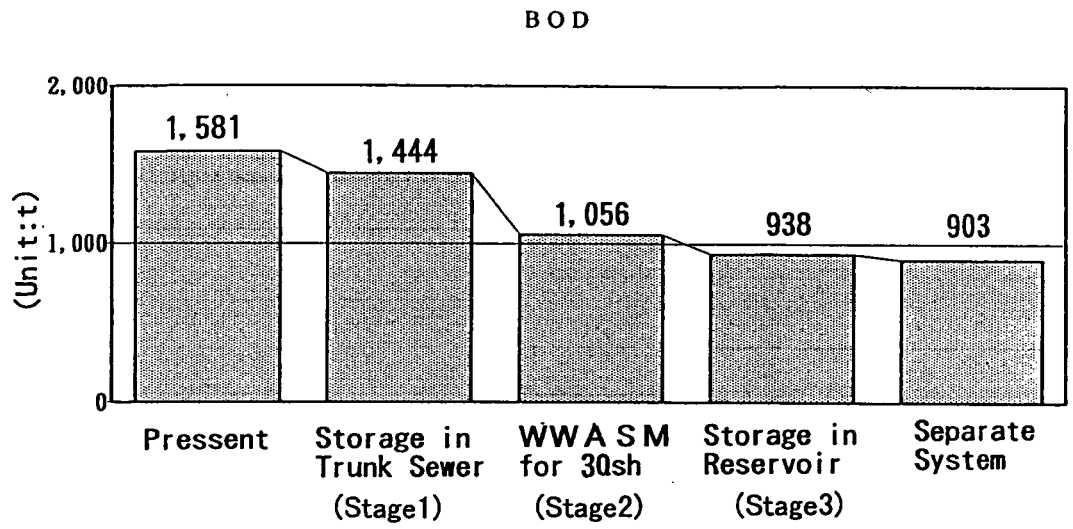


Fig. 14 Annual Total Discharge Load(BOD)

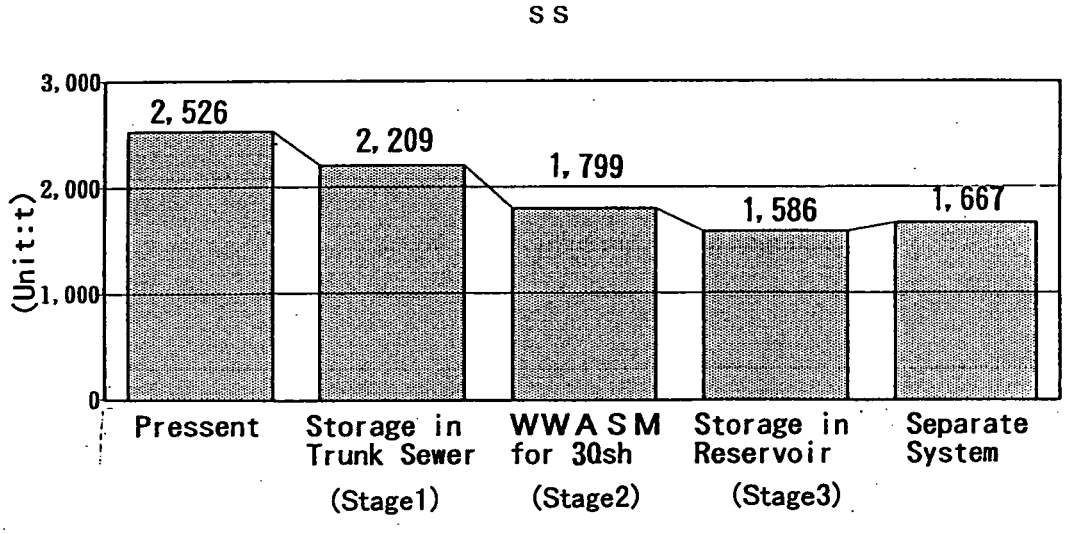


Fig. 15 Annual Total Discharge Load(SS)

CONCLUSION

Over the past 100 years, Osaka City has developed its public combined sewerage system, which now serves almost 100% of the City's population. However, the pollution load of sewer discharge in wet weather has reached such significant quantities that measures must be taken immediately. Therefore, as basic improvement strategies for Osaka City's combined sewer systems, measures are being implemented that mainly involve

① Reduction in solid pollutants accumulated in sewers
② Sewage storage in wet weather
③ Sewage treatment in dry weather

As a result of studies on the effects of the above improvement measures in a treatment district, it is thought that these measures will yield such positive results as

- In terms of wet weather sewage volume, the WWASM, implemented with the storage of initial precipitation, allows the discharge of about 70% of wet weather sewage after it is treated by the activated sludge process.
- Once Osaka City's basic measures have been completed, the pollutant load discharged from sewers in a year will be reduced by about 40% in terms of both BOD and SS, as compared to current levels.
- The total discharged load can be reduced to a level equal to that of a separate sewer system by these measures.

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Session 9

Disinfection and THM Precursors

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Recent Development of Disinfection Technologies in Japan

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ABSTRACT

Chlorine dosage should be 2 to 4 mg/l for secondary effluent with retention time of 15 minutes. Regarding the photoreactivation coliform removal efficiency should be more than 99.9% for UV radiation. As for ozone disinfection COD removal and color removal is expected. Official evaluation had opened in March,1997. These system will be adopted widely in Japan.

KEYWORD
Disinfection, UV, Ultraviolet, Ozonation, Chlorination, Japan, Wastewater, Pilot Plant, Coliform, Survival, Photoreactivation

INTRODUCTION

The primary role of municipal wastewater treatment plants is the sanitation of sewage and the history of sewerage construction is closely related to the prevalence of an infectious disease. The occurrence of an infectious disease is decreasing in recent years, but the primary role of the municipal wastewater treatment plants is still very important.

The effluent standards for the coliform number is set to be equal to or less than 3,000 /ml in Japan to keep the public water body safe. To meet the effluent coliform number standard, chlorination is the most frequently used method of disinfection, but ultraviolet (UV) radiation and ozonation are the promising alternatives due to the potential health and safety concerns.

Japan Sewage Works Agency have evaluated these disinfection methods for the future implementation. This report covers the recent development of disinfection technologies in Japan.

PILOT PLANT TEST

Pilot plant

Pilot plants, shown in Figure 1, were set up in the test and evaluation facility of Japan Sewage Works Agency (Research & Technology Development Division, Toda City) and the disinfection tests were carried out. The specification of each plant is shown in Table 1. The pilot plants capability are 36 m^3/day for ozonation and 100 m^3/day for chlorination and UV radiation, respectively.

Experimental method

The influent used for the disinfection tests was the secondary effluent of the neighboring municipal wastewater treatment plant owned by the Saitama Prefectural Government. The disinfection tests were carried out changing the disinfectant infection rate and the reaction time for the chlorination test and the ozonation test. The UV test was carried out changing the radiation volume (luminous intensity x reaction time). The filtration method with m-ENDO culture medium was used for coliform counting.

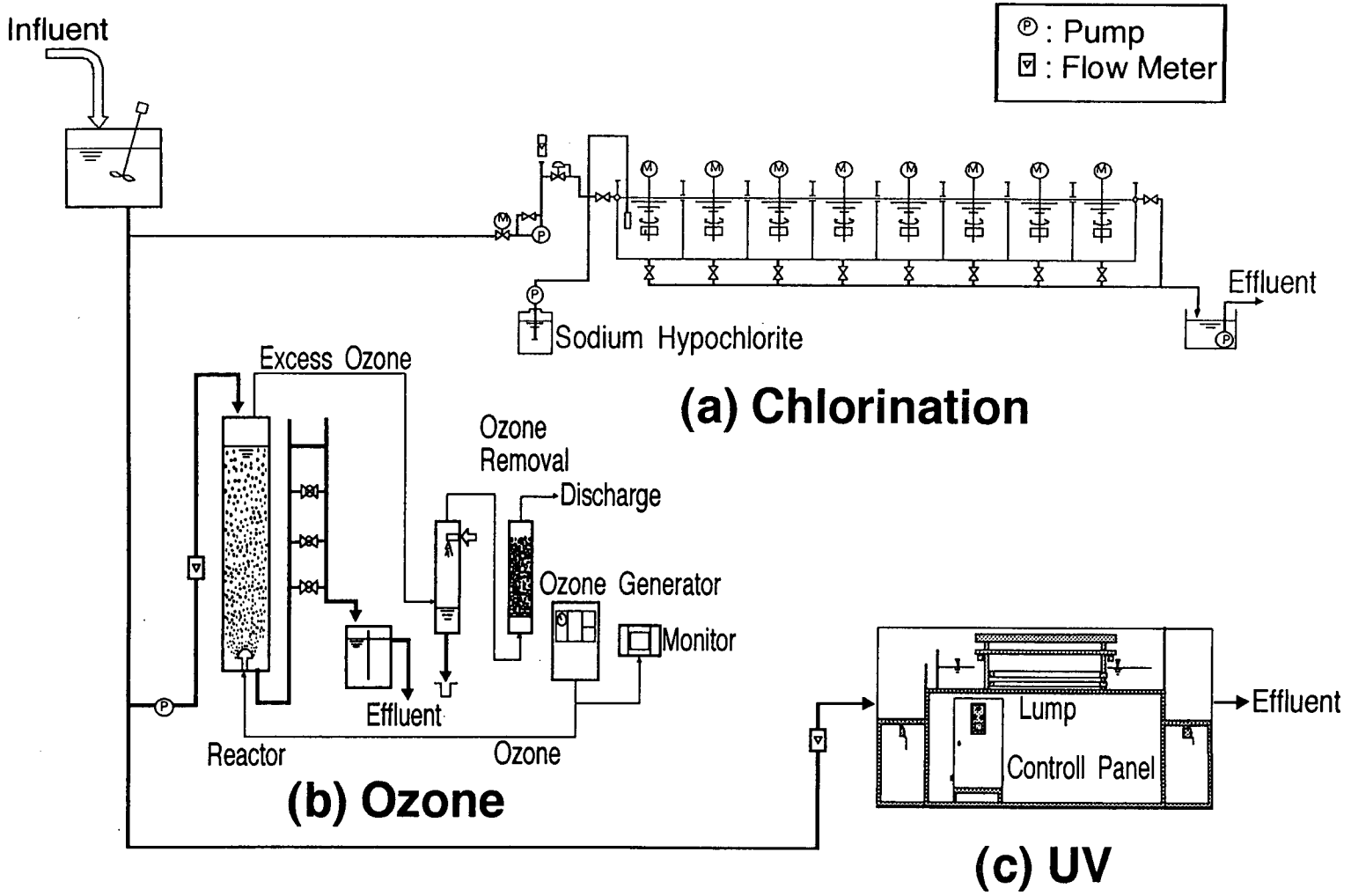


Figure 1 Schematic of Pilot plant

Table 1 Specification of Pilot Plant

Plant	Item	Spec
Chlorination	Capacity	100m^3/d of influent
	Chemical	Sodium hypochlorite
	Reactor	W:500,L:500,:H650mm,8chamber
Ozone	Capacity	36m^3/d of influent
	Raw Material	Oxygen from PSA
	Generating Ozone	25g O_3/h
	Reactor	D:250,H:4000mm,Counter flow
UV	Capacity	100m^3/d of influent
	Reactor	W:65,L:1865,H:130mm
	Lamp Length	760mm
	Number of Lamp	2(Low pressure mercury type)
	Electric Power	0.1kW

CHROLINE DISINFECTION

Historically, the disinfection of effluent from the municipal wastewater treatment plants had been conducted using chlorine gas as a disinfectant. The sodium hypochlorite solution has been mostly used for large and medium sized plants and the solid type chlorine compound has been used for small sized plants in Japan.

Table 2 shows the technical standards for secondary effluent from the public owned municipal wastewater treatment plants. The coliform number must be equal to or less than 3,000 no./ml.

Table 2 Technical Standard for Secondary Effluent

Item / Classification	pH	BOD (mg/l)	SS (mg/l)	Coliform (No./ml)
Secondary Effluent(High)	5.8~8.6	20 or less	70 or less	3000 or less

The reason that sodium hypochlorite solution is largely adopted in Japan is the comparative safety and easiness of controlling the injection volume. The reason that the solid type chlorine compound is commonly used in the small sized plants is the easy operation and maintenance.

Figure 2 shows the status of coliform number in influent, secondary effluent and final

effluent (after chlorination) of municipal wastewater treatment plants all over Japan. The coliform numbers in secondary effluent are less than 3,000/ml for 80 % of plants. The coliform number of final effluent is perfectly less than 3,000/ml for all the plants due to disinfection. Therefore, Figure 2 verifies that the plants performance are fairly well in terms of disinfection in Japan.

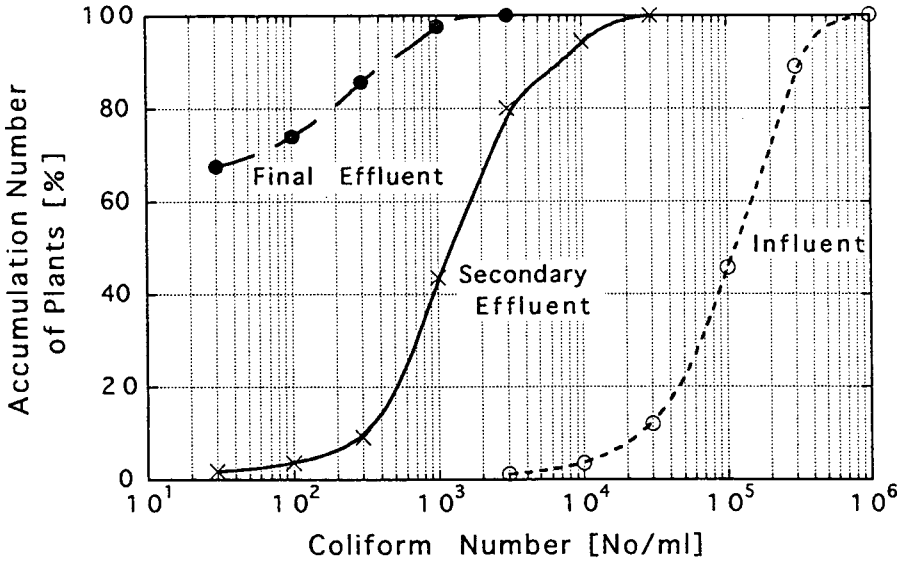


Figure 2 Coliform Number in Japan

Figure 3 shows the test results of chlorination for various types of effluent; primary effluent, secondary effluent, sand filtrate and secondary effluent with excess sludge.

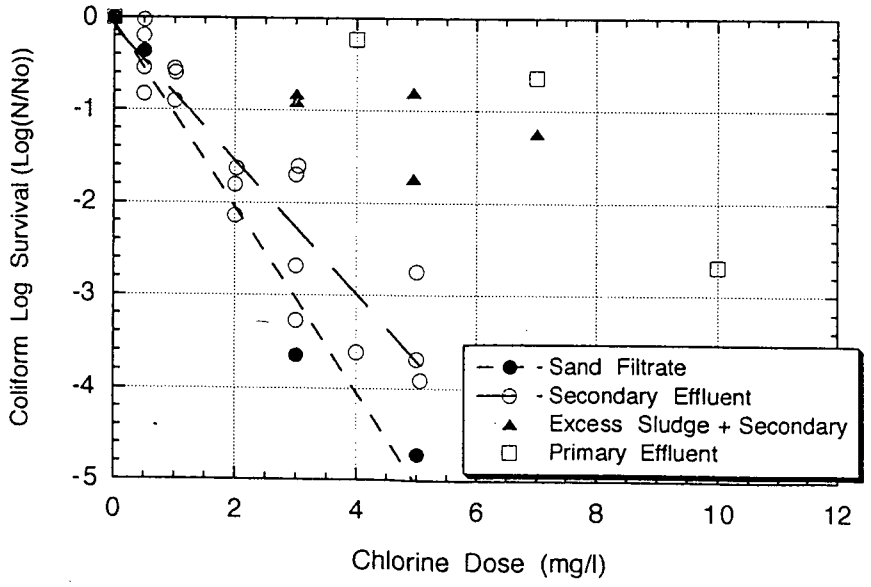


Figure 3 Chlorine Dosage and Coliform Survival

From the test results, the relationship between coliform survival and chlorine dosage, chlorination reveals a fairly high effect on secondary effluent and sand filtrate. Chlorination efficiency becomes worse if the plant effluent quality gets worse. Therefore, biological treatment performance should be controlled better so as to reduce the chlorine dosage.

These results, shown in Figure 2 and 3, suggest that 2 to 4 mg/L chlorine dosage with 15 min. retention time may be required for secondary effluent disinfection.

Figure 4 shows the relationship between Ct value (mg - min/L) and coliform survival for secondary effluent with low nitrification, where effluent average ammonium concentration is 4.9 mg/L (ranging from 0.1 to 13.7). Ct value, N and No in Figure 4 are defined as the followings.

Ct = (residual chlorine concentration) x (contact time)
N : secondary effluent coliform number after chlorination (no./ml)
No : secondary effluent coliform number before chlorination (no./ml)

Figure 4 reveals that the efficiency of chlorination for secondary effluent with moderate nitrification could be predicted by the Ct value.

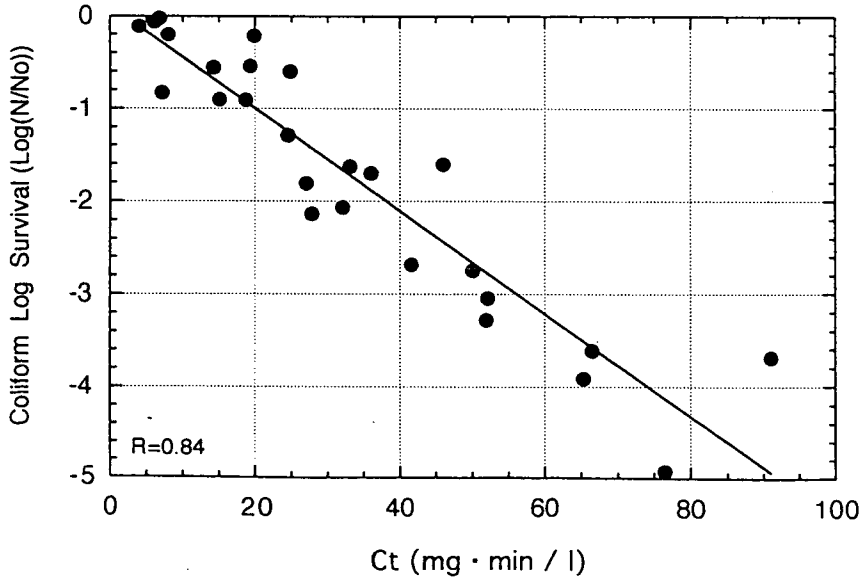


Figure 4 Ct and Coliform Survival

ULTRAVIOLET DISINFECTION

The disinfection methods with UV radiation have recently been introduced and

adopted for secondary effluent in Japan. Photo 1 shows the appearance of UV radiation pilot plant installed in the test and evaluation facility. Figure 5 shows the relationship between the UV radiation dosage and coliform survival. The available data in the field surveys are indicated as several lines in Figure 5.

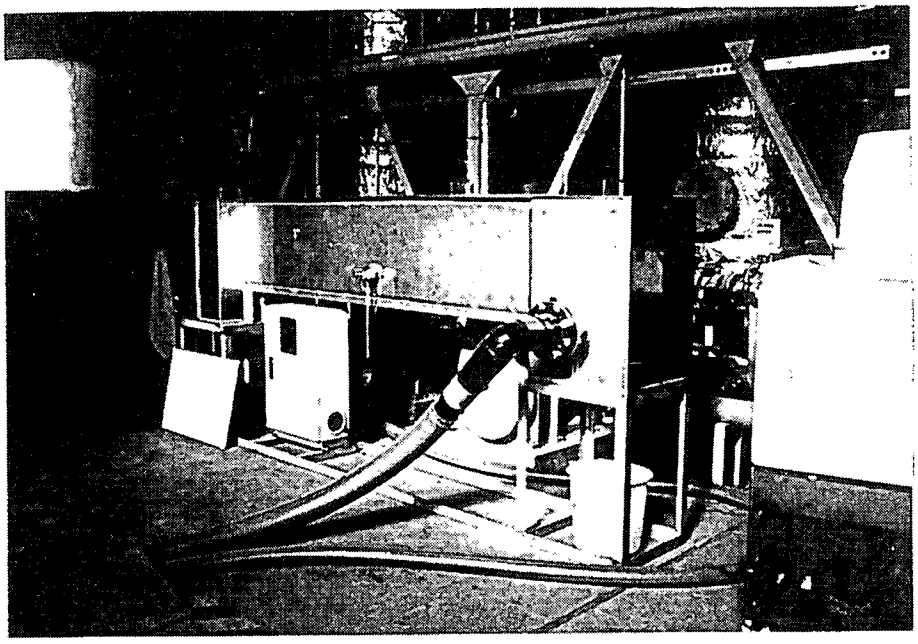


Photo 1 UV Test Plant

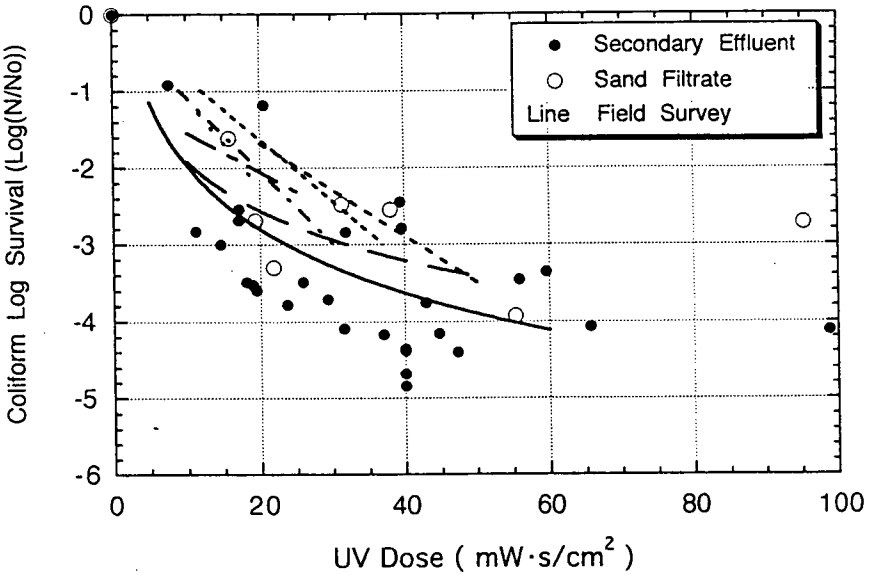


Figure 5 UV dosage and coliform survival

Deoxyribonucleic acid (DNA) molecule is the principal target of UV energy since DNA is the macromolecules whose function are the storage and transfer of cells' genetic information. The UV energy is absorbed in the DNA of microorganisms, causing structural changes in the DNA that prevent microorganisms from propagating.

When the DNAs in cells are damaged by UV radiation, the damaged DNAs may be repaired by photoreactivation phenomenon(1). Therefore, the extent of UV disinfection must be determined considering this photoreactivation phenomenon. Figure 6 shows the example of this photoreactivation for coliform bacteria based on the UV irradiation dosage and the light radiation time. As for the enterococus, no photoreactivation was observed. The results, obtained in the UV disinfection tests, suggested that the required UV irradiation dosage must be determined to remove 99.9 % of coliform bacteria considering this photoreactivation phenomenon.

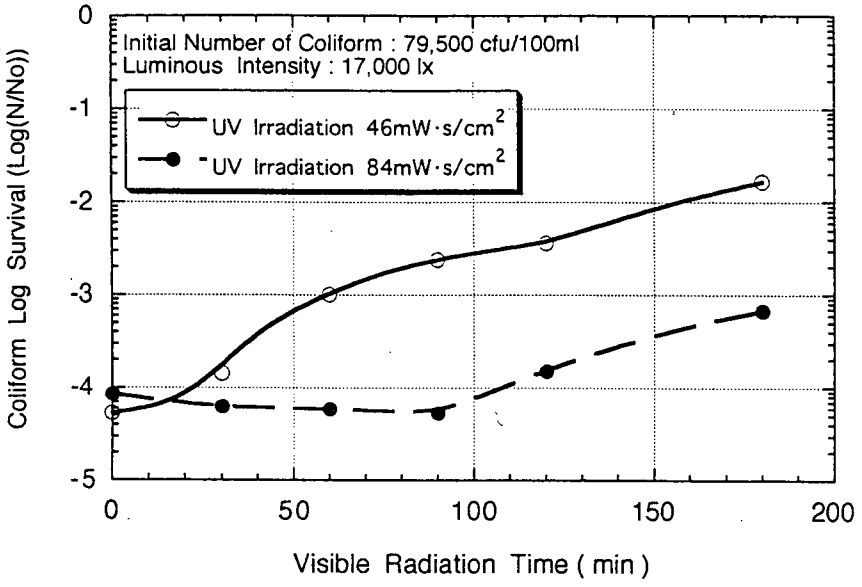


Figure 6 Photoreactivation of Coliform Bacteria

OZONE DISINFECTION

Ozone is an extremely reactive oxidant, and it is generally believed that bacterial kill through ozonation occurs directly because of cell wall disintegration. Photo 2 shows the appearance of ozonation plant installed in the test and evaluation facility.

Figure 7 shows the relationship between ozone dosage and coliform survival. No clear relation is obtained in the tests results since the required ozone dosage is widely fluctuated due to the characteristics of secondary effluent. Although the minimum ozone dosage is 5 mg/L for secondary effluent, but the actual ozone requirement in general is much higher.

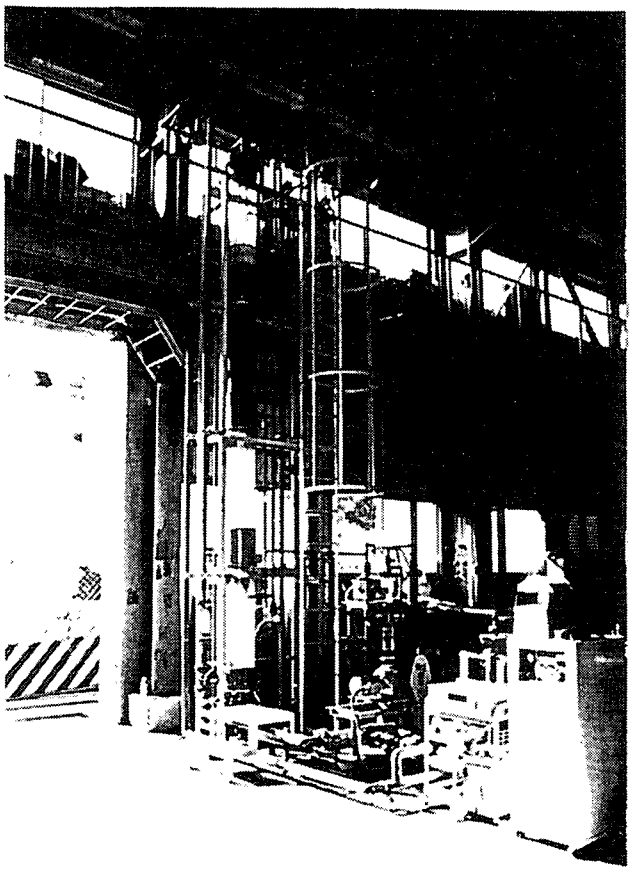


Photo 2 Ozonation Test Plant

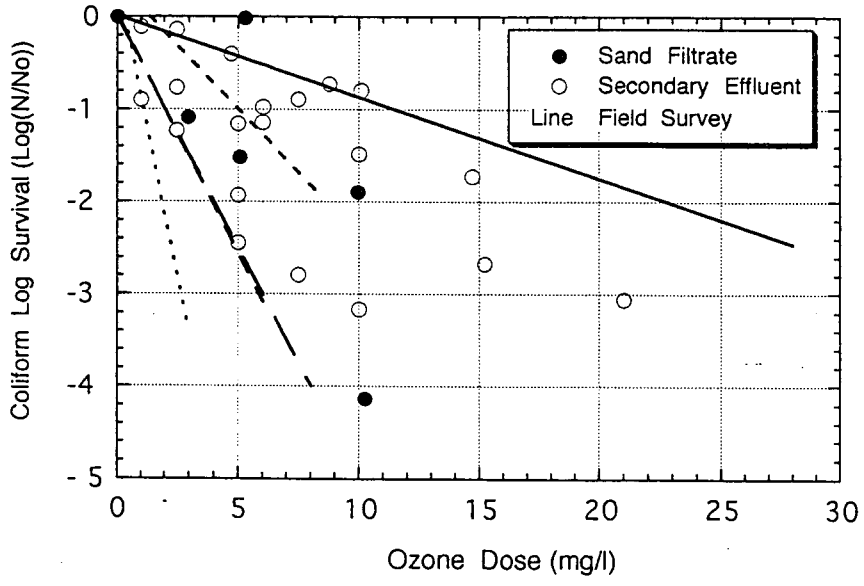


Figure 7 Ozone Dosage and Coliform Survival

Compared with other disinfection methods, the ozonation has the advantages in terms of COD removal and color removal. In Japan, therefore, the ozonation will be the promising disinfection method for the plants whose effluent COD standard are

stringent and/or where the decoloring of final effluent is required.
Figure 8 shows the relation between ozone dosage and COD removal and color removal.

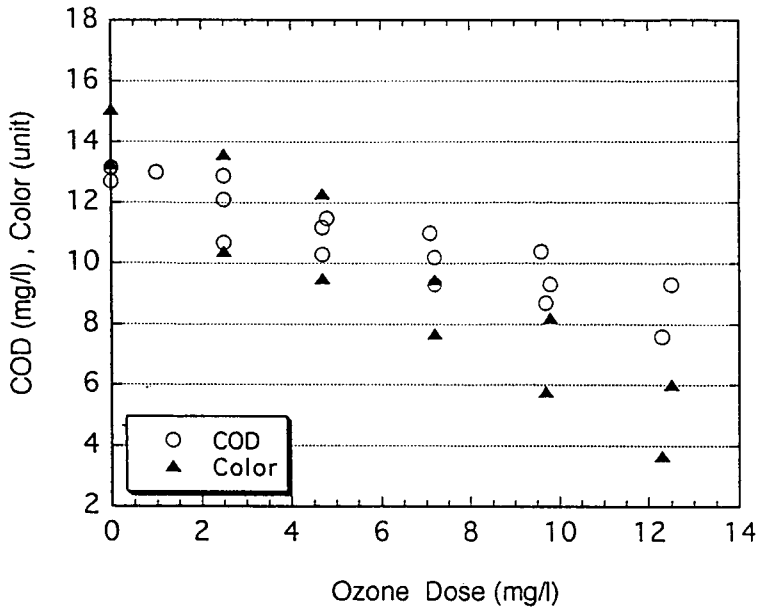


Figure 8 COD Removal and Ozone Dosage

CONCLUSION

The Japan Sewage Works Agency Technical Evaluation Committee submitted the main report on the latest disinfection methods in March 1997 based on the these tests results shown in this paper. This report covers chlorination, UV radiation and ozonation methods, and these three methods are competitive in terms of their disinfection performance, construction cost, and O&M cost. In Japan, only 8 plants adopted the UV disinfection method, and only 16 plants adopted the ozone disinfection method at present. Since each municipal wastewater treatment has different local conditions, this technical evaluation report on the latest disinfection methods will be very helpful for the plant designer to select an optimum disinfection method carefully in Japan.

REFERENCE

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VARIATION OF ORGANIC HALIDE FORMATION POTENTIAL OF DYES AND INTERMEDIATES BY OZONATION

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ABSTRACT

Effluents containing various dyes, intermediates and auxiliaries, which are typically biorefractory, are known to have high trihalomethane formation potential (THMFP) as well as intense color. In this study, six water-soluble dyes and five intermediates were ozonated to investigate the variations of total organic halide formation potential (TOXFP) and THMFP. The decrease in color and the change in biodegradability were also studied. The variation patterns of TOXFP and THMFP were roughly divided into two groups and the values of TOXFP decreased to 50.0 μ g/mg total organic carbon (TOC) and that of THMFP to 20.0 μ g/mgTOC through ozonation of about 2.50mgO_3/mgTOC. Rapid decoloration was attained by short-term ozonation. All the compounds except α- and β-naphthols were converted to be biodegradable. From the viewpoint of the removal of organic halides, long-term ozonation was found to be necessary.

KEYWORDS

Organic halide formation potential, Dyes, Intermediates, Color, Biodegradability

INTRODUCTION

Trihalomethanes (THMs) are suspected to be carcinogenenic. The production of THMs through chlorination process at drinking water plants has been perorted, causing a serious problem in ensuring the safety of tap water. From this background, a new legulation guideline concerning THMs in tap water was amended and the level was established as 0.1mg/L. The Environment Agency has taken this guideline into consideration and promulgated a new law to protect water supply sources. The new law emphasizes as important the control of the discharge of precursors to THMs from industrial wastewaters[1].

Effluents containing various dyes, intermediates and auxiliaries, which are typically biorefractory, are known to have high THMFP as well as intense color. As a result, the treatment of these wastewaters in terms of the decrease in THMFP should be considered[2], when they are dischared into water supply sources. In order to decrease

the TOXFP and THMFP from dye-containing solution, six water-soluble dyes and five intermediates were selected as target compounds in this study. The variations of TOXFP and THMFP were investigated, and further correlated with the variations of color and biodegradability.

MATERIALS AND METHODS

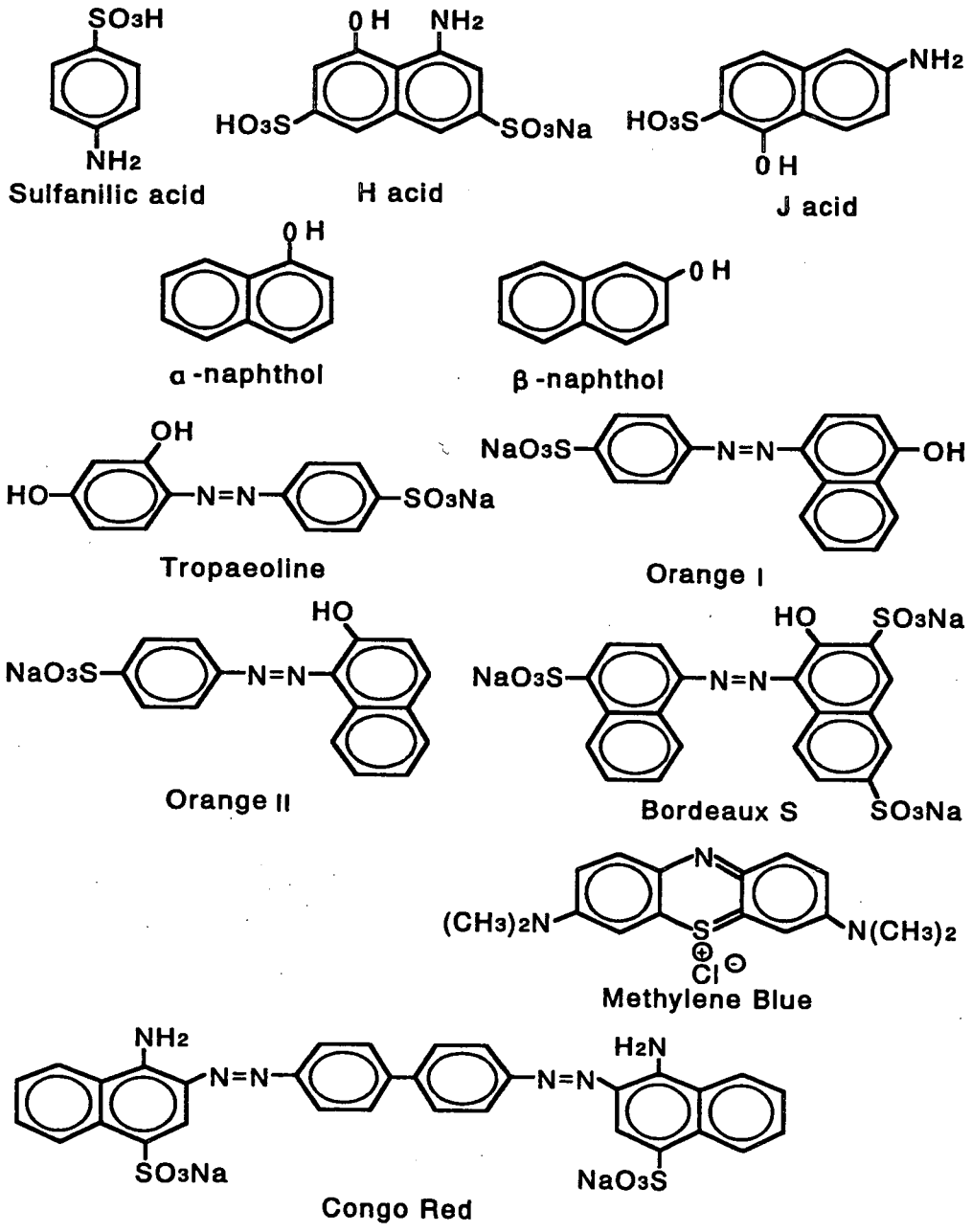


Fig.1 Molecular structure of dyes and intermediates

Materials

Six water-soluble dyes (Tropaeoline, Orange Ⅰ, Orange Ⅱ, Congo Red, Bordeaux S and Methylene Blue), which are known not to be effectively removed by both conventional biological treatment and coagulation/sedimentation, and five intermediates (Sulfanilic, H and J acids, α- and β-naphthols) were of commercially available reagent grade (Wako Pure Chemical), and were used without further purification. Most of the dyes used ccontain azo group (-N=N-), which is one of the most popular chromophores in dye molecule. Aqueous solutions of these compounds at a concentration of 1.44 mM/L were prepared using deionized distilled water. Figure 1 shows the molecular structure of dyes and intermediates.

Ozonation Apparatus

Figure 2 shows a schmatic diagram of the semi-batch type ozonation apparatus. A 1.6L solution of each of the dyes and intermediates was placed in a reactor 30cm high and 9.5cm inner diameter, and ozonated by bubbling ozonized oxygen gas through a glass bowl filter at a flow rate of 0.5 L/min. Ozonized gas was generated from pure oxygen by a laboratory ozone generator (Nippon Ozone, ON-1-2) at a concentration of between 22.5 and 26.5mg/L. Aliquots of the sample solution were periodically taken out, and then bubbled with nitrogen gas for 15 min to remove residual ozone. All experiments were conducted at a temperature of 22±2℃ under a pH of 4 ±0.5.

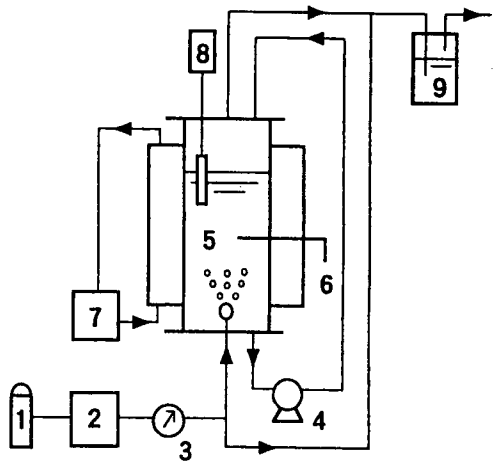


Fig.2 Schematic diagram of the reaction apparatus

1: Oxygen gas houlder, 2: Ozone generator, 3:Flow meter, 4: Pump, 5: Contact tower, 6: Sampling stopcock, 7: Cooler, 8: PH controller, 9: Exhaust ozone gas absorption tower

Analytical Methods

Aliquots of each of the sample solutions were diluted to a concentration of about 1～3mgTOC/L and chlorinated by excess of hypochlorite solution. The solutions were then stored in the dark at 20℃ for 48h. After chlorination, the concentration of THMs was determined by the head space method according to JIS K0125. The measurement was performed using a gas chromatograph (Hitachi, 263-50) equipped with a ^{63}Ni ECD detector and a capillary column (Ø3mm×3m) packed with 20% silicon DC-20 on

80/100 mesh Chromosorb WAW-DMCS support. After chlorination, an aliquot of the sample solution was adsorbed onto granular activated carbon for the measurement of total organic halide (TOX). The TOX content was analyzed using a TOX analyzer (Mitsubishi Kagaku, TOX-10Σ). Biological oxygen demand (BOD_5) was measured by JIS K0102. The sample water of the Tama River in Chofu was used to provide the microbial inoculumn. TOC was measured using a TOC analyzer (Shimadzu, TOC-500). Biodegradability was represented in terms of the ratio of BOD_5 to TOC (BOD_5/TOC)[3]. Visible absorbance was measured in a 1-cm cell using a UV-visible spectrophotometer (Hitachi, 100-50). Color ($\sum\lambda$) was determined by the sum of absorbances in the wavelength interval of 50nm from 350～700nm[4]. The concentration of ozone in the feed gas and that in the off gas were measured by iodometry. The amount of ozone consumed within the reactor was determined from the difference between them.

RESULTS AND DISCUSSION

Variations of TOXFP and THMFP

As shown in Table 1, the ratio of THMFP to TOXFP varied from 0.09 for β-naphthol to 0.61 for α-naphthol, demonstrating that in most of the target compounds, more than half of the organic halides were compounds other than THMs. It was also found that the position of the hydroxyl group had a significant effect on TOXFP and THMFP through the composition of α- and β-naphthols, and that TOXFP and THMFP cannot be easily estimated by the molecular weight and/or TOC content, because some low-molecular-weight or low-TOC-containing compounds such as Tropaeoline, Methylene Blue and Sulfanilic acid had high TOXFP and THMFP. The high values of TOXFP and THMFP for Tropaeoline, Methylene Blue and Sulfanilic acid are probably due to the 1,3-dihydroxy structure (the resorucinol structure), the substitution of active N,N-dimethyle amino group into the aromatic ring, that of amino group, respectively[5)~7)].

Table 1 Characteristics of dyes and intermediates

Dyes & intermediates (1.44×10^{-3}mol/L)	Molecular weight (-)	TOC (mg/L)	TOXFP (μg/mgTOC)	THMFP (μg/mgTOC)	THMFP/TOXFP (%)	BOD_5/TOC (mgO_2/mgC)
Tropaeoline	316.2	212.5	619.7	333.4	53.8	0.03
Orange I	350.3	279.0	95.4	18.4	19.3	>0.01
Orange II	350.3	214.2	108.3	19.9	18.4	0.05
Congo Red	696.7	580.0	42.5	20.7	48.7	0.03
Bordeaux S	604.5	347.0	51.0	13.8	27.1	>0.01
Methylene Blue	319.5	288.4	343.8	143.3	41.7	0.15
Sulfanilic acid	173.2	107.0	467.2	212.1	45.4	>0.01
H acid	341.3	154.4	323.2	39.4	12.2	0.03
J acid	239.3	158.0	327.8	65.8	20.1	0.06
α-naphthol	144.2	175.0	96.9	59.3	61.2	1.03
β-naphthol	144.2	174.8	18.8	1.7	9.0	1.22

Figures 3 and 4 show the variations of TOXFP and THMFP during ozonation, respectively. Altough the variations of TOXFP and THMFP with ozone consumed showed a similar behavior for the same dyes or intermediates, the target compounds were roughly divided into two groups: (1) compounds showing a maximum in the initial stage of ozone consumed of 0.50~1.10mgO_3/mgTOC and (2) compounds showing a uniform decrease with the increase of ozone consumed. In spite of the different variation patterns and initial values, ozonation of about 2.50mgO_3/mgTOC could decrease the TOXFP of all the target compounds to 50.0 μ g/mgTOC and the THMFP to 20.0 μ g/mgTOC. These results showed that the variations of TOXFP and THMFP caused by ozonation of dyes and intermediates depended on both the structure of target compounds and the degree of ozonation.

As one of the reasons for this phenomenon, the production of low-molecular-weight organic acids such as formic, glyoxylic, and formic acids, which have low TOXFP and THMFP values, could be assumed. On the other hand, the temporary increase in TOXFP and THMFP was probably caused by the hydroxylation of the aromatic ring and the subsequent production of compounds with hydroxyl groups at the 1,3-positions[5)~7)].

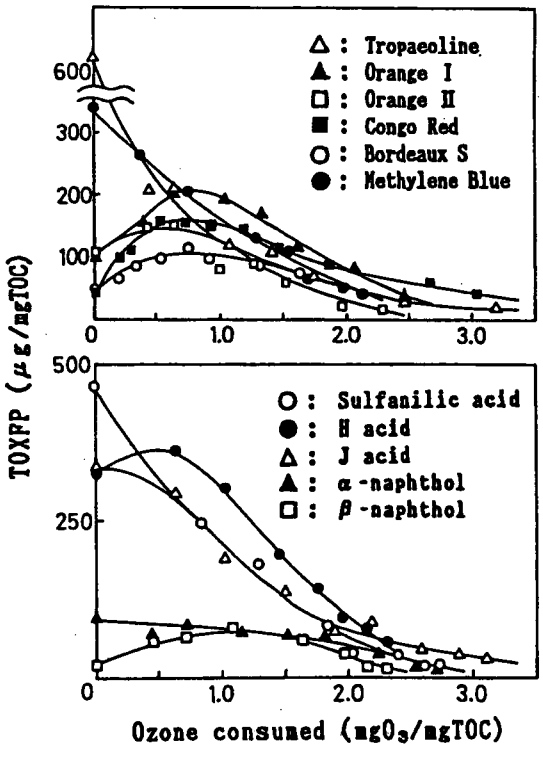


Fig.3 Variation of TOXFP with ozone consumed

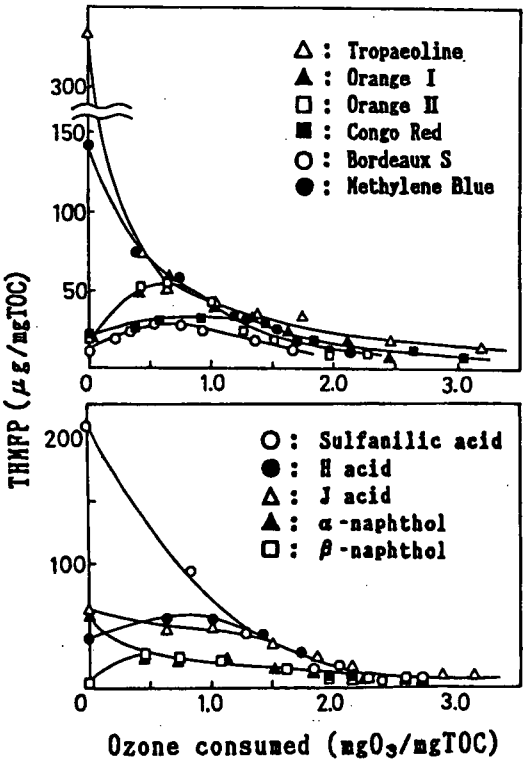


Fig.4 Variation of THMFP with ozone consumed

Decrease in Color

The six water-soluble dyes show a maximum absorption peak in the visible region, and Congo Red shows another peak at 345nm. The absorption spectrum uniformly decreased during ozonation without the production of a new peak (see Figure 5). Figure 6 shows the relationship between color and ozone consumed, indicating that a high level of decoloration was observed at low ozone consumption. That is, decoloration of more than 90% was achieved at 0.75~1.00mgO_3/mgTOC for all the dyes other than Congo Red, in which decoloration of about 87% was attained at 1.20mgO_3/mgTOC. These facts indicate the selective attack of ozone molecule on the chromophoric azo group.

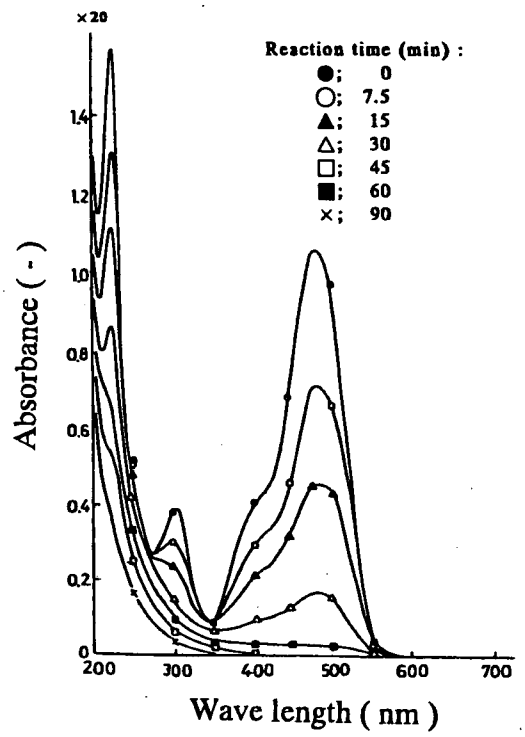


Fig.5 Absorption spectra of Orange II

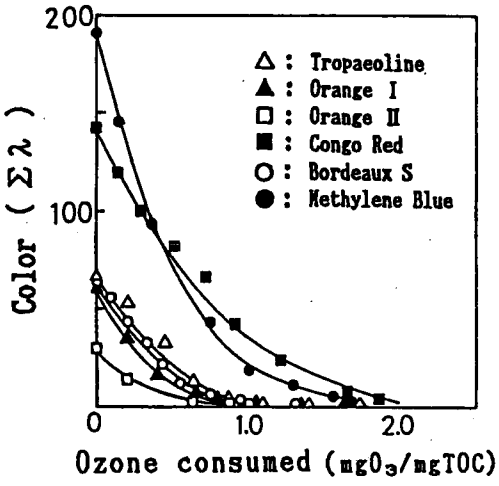


Fig.6 Decrease in color with ozone consumed

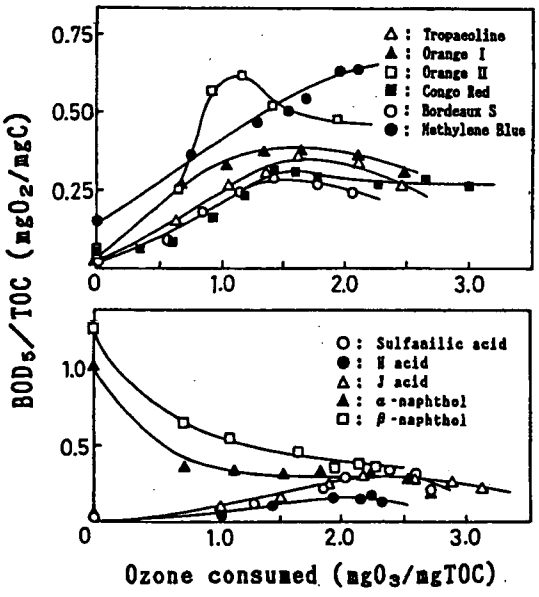


Fig.7 Variation of biodegradability with ozone consumed

Change in Biodegradability

Figure 7 shows the change in biodegradability. The initial BOD_5/TOC values for all the dyes were less than 0.15, indicating that the dyes were typically nonbiodegradable

before ozonation. During ozonation, the BOD_5/TOC values for all the dyes other than Methylene Blue rgadually increased with the increase of ozone consumed, showed a maximum of 1.20～1.70mgO_3/mgTOC, and then slightly decreased to a level of 0.25～0.45. In case of Methylene Blue, the BOD_5/TOC value uniformly increased with the increase of ozone consumed, and reached a level of about 0.64 at 2.00 ～ 2.10mgO_3/mgTOC. These facts suggest an enhancement in biodegradability. The existence of a maximum indicates that there is an optimum condition for the ozonation of the five dyes excluding Methylene Blue.

In case of Sulfanilic, H and J acids, an enhancement in biodegradability was also observed during ozonation, where a maximum value of 0.20～0.30 was obtained at 2.20 ～ 2.40mgO_3/mgTOC. On the other hand, α - and β -naphthols were initially biodegradable because of the high BOD_5/TOC values of 1.00 and 1.22, respectively. The BOD_5/TOC values of these compounds uniformly decreased to about 0.35 with the increase of ozone consumed.

Relationship between the Variations of TOXFP and THMFP and those of Color and Biodegradability

When dye-containing effluents are discharged into the environment, both color and biodegradability of them should been also taken into account as well as TOXFP and THMFP. Consequently, the relationship between the variations of TOXFP and THMFP and those of color and biodegradability was investigated.

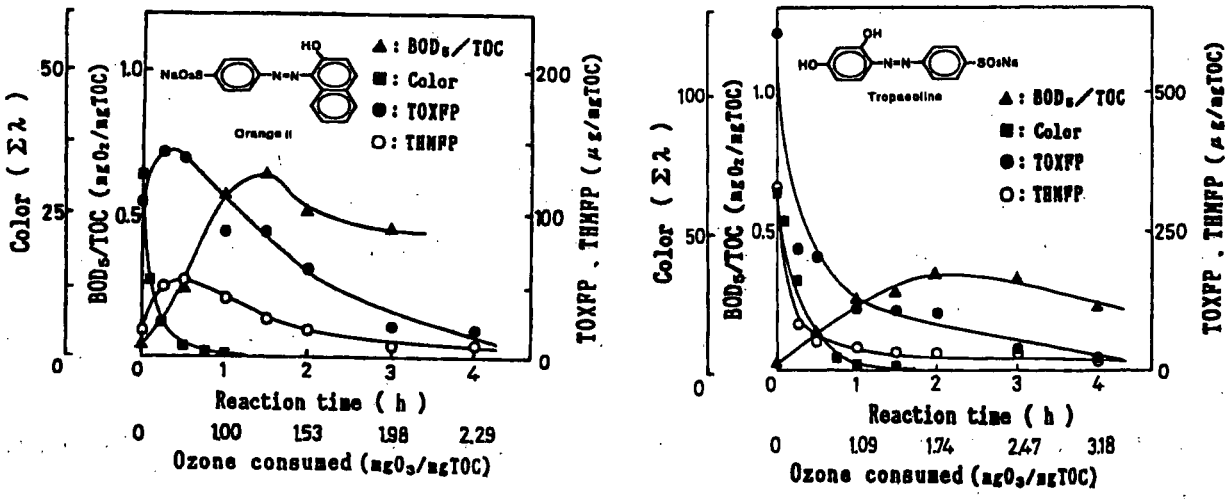


Fig.8 Variations of TOXFP, THMFP, color and biodegradability

Figure 8 shows the variations of TOXFP, THMFP, color and biodegradability for Orange II with a temporary maximum in TOXFP and THMFP and for Tropaeoline with a uniform decrease in TOXFP and THMFP. As shown in Fig.8, rapid decoloration was attained by short-term ozonation. That is, relatively short-term ozonation, which is

equivalent to 1.50mgO_3/mgTOC for Congo Red and 0.75～1.00mgO_3/mgTOC for other five dyes, could result in an more than 90% decoloration. Moreover, short-term ozonation was effective for the enhancement in biodegradability. However, it was not necessarily sufficient for the decrease in TOXFP and THMFP. These results indicate that long-term ozonation is necessary for the removal of precursors to organic halides.

CONCLUSIONS

Six water-soluble dyes and five intermediates were ozonated to investigate the variations of TOXFP and THMFP and to correlate those variations with those of color and biodegradability. The following items were concluded:

(1) The variation patterns of TOXFP and THMFP were roughly divided into two groups and the values of TOXFP decreased to 50.0 μ g/mgTOC and that of THMFP to 20.0 μ g/mgTOC through ozonation of about 2.50mgO_3/mgTOC.

(2) Rapid decoloration was attained by short-term ozonation.

(3) All the compounds except α- and β-naphthols were converted to be biodegradable.

(4) From the viewpoint of TOXFP and THMFP removals, long-term ozonation was found to be necessary.

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Electrochemical Decomposition Treatment of Dye-containing Colored Water by Use of Solid Polymer Electrolyte Membrane

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ABSTRACT

A novel electrolytic wastewater treatment method using solid polymer electrolyte (SPE) was developed and applied to the decomposition of various dyestuffs. A Nafion^R (Du Pont) membrane was used as the SPE and beta-PbO_2 was chosen for an anode material which can oxidize organic substances. Within 60-120 min, the dyestuffs served to the SPE electrolysis (amaranth, alizarin green G and gallocyanine) were decolorized to show no detectable color with the naked eye. Removal of organic components at 120 min was in the range of 74-58% (in COD) and 49-21% (in TOC) for these dyestuffs. As the decomposition products, several kinds of organic acids were detected in the treated water.

KEYWORDS

Dyestuff, Trihalomethane, Wastewater treatment, Decolorization, Solid polymer electrolyte, Lead dioxide, Electrolytic oxidation, Decomposition characteristics, COD, TOC

INTRODUCTION

Colored wastewater discharged from factories especially in dyeing industry contains refractory coloring compounds such as dyestuffs. Since these compounds usually indicate remarkably high trihalomethane formation potential, serious environmental problems may arise when such wastewater is discharged in the source area of public water supply. On this background, Japanese government has established the legislation in 1994 for

the effluents with high trihalomethane formation potentials to avoid the hazard of trihalomethanes in the tap water.
Furthermore, colored wastewater itself gives people so unpleasant feelings that some local governments in Japan have imposed stringent controlling measures on the color of effluents from the industrial facilities.
Recently emerged these two factors have been requiring adequate treatment of the colored wastewater.
On the contrary, there have been many difficulties in treating the wastewater of this sort since the dyestuffs are usually hydrophilic and indicate poor biodegradability. For these reasons, conventional water treatment methods such as flocculation, activated sludge treatment etc. are less effective for the removal of coloring compounds from the wastewater. Though a few methods such as chemical oxidation method or activated carbon adsorption method are expectable, treatment costs may generally reduce their applicability.
Electrochemical oxidation method may be classified as a kind of oxidative treatment method. Since this method has some promising features in cost and simplicity of the operation, many works have been reported so far [1]. Among them, our interest has been focused on a direct electrochemical oxidation method using a solid polymer electrolyte (SPE) membrane. Some expectable features of the SPE electrolytic oxidation method are the following:
(1) Utilizing SPE in place of liquid electrolyte media, it requires no additional electrolyte such as NaCl which is usually added to generate hypochlorite. While this electrochemically generated hypochlorite is employed for the oxidant, it may produce hazardous organic halides [2].
(2) It requires no oxidizing reagents which demand in general careful handling and larger cost.
(3) The treatment system may be compact due to applicability of high current density electrolysis.
In this study, SPE electrolytic oxidation treatment of dye-containing colored water has been carried out. Beta-PbO_2 was chosen as a high oxygen overvoltage anode material in place of precious metals such as platinum [3]. Decomposition characteristics of 3 different kinds of dyestuffs are described herein.

EXPERIMENTAL

Chemicals

3 kinds of dyestuffs with different chemical structures, amaranth (C.I. Acid Red 27), alizarin green G (C.I. Acid Green 25) and gallocyanine (C.I. Mordant Blue 10), were used for the target compounds for SPE electrolytic oxidative decomposition. The structures of these dyestuffs are shown in Figure 1. These dyestuffs were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and used as received. Other chemicals were of analytical grade.

The SPE membrane and preparation of the electrodes

A perfluorosulfonate ion-exchange membrane Nafion^R 117 (E. I. du Pont de Nemours) was used as the SPE membrane. The membrane (thickness 0.18 mm) was used after cutting in a circle (diameter 60 mm).

Beta-PbO_2 was electroplated on a porous titanium base (thickness: 0.5 mm, diameter: 36 mm) from a $Pb(BF_4)_2$ solution and used for the anode.

As the cathode, a carbon-supported-platinum catalyst dispersed gas diffusion electrode membrane was employed.

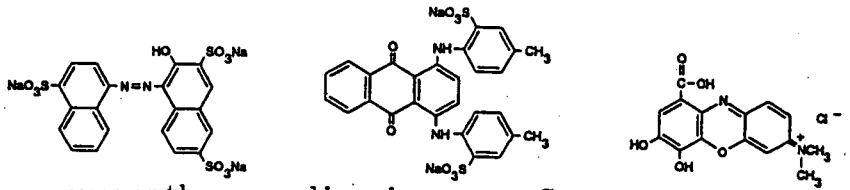


Figure 1. Structures of the dyestuffs.

The electrolytic cell

The SPE membrane was sandwiched between the anode and the cathode, and mounted in a round shaped flange type electrolytic cell. The cell housings were made of titanium (diameter 80 mm) and fine ditches were machined inside of the housings to serve as the paths for the solution and evolved gas. The geometrically effective area of the electrode in the cell was 10 cm^2.

The SPE electrolytic oxidation treatment system

Figure 2 shows the schematic diagram of the experimental system of the SPE electrolytic oxidation treatment. A solution (500 ml) of the dyestuff to be decomposed was circulated form a glass vessel to the electrolytic

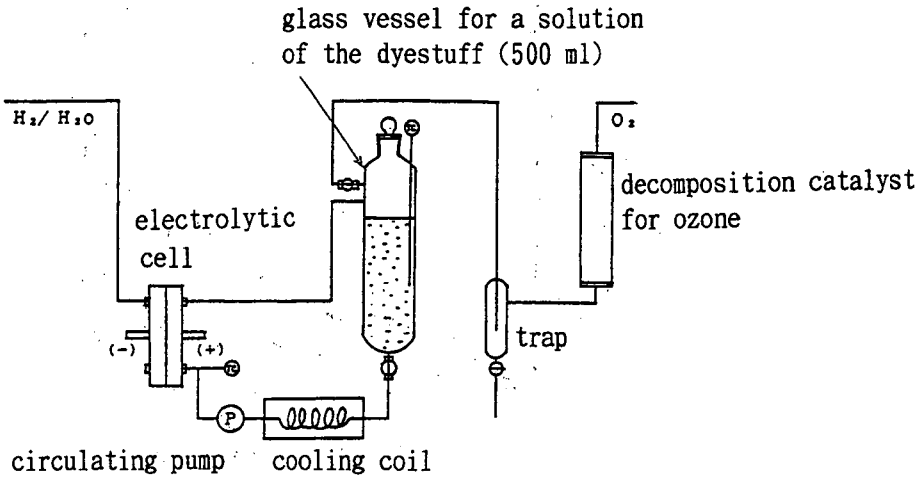


Figure 2. Schematic diagram of the SPE electrolytic oxidation experiment system.

cell by a pump whose bellows was made of PTFE. All pipings and joints used were of PTFE to avoid the wear of material by ozone gas evolved as by-product.

Galvanostatic (viz. controlling the current constantly) electrolysis was performed with an NL012-50 DC stabilized power supply (Takasago Seisaku-sho, Japan).

Evaluation of quality of the treated water

To evaluate the water quality characteristics resulting form the SPE electrolytic decomposition treatment of the dyestuffs, the following measurements were conducted. UV-visible absorption spectra of the sample solutions were measured with a Hitachi 320 spectrophotometer. Total organic carbon (TOC) and biological oxygen demand (BOD) were determined with a Shimadzu TOC-500 and an Ohkura BOD coulometer, respectively. Inorganic and organic anions were analyzed by a Yokogawa IC7000 ionchromatograph. Chemical oxygen demand (COD) with permanganate (100 centigrade) method was determined according to the procedures described in the Testing Methods for Industrial Wastewater (in Japanese Industrial Standard).

RESULTS and DISCUSSION

Decomposition of amaranth

Since there are a number of azo dyes and they hold a place of practical importance in the dyeing industry, the decomposition characteristics of amaranth were investigated rather in detail as a typical azo dye.

(a) Influence of current density on the decomposition of amaranth.

Influence of current density which was supplied to the cell galvanostatically was examined in the range of 0.1-0.4 A/cm^2 (Figure 3). Efficiency of TOC removal from the amaranth solution (initial concentration 113 mg/l) was

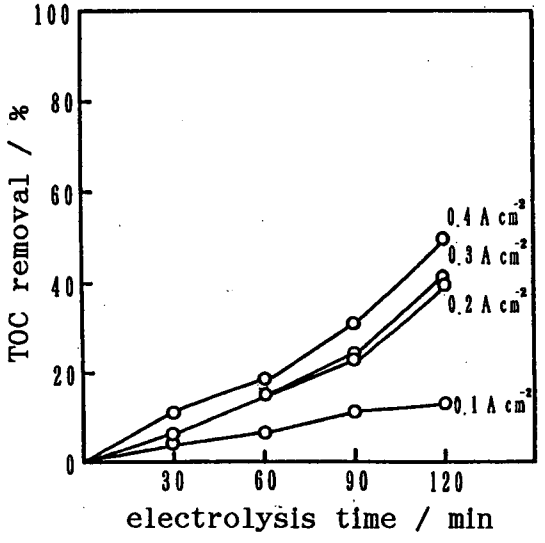


Figure 3. Influence of current density on the decomposition of amaranth by the SPE electrolytic oxidation.

saturated at 0.3 A/cm^2, hereafter the electrolysis experiments were performed at 0.3 A/cm^2.

(b) Uv-visible absorption spectra.

Figure 4 shows change in uv-visible absorption spectra of the amaranth solution by SPE electrolytic oxidation treatment (current density: 0.3 A/cm^2, cell voltage: 3.5 V). Absorption maximum in visible branch at 520 nm rapidly diminished along with the progress of electrolysis, and the treated water was entirely decolorized at 120 min showing no detectable color with the naked eye. This result indicates that main chromophore -N=N- group in the amaranth was destroyed completely at that time. In uv branch, absorption band originated from aromatic rings also diminished though it was not as fast as in the case of visible absorption. This implies that aromatic rings in amaranth are more resistant than azo group against cleavage by electrolytic oxidation.

(c) Removal of organic components.

Figure 5 shows the removal effect of organic components from the amaranth solution by SPE electrolytic oxidation. COD of the solution decreased sharply in early stage of the electrolysis, but COD removal efficiency gradually went down with the progress of electrolysis. On the other hand, TOC decreased with almost constant rate from the beginning of the electrolysis. At 120 min, 74% of COD removal was achieved, while TOC removal was 49%.

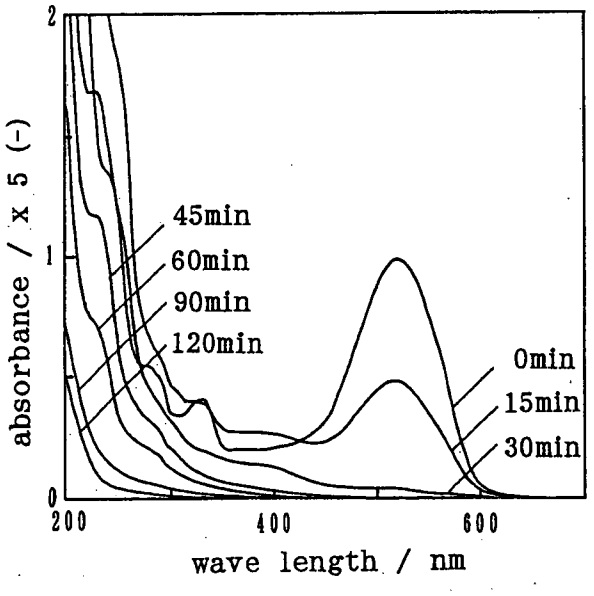


Figure 4. Absorption spectra of the amaranth solution treated with SPE elctrolytic oxidation. (current density=0.3 A/cm^2)

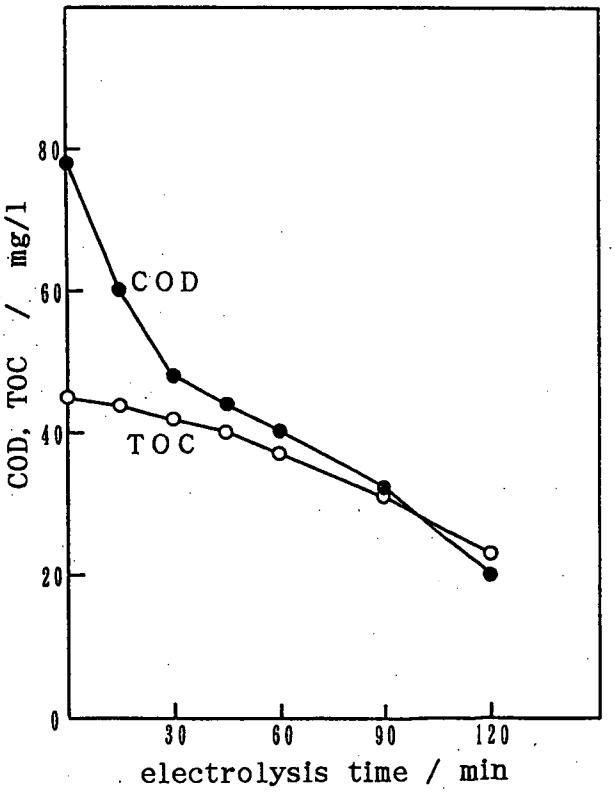


Figure 5. Decrease in COD, TOC of the amaranth solution treated with SPE elctrolytic oxidation.

From the BOD measurement data, biodegradability of the sample solution increased by electrolytic decomposition of amaranth. BOD of the amaranth solution with initial value 0 mg/l increased as large as 12 mg/l after 120 min's electrolysis. This result suggests the possibility of combined treatment of biological method with the electrolytic oxidation.

(d) pH change, formation of organic acids and inorganic anions.

Figure 6 indicates pH change of the treated water with time elapsed from the beginning of electrolysis. pH reached 3.2 at the last stage of electrolysis. One of the reasons of this pH decrease might be attributed to the formation of organic acids, since some lower aliphatic acids were detected in the treated water by ionchromatograpy. Figure 6 also shows this situation. Remarkable formation of oxalic acid was observed in the middle to last period of the electrolysis, while formic acid formation showed a maximum in the middle period. By contrast, acetic acid was not found at any occasions.

As for inorganic anions, concentration of sulfate ion increased almost proportionally to the electrolysis time (Figure 7). The origin of the sulfate ion was considered to be sulfonic groups attached to the naphthalene skeletons of amaranth. At 120 min, 89% of sulfonic group in the amaranth was oxidized to sulfate ion and released into the treated water. In regard to nitrogen atoms in azo group, on the contrary, little nitrate ion was detected throughout the electrolysis.

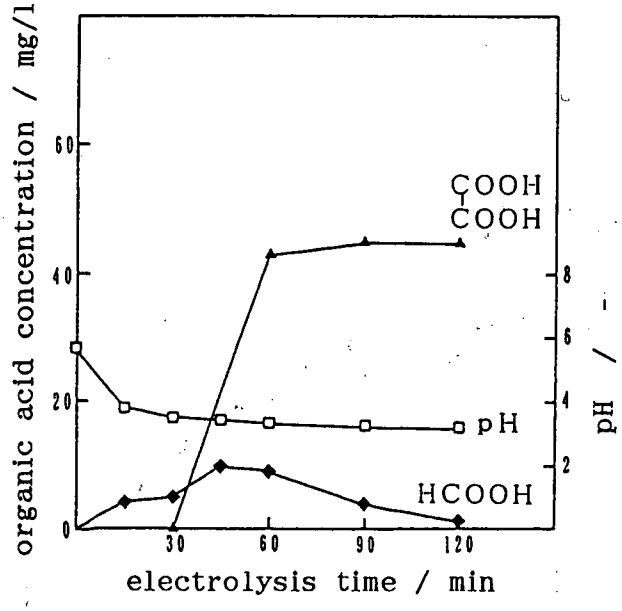


Figure 6. pH change, formation of organic acids in the amaranth solution treated with SPE elctrolytic oxidation.

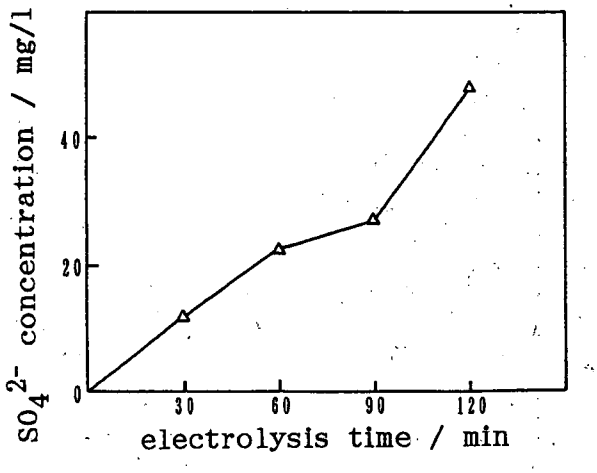


Figure 7. Sulfate ion released in the amaranth solution treated with SPE elctrolytic oxidation.

Decomposition of alizarin green G

An alizarin green G solution (96 mg/l) was treated by SPE electrolytic oxidation (current density: 0.3 A/cm^2, cell voltage: 3.3 V). The decolorization characteristics are shown in Figure 8. Absorption maximum in visible branch nearby 600-640 nm diminished sharply and any color was not recognized by eyesight at 60 min.

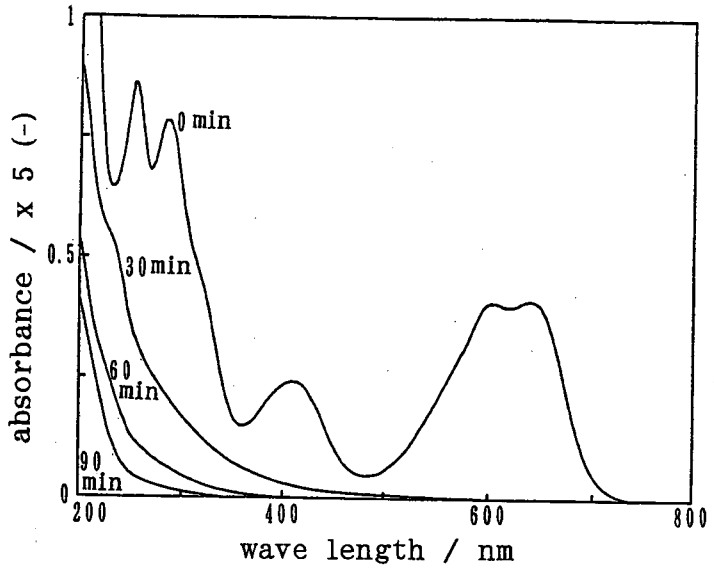


Figure 8. Absorption spectra of the alizarin green G solution treated with SPE elctrolytic oxidation.
(current density=0.3 A/cm^2)

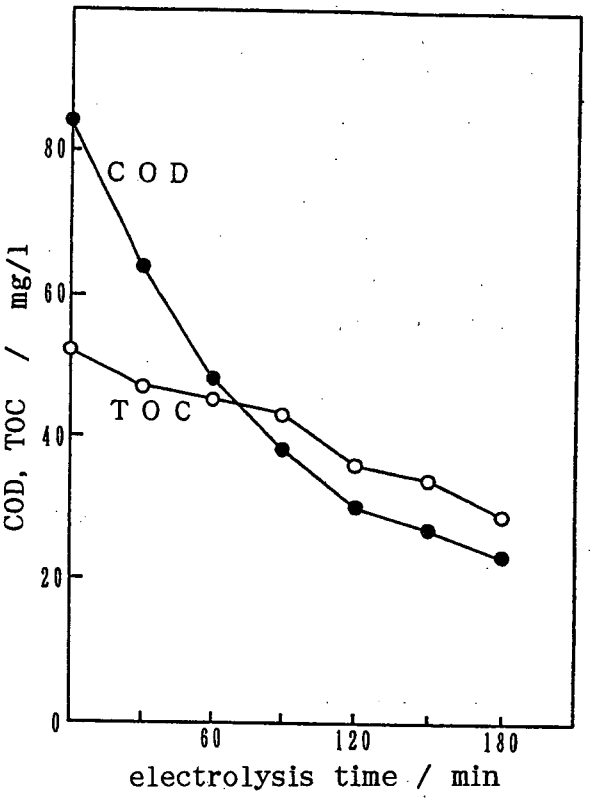


Figure 9. Decrease in COD, TOC of the alizarin green G solution treated with SPE elctrolytic oxidation.

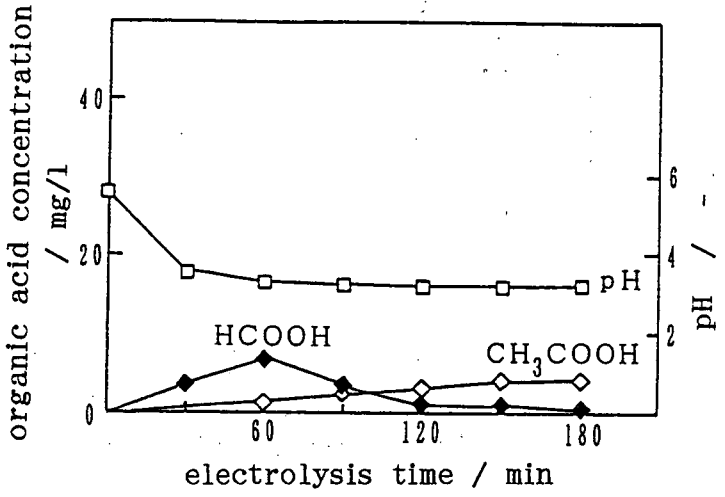


Figure 10. pH change, formation of organic acids in the alizarin green G solution treated with SPE elctrolytic oxidation.

Removal characteristics of organic components from the alizarin green G solution are shown in Figure 9. At 120 min, COD removal and TOC removal were 64% and 31% respectively.

Figure 10 indicates pH change and formation of organic acids. Formation of formic acid had a maximum at 60 min. Formation of acetic acid which was not found in the case of amaranth was slightly observed in this case. In addition, sulfate ion showed similar behavior as in the case of amaranth, that is, 76% of sulfonic group in the dyestuff was released as sulfate ion at 120 min.

Decomposition of gallocyanine

Figure 11 shows decolorization characteristics of a gallocyanine solution (80 mg/l) treated by SPE electrolytic oxidation (current density: 0.3 A/cm^2, cell voltage: 3.2 V). And removal characteristics of organic components are shown in Figure 12. This dyestuff is more resistant than the other dyestuffs against electrolytic oxidation since COD removal and TOC removal at 120 min were 58% and 21% respectively.

In regard to organic acids formed by the electrolysis, formic acid mainly appeared in the early stage of oxidation (Figure 13).

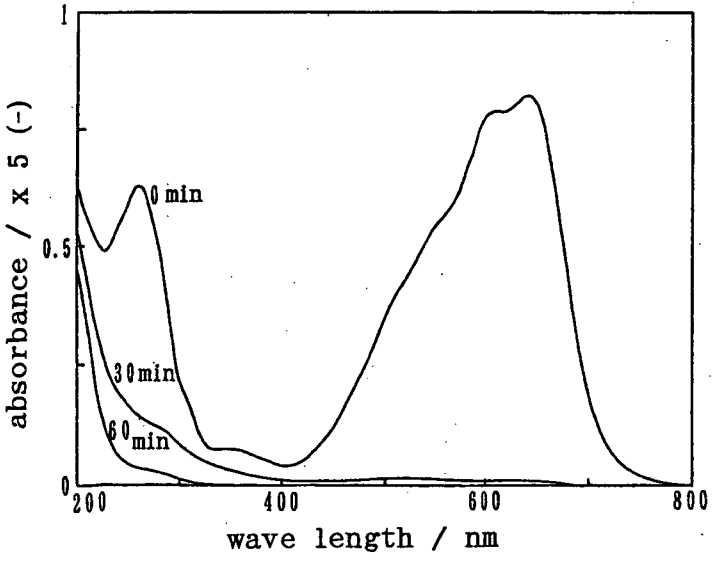


Figure 11. Absorption spectra of the gllocyanine solution treated with SPE elctrolytic oxidation.
(current density=0.3 A/cm^2)

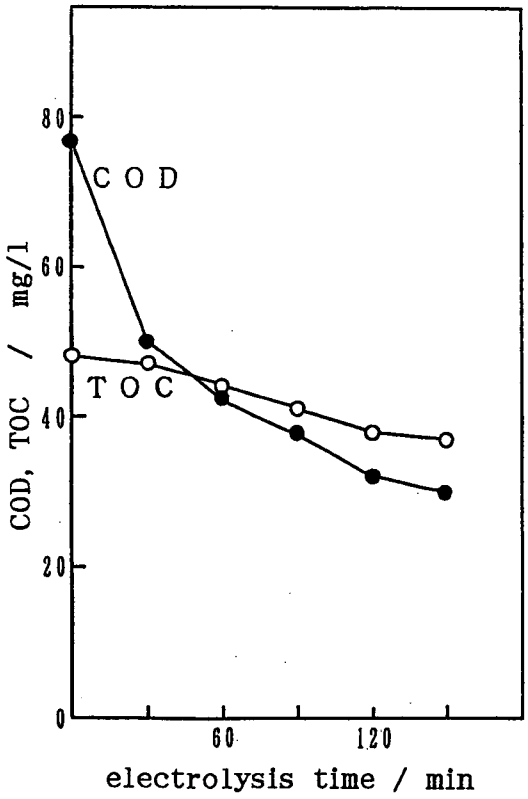


Figure 12. Decrease in COD, TOC of the gallocyanine solution treated with SPE elctrolytic oxidation.

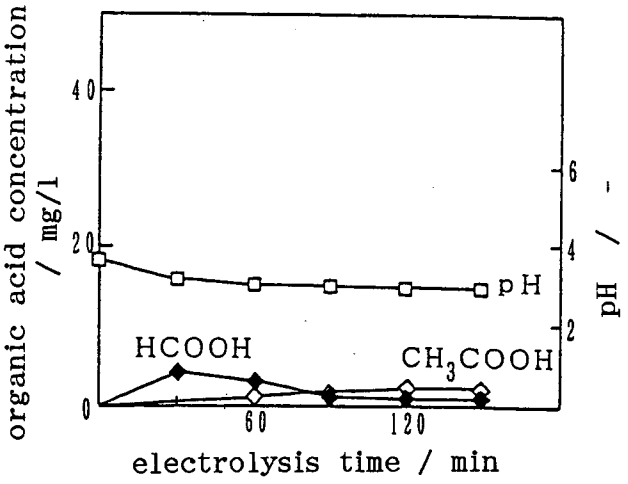


Figure 13. pH change, formation of organic acids in the gallocyanine solution treated with SPE elctrolytic oxidation.

As a matter of course, sulfate ion was not detected in the treated water since gallocyanine has no sulfonic groups in its chemical structure.

CONCLUSIONS

It has been demonstrated that the SPE electrolytic oxidation treatment method is effective for the decolorization of 3 different kinds of dyestuffs giving almost colorless treated water within 60-90 min of electrolysis. 49-21% of the initial TOC was also removed. If further removal of TOC is necessary, combination of the biological treatment with this method may be possible due to the improvement in biodegradability by electrolytic oxidation.

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Session 10

N and P Removal

"Experience with Full-Scale Plants for Phosphorus and Nitrogen Removal in Germany and Comparison of their Sludge and Energy Balances"

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UNIVERSITÄT HANNOVER
Prof. Dr.-Ing. K.-H. Rosenwinkel

Experience with full-scale plants for phosphorous and nitrogen removal in Germany and comparison of their sludge and energy balances

Karl-Heinz Rosenwinkel, Wiebke Hinrichs, Thomas Gigerl

Abstract

In this paper the design data, flow sheets, operating results and especially the aspects of sludge treatment and energy production of the process of anaerobic stabilization by three municipal wastewater treatment plants are presented. According to that a case study is carried out to demonstrate the energy supply of a wastewater treatment plant by different approaches of the activated sludge scheme. The energy potential of the sludge is shown at the three full-scale plants Hannover-Gümmerwald, Bremen-Seehausen and Hildesheim. To evaluate the sludge treatment regarding aspects like sustainability and improving the energy balances of wastewater treatment plants a survey about performing a Life Cycle Assessment is given.

Zusammenfassung

Anhand dreier großtechnischer Kläranlagen werden die Dimensionierungsgrundlagen, Fließschemata und im besonderen die Auswirkungen der Schlammbehandlung auf den Energiehaushalt dargestellt. Um die Wechselwirkung zwischen Abwasser- und Schlammbehandlung auf die Energiebilanz aufzuzeigen, werden mögliche Schlammbehandlungsverfahren vorgestellt. Zur Bewertung der Schlammbehandlung in Fragen der Nachhaltigkeit und Energiebilanzierung wird ein Abriß über die Durchführung eines Life Cycle Assessment gegeben.

1 Introduction

Because of recent regulations in the Federal Republic of Germany and in the countries belonging to the European Union and also due to increasing eutrophy in North Sea and Baltic Sea, the most imminent ecological problems are the elimination of oxygen consuming carbon compounds and the reduction of nutrient salt loads. Since the end of the 70s, several methods have been developed to biologically elimination of nitrogen and phosphorous from the wastewater. Parallel to an increase in efficiency of wastewater treatment plants, the requirements for the effluent quality of wastewater treatment plants were tightened.

Table 1 Requirements for the effluents from municipal wastewater treatment plants in the FRG and the EU, (*) for „sensitive areas",(**) „normal areas"

Requirements FRG					
Size [P. Equiv.]	COD [mg/l]	BOD [mg/l]	NH_4-N [mg/l]	N min.[mg/l]	$P_{tot.}$ [mg/l]
5000 – 20.000.	90	20	10	18	-
20.000 - 100.000	90	20	10	18	2
> 100.000	75	15	10	18	1
Requirements EU-Standards					
Size [P. equiv.]	COD [mg/l] (**)	BOD [mg/l] (**)	NH_4-N [mg/l]	N tot.[mg/l] (*)	$P_{tot.}$ [mg/l] (*)
10.000 - 100.000	125 or 75 %	25 or 70-90 %	-	15 or 70-80 %	2 or 80 %
> 100.000	125 or 75 %	25 or 70-90 %	-	10 or 70-80 %	1 or 80 %

To meet these requirements wastewater treatment has to be improved by applying stabilized nitrogen and phosphor elimination. These technically large scale processes in turn cause higher costs for operators of municipal sewage treatment plants for both sewage and sludge treatment. By extending municipal sewage treatment plants investigation costs as well as operation costs such as staff, energy and disposal of residues, are affected. For operators of sewage treatment plants the contrary assignments of fulfilling the required minimum standards for the effluent and economic responsibilities can lead to conflicts in some topics.

To give an example of a conflict mentioned above one might take a look upon nitrification. Recently tightened minimum requirements regarding nitrification can be met by enlarging the sludge age. Larger sludge age requires more energy.

Taking into account the energy potential of sludge in the case of digestion alternative to combustion it becomes obvious that both sewage treatment and sludge treatment have to show in the balance-sheet to accomplish an overlapping optimization of the technical processes.

Two of the observed conflicts are shown in the following table.

Table 2 Examples of possible conflicts between advanced wastewater treatment and sludge treatment

Taken measures	Advanced wastewater treatment	Sludge treatment
Large sludge age	The establishment of a stable nitrification demands sludge ages > 10d	High retention times lead to a partially aerobic stabilization of the activated sludge, this reduces the organic and enlarges the mineral portion of the activated sludge
Large preliminary treatment	Negative effects on denitrification and biological phosphor elimination, since only a limited amount of easy degradable COD reaches the second treatment step	Higher amount of primary sludge with higher energy content

In the following theoretical example the connection of the different operating methods of sludge activation and the usable energy potential of sludge is shown. For this the removal efficiency as well as the sludge and energy balances of three full scale treatment plants with anaerobic digestion of the primary and excess sludge are compared with a case study of aerobic/anaerobic stabilization.

2 Case study aerobic stabilization – anaerobic stabilization

To consider the energy balances of sludge treatment in wastewater treatment plants two operation methods are described in the following.

In the following example energy and sludge balances of two model plants are described. The two investigated alternatives are on the one hand an operating method with anaerobic stabilization of primary and excess sludge and on the other hand an operating method with simultaneous aerobic stabilization of excess sludge and anaerobic stabilization of the produced primary sludge. The given energy balance includes the aeration tank, the sludge treatment and the electrical power gained from biogas. Calculations have been done for sewage treatment plants with 10.000 to 1.000.000 PE[1].

2.1 Measurements

The measurement of sludge activation was done according to the ATV guideline A 131. The following influent concentrations were assumed as well as retention time of 1 hour in the pretreatment – which leads to a 25 % decrease in all substance parameters. Also given was a combined sewer system, which leads to a 25 % increase in DS_0 [ATV, 1991].

Table 3 Parameters for model plants after pretreatment

Parameter	*Value*
Temperature	10°C
$Q_{average}$	0,2 m³/(P * d) including infiltration water
$B_{d,BOD}$	47 g/(P * d)
$B_{d,COD}$	95 g/(P * d)
DS_0	45 g/(P * d)
N	10 g/(P * d)
P	2,3 g/(P * d)

2.2 Sludge

The sludge age in the activated sludge tanks needed for the nitrification was 15 days in the case of anaerobic stabilization and 25 days for the aerobic stabilization of the excess sludge. The dried solid matter content of sludge of the primary treatment $DS_{primary\ treatment}$ was calculated according to the following equation

$DS_{primary\ treatment} = DS_0 * 1{,}25 * PE/1000$ [kg DS/d]
The amount of excess sludge from after anaerobic stabilization $DS_{excess\ sludge}$ was calculated as follows:

[1] PE:Population equivalents

$DS_{excess\ sludge} = 0,7 * ExcessSludge_{,BOD} * B_{d,BOD}$ [kg DS/d]

The anaerobic stabilization includes the treatment steps, water reduction to a water content of 95 % and 20 days of anaerobic digestion at 35 °C.

2.3 Energy production

For power generation from block heating works are used. Waste heat gained from cooling systems by heat exchanger can be used for further heating. Based on the expected daily amount of biogas V_G and an efficiency of 0,62 for m^3 biogas/kWh_{el} for widely used block heating works. the power $P_{block\ heating\ works}$ of these combustion engines was calculated according to the following equation [Oswald-Schulze-Stiftung]:

$P_{block\ heating\ works} = V_G/0,62$ [kWh_{el}/d]

2.4 Energy uptake for activated sludge tanks and digestion

According to recommendation of the ATV a simplified approach for calculating the demand of energy for the digester and the activated sludge tank is used. In the activation tank the electrical power is used for aeration, upheaval and recirculation. To achieve and to maintain the necessary temperature for the digestion temperature the waste heat of combustion engines is used.

Table 4 Calculation of the energy need for sludge activation; $p_{spez.}$ is a function of the digester capacity>

Energy need	*Calculation*
Activated sludge tanks	
Total E_{BB}	0,04 tank capacity [kWh/h]
Digesters	
Total $E_{Digester}$	p_{spez} *digester capacity/1000 [kWh/h]

2.5 Results

The following figure stresses the connection between the population and the required tank size depending on the chosen operating method for sludge treatment. The operating method with simultaneous aerobic stabilization requires bigger activation tanks to allow older sludge ages. This, of course, causes higher investments and operating costs. Bigger activation tanks and bigger sludge volumes take up more energy for aeration, mixing the sludge and recirculation.

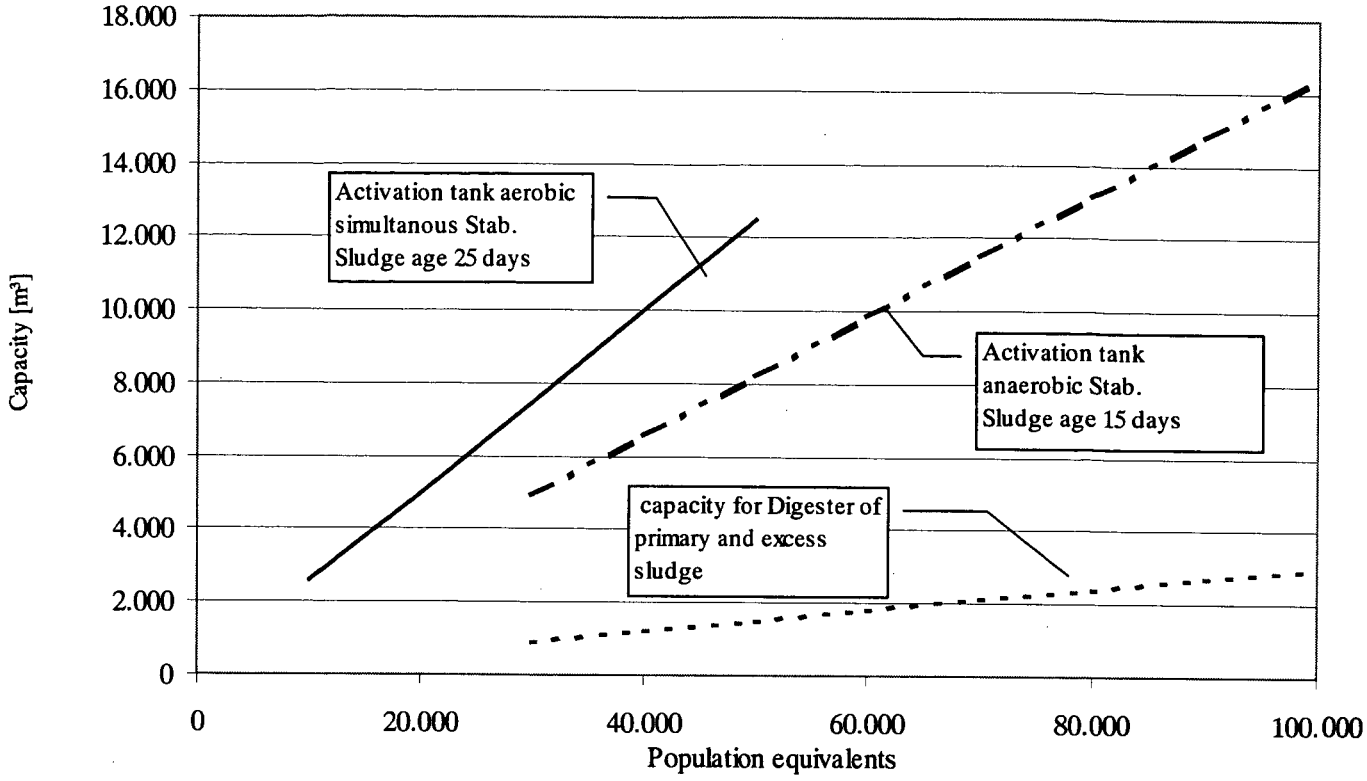


Figure 1 Volumes of activation tanks and digesters of the case study

The operating method with anaerobic stabilization of primary and excess sludge requires smaller activation tanks, but need a digester instead. Regarding the energy production by block heating works only 1/3 of the produced energy is electric. Nearly the half of the produced energy is still heat and more or less 20 % of the energy is lost.

The following picture shows the correlation of energy need for sludge activation of both operating methods and energy production by combusting biogas . The energy production by biogas is shown as positive value while the negatives values indicates an energy consumption. From an energetic point of view it becomes obvious that the anaerobic stabilization of primary and excess sludge supports a big portion of its own energy need for activation. Assuming that with further progress in isolation materials the efficiency of block heating works can be advanced, the energy need for the whole wastewater treatment plant could be supplied by biogas combustion.

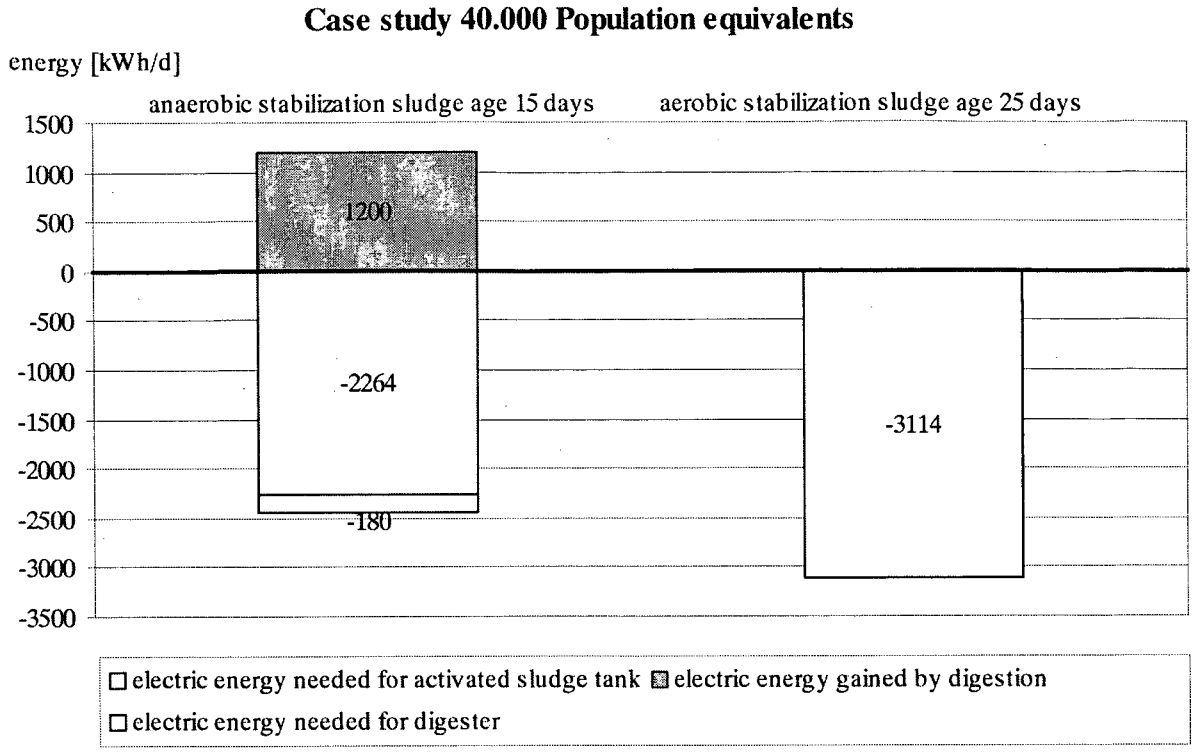


Figure 2 Case study 40.000 population equivalents

Apart from the energy topic the disposal of the digested sludge is still a problem. Operational conflicts as mentioned earlier may be the following:

Table 5 Rating of selected causes and effects of the examined sludge treatment processes

Anaerobic stabilization of primary and excess sludge		
rating	Cause	Effect
+	Higher biogas portion	Improvement of electrical power production in quality and quantity
-	Treatment of bigger amounts of sludge	Larger digesters and gas tanks + disposal of digested sludge + more land use
Aerobic simultaneous stabilization of excess sludge		
rating	Cause	Effect
+	No sludge treatment	no digesters and gas tanks + no investment
-	No energy gain	need of external energy for operation
-	Larger activated sludge tanks	higher investment and operation costs

This theoretical example shows that even for small wastewater treatment plants it is not reasonable to use aerobic stabilization of the excess sludge simultaneously in the activation tank. Enlarging the activation tank for a stable nitrification leads to a partial aerobic stabilization of the excess sludge, part of the organic

fraction of the sludge will still not be used by energetic means, but will be converted to CO_2 by biological processes.

3 Case study: incineration of raw or digested sludge

An investigation of Born et al. (1994) did an overall balance of digested and raw sludge combustion.. Aim of the investigation was to find out energetic advantages and disadvantages of different sludge treatments Raw sludge exceeds the energy potential of digested sludge by 40 %. For an overall balance of sludge combustion the amount of biogas produced from sludge digestion is important.

Three operating methods of sludge treatment were exemplary analyzed in regard of energy.

Variant A: digestion/dewatering/drying/incineration

Variant B: dewatering/drying/incineration

Variant C: dewatering/incineration

The following assumptions form the basis of calculation:

- Quantity of dry solids 3000 kg DS/h equivalent to an waste water treatment plant of 1 million population equivalents
- Ratio of organic and inorganic matter 2:1
- Degradation of organic matter during the digestion 50 %
- Mechanical dewatering up to 30 % DS
- drying of 30 % DW up to 60 %
- caloric value 21.000 kJ/kg DS_{org}
- excess air during incineration n=14
- utilization of energy by operation of back pressure turbine

Figure 3 shows the balances of all three variants. Exclusively for variant A the energy balance is positive. Utilization of biogas for power generation and for heating led to this result.
In case of incineration of the non digested but dewatered sludge (Variant B) a higher quantity of dry solids pass through the thermal treatment which negatively influences the energy balance. Compared to the incineration of digested sludge (Variant A) a reduction of produced thermal energy of 25 % can be calculated. External electrical energy has to be supplied to the process.
From an energetic point of view the variant C is the last effective one. Incineration of only dewatered sludge produces 10 % less thermal energy but the need for electrical power is more than that of variant A.
Overall the study showed that variant A which involves the incineration of digested and dewatered sludge is the best operating method by energetic means.
Furthermore it is easier to dewater digested sludge than undigested sludge and the digested sludge is less likely to produce bad odors when stored before finally disposition.

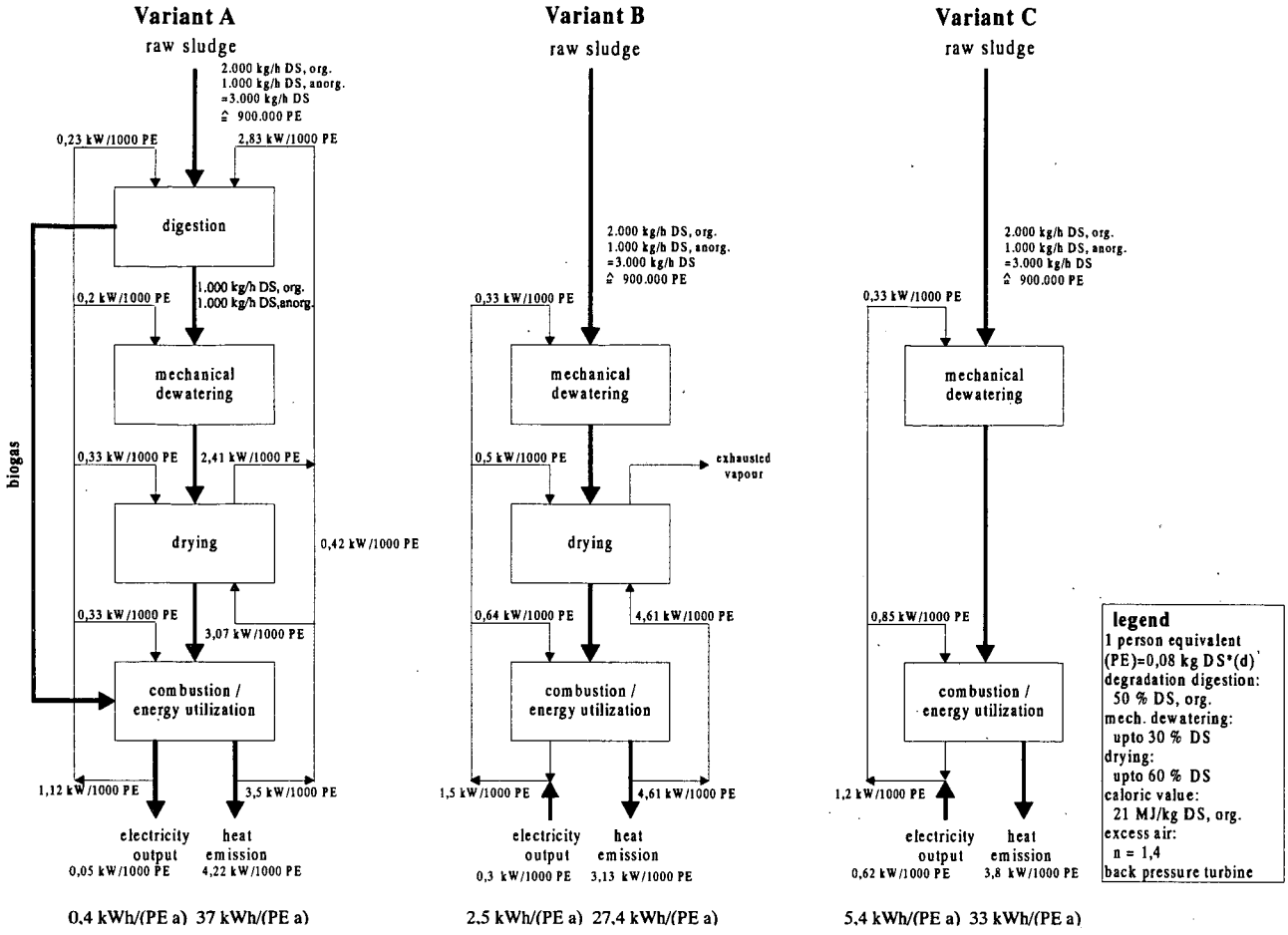


Figure 3 Energy balances for different operating methods of sludge treatment [Born, 1994]

In concrete case decision should be made after looking closely at all circumstances.

4 Wastewater Treatment plant Hildesheim

4.1 Wastewater Treatment Plant Hildesheim

The extension of the wastewater treatment plant Hildesheim by a biological stage with nitrification, denitrification and biological phosphorous removal was conceived in 1982/1983. At this time, practical experiences with full scale plants for biological phosphorous removal were available only from plants in South Africa, where, as a rule, the wastewater is rather concentrated, that is the sedimented BOD ranges from 300 to 400 mg/L. In contrast, in Hildesheim one can expect concentrations below 100 mg BOD/L on rainy days or with high amounts of sewer infiltration water. The plant is run using the ISAH-process, the main asset of which is that the return-sludge is denitrified in a separate anoxic tank in order to prevent any possible impairing of the phosphate removal through return nitrate. If necessary, additional substrate can be fed from the anaerobic tank. Of the four lines planned for the activated sludge plant, two were built and started in July 1987, in order to use operation experiences for the construction of the other two. The first of these was started at the end of 1996, the second is about to be initiated very soon.

Table 6 Dimensioning Data (2 lines) of the wastewater treatment plant Hildesheim

aeration tank	V = 2 * 7.100 m^3 = 14.200 m^3 t_R = 11,3 h Aeration aggregates: 6 mammoth rotors per tank Aeration capacity. 288 kg O_2/h per tank V_{anox} = 2 * 625 = 1250 m^3 V_{an} = 2 * 875 = 1750 m^3
secondary clarification	V = 2 * 3360 = 6720 m^3 A = 2 * 1018 = 2036 m^2 Effluent through submerged pipes

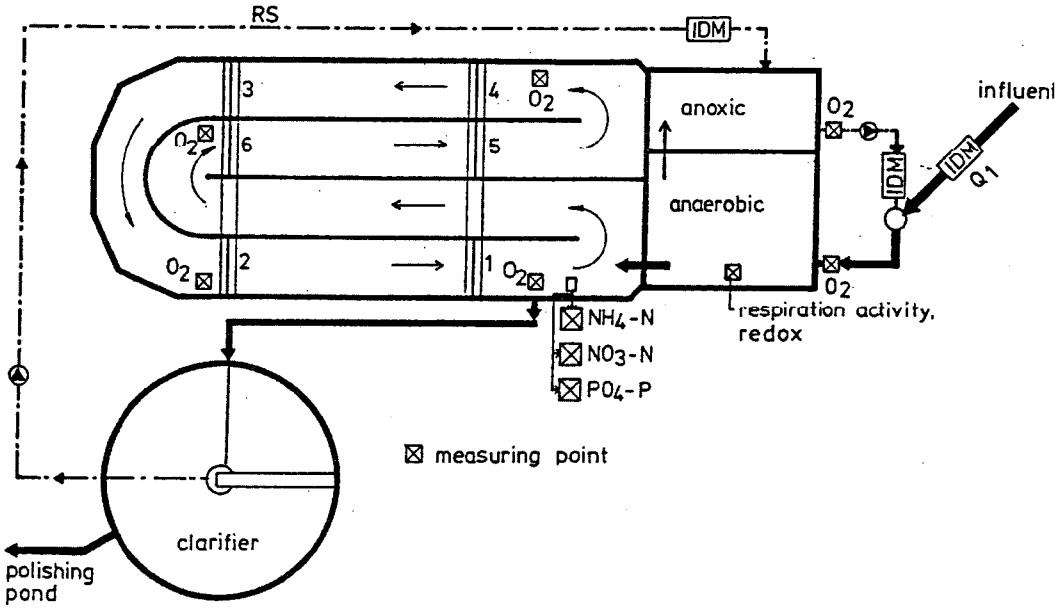


Figure 4 Flow diagram of the wastewater treatment plant Hildesheim

The following results were gained from the operation data of the year 1992. Comparing these data with those for the dimensioning data for 4 lines, a work load of 80 % is already reached, even though only 50 % of the scheduled volume of the entire plant were existent. In spite of this relatively high load, the effluent data of the wastewater treatment plant were satisfactory for the parameter *nitrogen* (in mineral form). The reason for the high effluent data in regard to the parameter *total phosphorous* is the nitrate concentration in the influent, which is at times very high (up to 6 mg/L); this is due to the input of spring water with high nitrate loads into the sewage system. Moreover, the average contact period in the anaerobic tank is 54 minutes (in 1992), which is quite short. Both phenomena have a negative effect of the effluent data in regard to the parameter *total phosphorous*.

Table 7 Load data of the wastewater treatment plant at Hildesheim for the operation with 2 lines in 1992 (average data), (*) in regard to the loads in the effluent of the primary sedimentation tank

	Operation 1992 (2 lines)	*Dimensioning (4 lines)*
Q	28.944 m^3 /d	37.500 m^3 /d
DS	3,12 g/l	3,0
BOD	7.786 kg/d	9.500 kg/d
NH_4-N	1302 kg/d	2.025 kg/d
$P_{tot.}$	348 kg/d	375 kg/d
Sludge Loading	ca. 0,11 kg BOD/(kg DS * d) (*)	0,06 kg BOD/(kg DS * d)

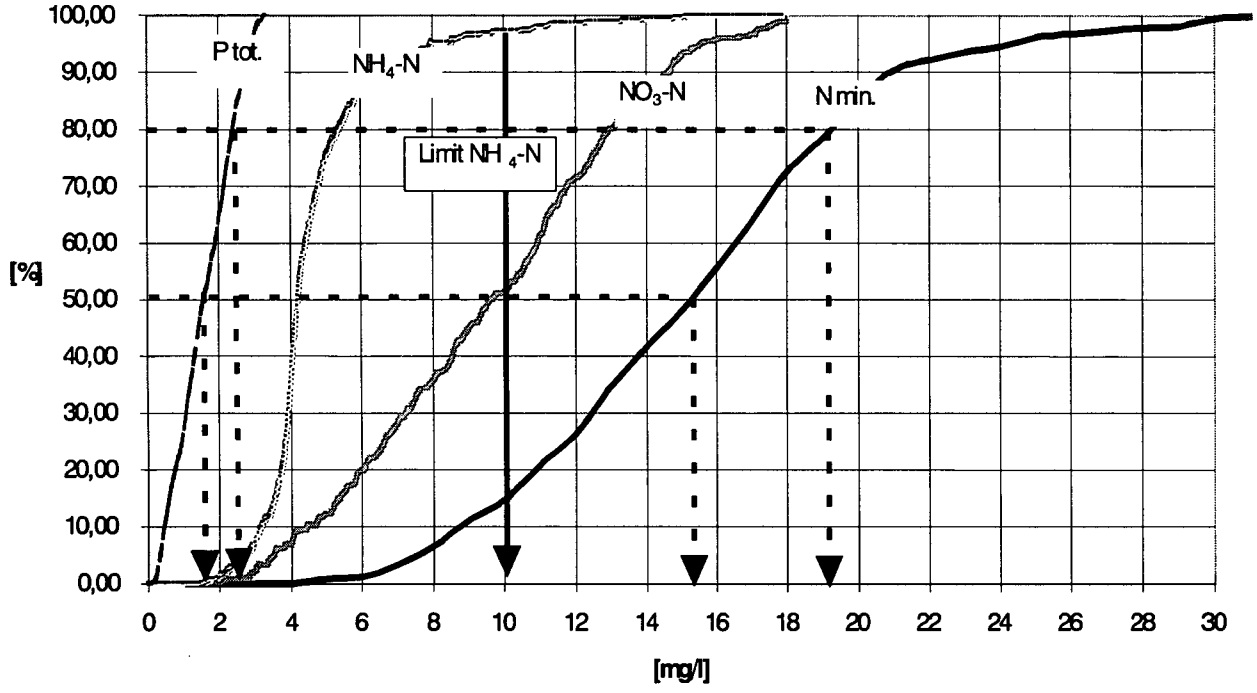


Figure 5 Cumulative frequency for the parameters mineral nitrogen in the effluent of the secondary clarification at the wastewater treatment plant at Hildesheim as average of the year 1992 (results with 2 lines only)

For the analysis period (1992), the relevant limit was only 10 mg/L for the parameter NH_4-N. For the parameter $P_{tot.}$, no limit was imposed up to the end of 1992. Yet, the limit of 2,0 mg $P_{tot.}$/L, which was introduced in 1993, could be observed already in the average effluent concentration of 1992. These operation data could be achieved without any supporting simultaneous precipitation. Since December 1996, the third of four lines has been operated. The first analysis of the operation data for the period between 12/1996 - 3/1997 evinced these average effluent concentration: 11,5 mg/L for $N_{min.}$, and 0,98 mg/L for $P_{tot.}$. This improvement was apparently due to the favorable impact of the third line.

4.2 Sludge and energy

In the wastewater treatment plant Hildesheim the fractions excess and primary sludge are currently treated in different anaerobic digesters.

The primary sludge undergoes anaerobic treatment until stabilization in an egg-shaped digester with a volume of 4.500 m^3 for 16 to 18 days at temperatures between 37° and 39° C.

The excess sludge is digested in two parallel operated digesters. Each of the digesters has a capacity of 1.700 m^3. Over of period of 20 to 22 days the excess sludge undergoes anaerobic stabilization at temperatures between 31° to 33° C.

Table 8 Selected parameters of the primary and excess sludge of the WWTP Hildesheim

Parameter	*Primary sludge:*	*Excess sludge*
DS	4,74 %	3,29
Ignition loss	67,51	72,51
DS digested	2,82%	1,99
Ignition loss digested	51,05%	65,23

The anaerobic stabilization of the excess sludge leads to a biogas production of 4,0 L/(P*d) whereas the anaerobic stabilization of the primary sludge causes a biogas production of 16,6 L/(P*d). To compare these amounts a biogas produced it is necessary to take into account the amounts of produced sludge as well. The treatment plant at Hildesheim has a daily production of 80-100 m^3/d of primary sludge and 70-90 m^3/d excess sludge. This indicates a higher organic content in the primary sludge, which is responsible for the higher biogas production.

To be able to evaluate the biogas production properly it is necessary to consider the biogas production in relation to the mass of volatile suspended solids (VSS) entering the plant.

The biogas production per kg VSS is very high in the plant Hildesheim compared to literature data. For primary sludge a biogas production of 1046 L/kg VSS and for excess sludge a biogas production of 419 L/kg VSS was measured. The Hildesheim treatment plant can cover its own energy to about 50 % by producing electrical power from biogas.

5 Wastewater Treatment Plant Bremen-Seehausen

5.1 Wastewater Treatment Plant of Bremen-Seehausen

In 1989, the municipal wastewater treatment plant at Bremen Seehausen consisted of a preliminary clarification plant topped with a two-stage activated sludge plant; because of the high work load, nitrification could not be run in the latter. The limits for phosphorous could be observed by constructing a dosing station for precipitation agents in 1989. In order to observe the demanded limits in regard to the parameters nitrogen and phosphorous, the plant had to be extended. For reasons of space and economy, the extension of the wastewater treatment plant had to be designed in a way that the existing two-stage activation plant could be smoothly integrated into the new plant. The new activation plant was initially dimensioned for 50% of the influent according to the German wastewater guideline A 131, and then extended following the ISAH-process described above.

The dynamic simulation of this option showed that due to the reduced work load the old plant was only able to nitrify; denitrification was not possible. As a result, the nitrate values in the effluent of the entire plant would have continued to be high. This would have impaired the chances to observe the demanded limits, and it could have led to denitrification in the secondary clarification unit, a phenomenon which might have led to loss of biomass.

In order to still reach the demanded clarification performance for the combination of the two plants, several extension options were designed for the old plant via dynamic simulation; the different options were compared in regard to their degradation performance. Considering the saving potential inherent in using the old parts of the plant, the most favorable option was the reconstruction of the old plant as one-stage plant.

The tank of intermediate clarification of the former two-stage plant was now used as tank for secondary clarification of the new part of the plant. Thus, it was possible to do without further tanks for secondary clarification. The old plant was redesigned as one-stage plant for nitrification/denitrification and built in cascade form. Additional measures for nitrogen reduction could thus be dispensed with.

Table 9 Dimensioning data of the wastewater treatment plant at Bremen-Seehausen

old plant	*Modul*
Aeration tank	$V = 24.500\ m^3$
Secondary clarification	$V = 14.112\ m^3$
	$A = 5.040\ m^2$
new plant	*Modul*
Aeration tank	$V_{AN} = 8.140\ m^3$
	$V_{DN} = 25.700\ m^3$
	$V_{N} = 54.300\ m^3$
	$V_{DN\text{-}RS} = 5.560\ m^3$
Secondary clarification	$V = 31.293\ m^3$
	$A = 11.176\ m^2$

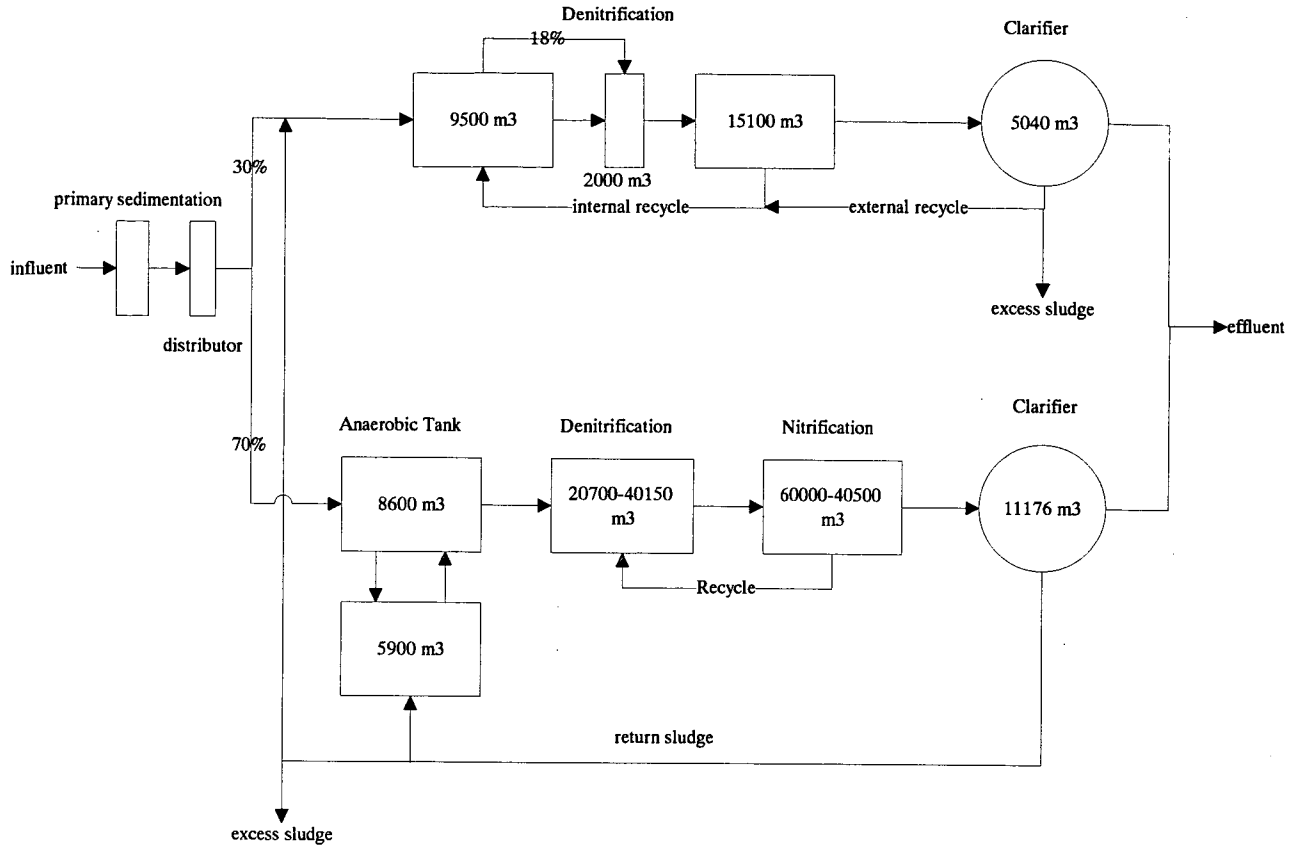


Figure 6 Flow diagram of the wastewater treatment plant at Bremen-Seehausen, accepted extension option [HARTWIG, KRUSE/1996]

Table 10 Operation data of the wastewater treatment plant at Bremen-Seehausen, (*) no data available

	Dimensioning	Operation data December 1996
$Q_{dry\ weather}$	143.000 m³/d	120.400 m³/d
$Q_{storm\ water}$	14.300 m³/h	- (*)
BOD	41.700 kg/d	29.761 kg/d
N_{tot}	11.200 kg/d	7.897 kg/d
P_{tot}	2.300 kg/d	1190 kg/d
DS (Average of both plants)	3,4	3,7
Sludge Loading		
Average of both plants	0,11 kg BOD/(kg DS * d)	0,08 kg BOD/(kg DS * d)
old plant	0,15-0,16 BOD/(kg DS * d)	0,09 kg BOD/(kg DS * d)
New plant	0,10 kg BOD/(kg DS * d)	0,08 kg BOD/(kg DS * d)

Comparing this extension option with the original concept, the effluent concentrations in the entire effluent are better, which is particularly due to the reduced effluent concentrations from the old plant. The reconstruction works at the old wastewater treatment plant were finished at the end of 1996. The new part of the plant was started on 01.07.1996.

5.2 Sludge

The primary sludge resulting from the primary treatment is mixed with the excess sludge from activation - which is thickened separately- and fed to the digester. The retention time in the digester is currently 17 days at a temperature of 37 °C, so that the digestion process has reached a degree of stabilization of 54 %. After digestion water is withdrawn from the sludge by centrifuges the remaining thickened sludge – nearly 90 % - is used as fertilizer in agriculture.

The following table shows the produced amounts of sludge of each treatment step, their DS and VSS content. By thickening the excess sludge the volume is reduced while simultaneously increasing its DS content. The organic components in the sludge remain unchanged. During digestion of the sludge the organic components of excess and primary sludge are oxidized to CO_2 so that the VSS content is reduced. The volume of the sludge in the digester is not reduced by this. The following treatment steps, dewatering and centrifugation, only cause a reduction of sludge volume and therefore an increase of the DS content. These steps have no influence on the organic components and the VSS content remains the same.

Table 11 Selected parameters of the sludge treatment of Bremen-Seehausen (*) stage1, (**) stage 2, (***) sum of stage 1 and stage 2

	Volume [m³/d]	*DS* [g DS/L]	*VSS* [%]	*Load VSS* [kg/d]
Primary sludge (PS)	1.136,0	34,9	77,1	30.567,4
Excess sludge (ES)	3.223,0 (*)	5,5(*)	75,6(*)	20.824,0(***)
	2.364,0 (**)	5,1(**)	59,6 (**)	
Thickened sludge only ES (TS)	498,0	60,1	68,8	20.591,7
Sludge fed to the digester (TS+PS)	1.634,0	39,9	70,4	45.898,4
Digested sludge	1.688,0	23,0	53,4	20.732,0
Sewage sludge dewatered 8%	50,7	143,0	53,4	3.874,8
Sewage sludge dewatered 21%	145,0	214,0	53,4	16.571,6

From the point of view of energy production the organic portion of the treated sludge is important, since this portion produces biogas instead of CO_2 during the digestion process. The table above shows that the organic portion of the sludge is reduced from 70,4 % before the digestion to 53,4 % after digestion, this means that about 17 percentage steps of the organic portion are used up by digestion.

5.3 Energy

The biogas of the gas tank is used for the production of electricity with the help of block heating works. Each year 8.460.770 Nm^3/a[2] biogas are produced and about 812.000 Nm^3/a biogas from external sources are used.

The block heating works need about 8.460.770 Nm^3/a, the torches use up 13.500 Nm^3/a and the heating needs 13.430 Nm^3/a. Adding the electricity gained from wind, 568.642 Nm^3/a, a total energy of 10.451.880 kWh/a is produced by the treatment plant itself. Since this is not enough to cover the energy need of 15.000.000 kWh/a another 4.566.092 kWh/a are supplied by external sources.

This makes clear that the wastewater treatment plant Bremen-Seehausen is able to cover to 2/3 of its energy demand by biogas combustion and wind energy.

6 Wastewater Treatment Plant Hannover Gümmerwald

6.1 Wastewater Treatment Plant Hannover Gümmerwald

The wastewater treatment plant Gümmerwald was taken into operation in 1983 and is part of the wastewater treatment plant association Herrenhausen-Gümmerwald. In addition to sewage which cannot be treated in Herrenhausen for capacity reasons sewage from several other suburbs and communities is processed.

A intercepting sewer connecting Herrenhausen and Gümmerwald allows an adaptation of the amount of sewage treated in each plant so that certain situations like repair work can be handled easily. Special about the plant Herrenhausen is the treatment of digested sludge. In the normal operation mode the whole filtrated water is mixed with the influent water going to the primary treatment. However it is also possible to add it to the main treatment step. A block heating engine is used for biogas combustion.

[2] Nm^3 = Normkubikmeter, temperature: 0°C, pressure: 1013 mbar

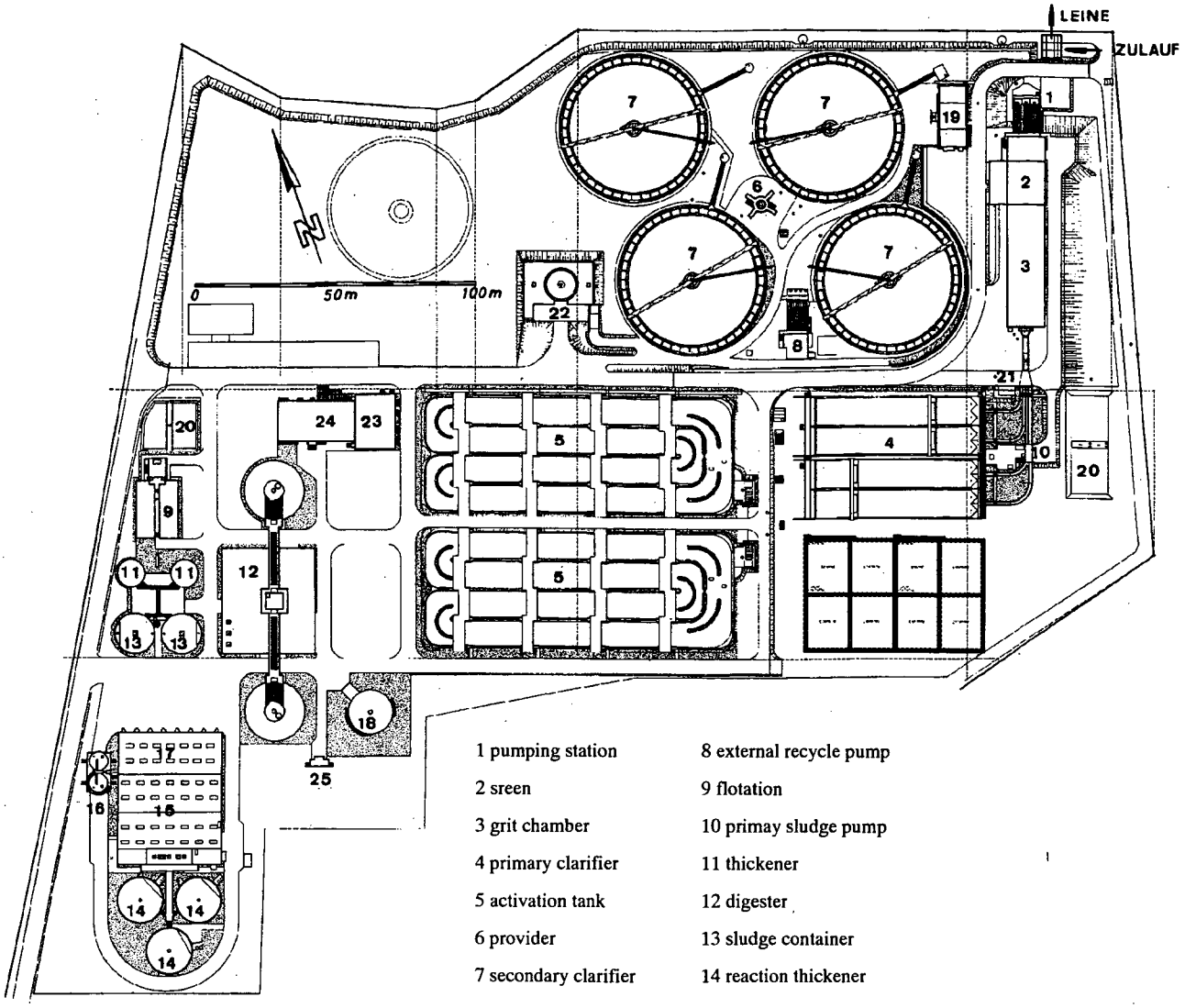


Figure 7 Flow diagram of the wastewater treatment plant Hannover-Gümmerwald

6.2 Anaerobic tank

The step for the improved biological phosphorous elimination consists of two lines with 4 tanks each. The first tank was planned for reentering sludge (RS-denitrification-tank). By opening the sewage afflux canal (ISAH operating method) untreated sewage can be used as additional substrate in the RS- denitrification -tank. When high amounts of sewage come in for short periods of time it is furthermore possible to use part of the sewage flow from the last anaerobic tank by having re-circulation pumps pumping the sewage into the RS- denitrification -tank. This increases the retention time in the tank and therefore the phosphorous resolution.

Yet another possibility to lower the phosphorous concentrations in the efflux at short notice it is planned to add the extra substrate acetyl. If it is still not possible to fulfill the requirements iron II chloride has to be used to precipitate the phosphorous.

6.3 Anaerobic-tank

The exact size of the tank is:

- 4 tanks of 1350 m^3 = 5400 m^3 each
- depth 4,50 m
- substrate connection 1,50 x 1,50 m = 2,25 m^2

6.4 Tank with circulating flow

The activation step of the wastewater treatment plant Gümmerwald consists of two separate circulation ditches which run back and forth four times each. The ditches are 100 m long and the aeration is supplied by 8 mammoth rotor pairs in each tank.

The exact size is:

- volume 2 x 15.000 m^3
- depth 3,55 m
- length 108,50 m
- width 41,10 m

6.5 Secondary clarifier

The secondary clarifier consists of four settling tanks with vacuum scraper. In the course of extending both, Gümmerwald and Herrenhausen, a new secondary settlement tank was added and taken into operation.

The exact sizes of the old secondary clarifier:

- Volume per tank 5.000 m^3
- depth 2,55 m
- surface 1962 m^2

6.6 Dimensioning

The wastewater treatment plant Gümmerwald was planned for the following dimensions.

Table 12 Dimensioning and operation data of the WWTP Hannover-Gümmerwald (*) no data available

	Dimensioning Data	*Operation data*
Influent AT	Concentrations	Concentrations
BOD	22.000 kg BOD /d	21.000 kg BOD/d/
Daily $Q_{\text{dry weather}}$	80.000 m^3/d	60.000 m^3/d
Max $Q_{\text{dry weather}}$	1,25 m^3/s	(*)
Min. $Q_{\text{dry weather}}$	0,55 m^3/s	(*)
$Q_{\text{storm weather}}$	1,7 m^3/s	(*)

6.7 Sludge

The primary sludge is treated in two separate round thickeners with 500 m^3 volume each. Afterwards it is stored together with the excess sludge from the secondary clarifier in a digester. This digester consists of two tanks which have a capacity of 1.500 m^3 each. The digestion takes place at a temperature of 38 °C for 24 days. The produced amount of biogas is stored in a dry gas container with a volume of 1.500 m^3. The digested sludge is stored temporarily in two tanks, each 1.750 m^3 big.

Table 13 DS and ignition loss of primary, excess and digested sludge of the wastewater treatment plant Hannover-Gümmerwald

	DS [%]	*Ignition loss[%]*
Primary sludge	6,5	65,8
Excess sludge	4,9	70,2
Digested sludge	3,7	51,2

The organic fraction of both, primary and excess sludge, can be reduced to an ignition loss of 51,2 % by anaerobic stabilization. The average amount of 8.294 m^3/d biogas is produced during the process of anaerobic stabilization. With this the wastewater treatment plant Gümmerwald can cover 56 % of its energy need.

7 Conclusion

If the effluent concentration requirements which will become law in 2005 and the advanced wastewater treatment with nitrogen and phosphorous elimination are set as a goal it is necessary to take a close look on energy flows, sludge flows and requirements for the reduction of nutrients.

Since 1/5 of the energy demand of municipal facilities is used wastewater treatment plants it is for economic reasons to optimize such plants.

7.1 Energy balances Hildesheim - Bremen - Hannover

The analysis and evaluation of operation journals shows that the investigated wastewater treatment plant are able to cover a big part of their energy needs by biogas combustion which is produced during anaerobic sludge stabilization. All three treatment plants use similar sludge treatment methods. The following table shows average digestion temperatures and the average retention times of the sludge in the digester. It is a mesophilic digestion process. The reduction of the organic fraction in the sludge is a measure degree of stabilization.

Table 14 Results and overview of the sludge treatment and the energy supplies of the examined wastewater treatment plants Hildesheim, Bremen-Seehausen, Hannover-Gümmerwald

	Hildesheim	Bremen-Seehausen	Hannover-Gümmerwald
Sludge			
Sludge treatment facility for dewatering	centrifuge	centrifuge	chamber filter press
Digestion Temperature [° C]	37 – 39 PS 31 – 33 ES	37	37
Duration of digestion [days]	16 – 18 PS 20 – 22 ES	17	17
Decrease of carbon content of sludge [%]	16	25	25
Energy			
Population	195.000	700.000	650.000
Energy need [kWh/a]	5,5 Mio	15 Mio.	13,1 Mio.
Energy need [kWh/(P a)]	45,6	21,4	20,1
Energy production [kWh/a]	2,9 Mio.	10,5 Mio.	7,3 Mio.
Energy production [kWh/(P a)]	14,9	15	11,2
Coverage of energy need by biogas combustion [%]	53	67	56

- The anaerobic stabilization of primary and excess sludge produces biogas which can be used for power generation
- Operating methods which reduce the carbon content of the sludge are a disadvantage by means of power generation since the carbon is only respired and not used for energy purposes.

Here presented data gives an overview on the energy potential of sludge and shows how much of the energy need of a municipal wastewater treatment plant can be covered by the plant itself. Some aspects like disposal problems and environmental questions are not covered in this paper since not enough data is available so far. To give a detailed overview, which goes beyond the correlation of power generation and sludge it is necessary to list all material and energy flow regarding sludge. For this purpose a Life Cycle Assessment (LCA) is favorable.

The following gives a brief summary about LCA and its use for the sludge circle. To get several points of view on the subject and to the circumstances into account which matter more for other areas that Germany it is an interesting perspective to work in cooperation with a technological equal partner like Japan.

7.2 Life Cycle Assessment

According to the International Organization for Standardization (ISO) the following steps for the evaluation of a product are requirement:

- Goal definition and scoping
- Inventory analysis
- Impact assessment
  - Classification
  - Valuation

The topic sludge can be explained by the following points:

- Avoidance of sludge
- Avoidance danger potential of sludge
- Using energy potential of sludge
- Recycling the valuable materials of the sludge

Sludge avoidance in biological wastewater treatment is only possible to a certain extend. Some new methods for sludge avoidance involve membrane biology. These methods produce a low amount of excess sludge compared to normal activation treatment with after treatment. The potential of sludge is due to its energetic and material resources. Sludge can be used as a fertilizer, sludge can be used for power generation by burning the biogas from sludge digestion. Last but not least sludge is a residence waste with all the accompanying problems.

Since sludge can be harmful, for example because of heavy metal accumulation or chlorinated hydrocarbons it has to be investigated what effects it has on the environment. For the heavy metal content the sewer system is as well important. Sludge form treatment plants supplied with sewer form a combined sewer system has a higher heavy metal content than the sludge of a plant connected with a separate system, in which the heavy metals are discharged with the storm water into the receiving waters [Boller].

7.2.1 Goal definition and scoping

The goal definition and the scoping establish the purpose of the examined topic on which the functional unit as a central measure will be defined. In addition to that the system boundaries of the study and the level of detail required for the LCA has to be set.

Possible goals of sludge treatment are:

- Sludge as resource and valuable materials
- Reduction of external energy used for advanced wastewater treatment
- Land use of digesters, landfilling and agricultural purpose
- CO_2 production during activation and combustion of biogas
- Hazardous content of sludge

The functional unit should cover all representative product or operating method alternatives according to the goal definition and scoping. More complete is the determination of the system boundaries and the level of detail.

7.2.2 Inventory analysis

For an inventory analysis the flow of resources and energy and the emissions of parameters influencing the environment has be contributed to the following components of a advanced wastewater treatment plant.

- Activation tanks
- Digester and gas tanks
- Facilities for sludge treatment like drying, dewatering, incineration etc.
- Facilities for energy production, block heating works, gas combustion engines etc.

The following parameters should be taken into account: consumption of material and energy for building, operation and abridgement of the plant as well as the use of land on which the plant is built on and the treatment of residue.

7.2.3 Classification

For an efficiency analysis or a classification all effects and emissions of investigated parameters – for example CO_2 for global warming – have to be recorded at all stages of the sludge cycle and for all sludge fractions. Emissions of substances have to be seized according to their relevance's in the ecosystem and whereas necessary combined to useful aggregated parameters. For example the efficiency potential of 1°kg CH_4 equal the potential of 40 kg CO_2 in regard to the problem of global warming. To aggregate different substances to only one potential parameter like CO_2 a lot of research has to be done.

7.2.4 Evaluation

When evaluating different operating methods for wastewater treatment regarding the goal definition the results of the inventory analysis have to be compared to those of the efficiency analysis. This allows to find the ecologically and economically best operating method for sludge treatment.

7.2.5 Sludge as energy source

Treatment plants with proper operating methods produce enough sludge to cover 60 % of their own energy demand. For an analysis of energy flows the energy used for preparation of sludge for digestion has to be compared to the energy produced by digestion. High organic loads in the sludge had to higher energy yields so that aerobic simultaneous stabilization has to be rated as unsuitable for energy production from sludge.

7.2.6 Sludge as residue

The residue sludge can be disposed by combustion, landfilling or it can be used as a fertilizer in agriculture. For combustion a dewatered sludge with a high organic load is necessary. Landfilling need a dewatered digested, that means biologically inactive, sludge with a less carbon content. For agricultural use digested sludge with a high content of nitrogen and phosphorous is important, because of further fertilizing the land.

A further possibility is the recycling of nutrient salts from sludge which could be especially interesting for Phosphorous, for which the world resources are limited.

The following is only focusing on the disposal of sludge since a LCA for a complete analysis of the sludge cycle would exceed a paper like this. For a LCA the global aspect of sludge treatment is important. Usually CO_2 emission functions as guideline, in addition to CO_2 parameters describing risks for human beings and the environment as well as parameters for eutrophication, acidification, odor etc. are part of the LCA. The following table shows disposal paths of sludge, goals and substance parameters are listed.

Table 15 Possible goals of a LCA for sludge disposal paths

Disposal path	*Goal*	*Evaluation parameters*
Incineration	Reduce of: Global warming, human toxicity, odor	CO_2, CH_4, PAC, AOX
Landfilling	Reduce of: Human and ecotoxicity, eutrophication	Heavy metals, PAC, AOX, N, P
Agricultural use	Reduce of: Human and ecotoxicity, eutrophication, acidification	Heavy metals, PAC, AOX, N, P

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Proper control manual for Anaerobic－Anoxic－Oxic (A 2 O) process

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1. Abstract

With regard to the removal of the nutrients for preventing the eutrophication of closed water body like Tokyo Bay, nitrogen and phosphorus removal method in wastewater treatment plant is required to be established.

Recently, the anaerobic－anoxic－oxic (A 2 O) activated sludge process has been adopted in some wastewater treatment plants in Japan.

It is one of the effective advanced wastewater treatment methods that can eliminate the nutrients biologically.

However, A 2 O process is more complicated than the conventional activated sludge process, because optimum condition as for nitrogen removal is contradictory to those for phosphorus removal.

And it requires the operation based on more careful and continuous monitoring.

Recently, Bureau of Sewerage of Tokyo Metropolitan Government could obtain the proper control manual for A 2 O process.

The optimum values of the typical operation indices are as follows.

(1) Sludge Retention Time, between 1 2 and 1 5 days.
(2) Return Sludge Ratio, about 5 0%.
(3) Mixed Liquor Recycling Ratio, about 1 5 0%.
(4) Dissolved Oxygen at the outlet of the oxic tank, between 1.5 and 3.0 mg／l .
(5) Mixed Liquor Suspended Solid, between 1,500 and 3,000 mg／l.

2. Key Words

Anaerobic－anoxic－oxic(A 2 O), Nitrogen removal, Phosphorus removal,
Nitrification, Denitrification, Phosphorus release,
Excess uptake of phosphorus, Oxidation－reduction potential (ORP)

3. Introduction

Recently in Japan, the anaerobic－anoxic－oxic (A 2 O) process has begun to be employed as a biological nutrient removal process. This process is based on two

different processes ; biological phosphorus removal and biological nitrogen removal.

In addition to organic matter that can be removed by conventional activated sludge process, it can remove nitrogen and phosphorus at the same time.

The Bureau of sewerage of Tokyo Metropolitan Government conducted a study to establish the proper control manual for operation of the A 2 O process facility, intending to remove nitrogen and phosphorus steadily and rationally.

The first step of the study was collection and analysis of basic data on process characteristics of the A 2 O system. In the second step, control factors and their optimum values for the A 2 O process were studied using water quality analyzers installed at the experimental plant. In the third step, analyzing the results of the study, proper control manual for the operation of A 2 O process was obtained from various points of view.

4. Outline of Tokyo

Tokyo lies near the center of Japanese archipelago. The total area of Tokyo Metropolis amounts to 2,183 square kilometers. Tokyo's climate is warm, with an average annual temperature of 15 degrees Celsius and average annual rainfall of 1,800 millimeters.

As of today, there are approximately 11.8 million people living in the Tokyo metropolitan area.

There are about 120 large and small rivers and waterways in Tokyo. Most of these flow into Tokyo Bay.

The water quality in Tokyo Bay has improved in comparison with the late 1 9 6 0 ' s, but the phosphorus and nitrogen concentrations are still high and eutrophication is still a chronic problem. This often causes Red tide, or deterioration in water quality due to propagation of phytoplankton, especially in summer.

Table.1 shows the status of the red tide in Tokyo Bay.

Table.1 Status of Red Tide in Tokyo Bay

Year	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
Days	80	82	78	69	84	74	68	80	106	120

5. Outline of Sewage of Tokyo

As of March 31, 1995, 100 percent of all residences in the Ward Area had sewers, as did 85 percent of all residences in the Tama Area, resultinging 95 percent dissemination ratio for the city as a whole.

We have 12 sewage treatment plants and 78 pumping stations in the Ward Area as of today. In this area, the average of total throughput is about 4.7 million M 3 a day.

Treated sewage water accounts for 91 percent of all metropolitan wastewater, and

therefore has a tremendous impact on the water quality of metropolitan rivers and Tokyo Bay. Table.2 shows the Effluent Quality of each treatment plant.

The" Master Plan for the Second−Generation Sewerage" was announced in 1992.

With this plan, efforts are being made to further improve the quality of treated sewage water through the gradual construction of advanced wastewater treatment facilities within existing sewage treatment plants.

Table.2 The Effluent Quality of each treatment plant (Ward area,1995)

(mg/l)

Item	Wastewater Treatment Plants									
	A	B	C	D	E	F	G	H	I	J
BOD	3	4	2	6	2	3	3	2	2	2
SS	2	4	2	6	1	4	2	3	3	0
T-N	19.1	30.1	14.5	20.8	10.4	22.9	19.9	14.7	14.6	17.8
T-P	1.2	1.5	1.3	1.5	0.6	2.0	1.4	1.7	0.9	1.2

6. Experimental plant and Methodology of the study

6. 1. Plant under Study

Figure. 1 shows the process flow diagram for the experimental plant and locations of water quality meters.

The bioreactor is a plug flow type deep layer tank with 13m(Wide) x 64m(Lenghs) x 10m(Depth) in size.

It is consisted of anaerobic tank, anoxic tank and oxic tank from the upper stream.

Partitions are built to separate each tank and to prevent short-circuit flow and reverse flow. The anoxic tank is divided into three parts and the oxic tank is divided into two parts by the partitions.

Flow rate of influent is controlled by the movable weir.

Dissolved oxygen (DO) level in the final circuit of the oxic tank is maintained at a constant level by the air flow control valve.

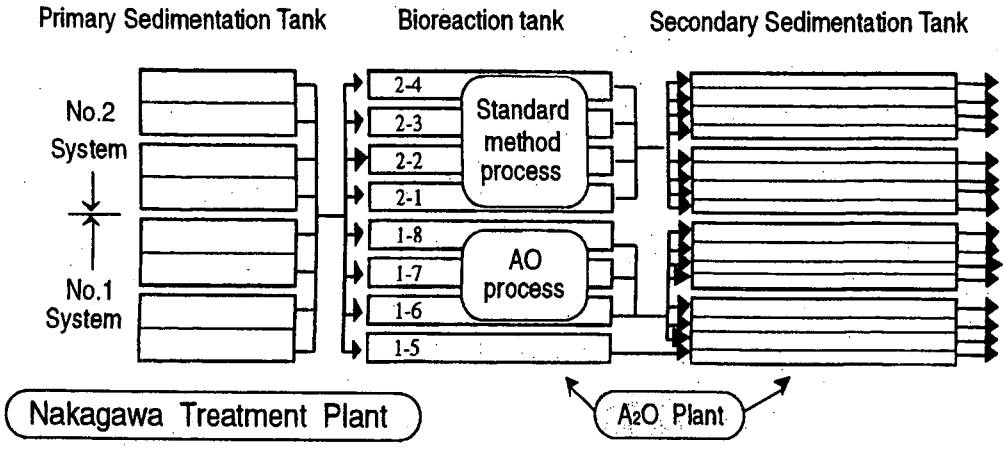
To mix the activated sludge, mechanical agitators are installed in each of the anaerobic tank and the anoxic tank, and a ceramic diffuser is placed in the oxic tank.

Three submerged pumps are installed in the final circuit of the oxic tank to recycle aerated water to the anoxic tank. The flow of recycled water is controlled to keep it in a desired ratio to the flow rate of influent into the bioreactor.

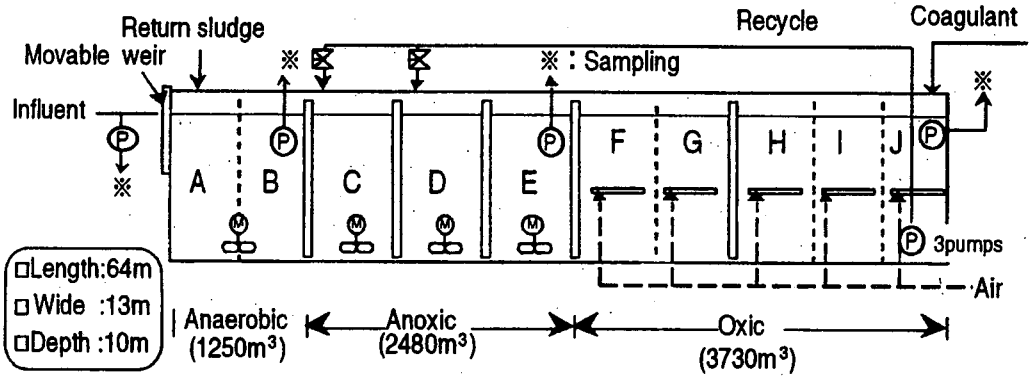
6. 2. Methodology

In the first step, to gain an understanding of the basic characteristics of the A2O process and operational conditions of the bioreactor (influent rate, return sludge ratio, nitrified mixed liquor recycling ratio, and DO level of the oxic tank), water quality data are collected from daily examinations and so on. These data were analyzed using computer.

In the second step, to determine operational conditions for the A 2 O process, correlation between the data measured by the water quality meters placed in the plant and the results of real water quality analyses were studied.



Bioreaction tank (No.1-5 line)



Set Location of Water Quality Meters

position / Sensor	Influ-ent	Anaerobic A	Anaerobic B	Anoxic C	Anoxic D	Anoxic E	Oxic F	Oxic G	Oxic H	Oxic I	Oxic J	Recircu-lation	Coagu-lant	Return sludge	Excess sludge	Sedimen-tation tank	Total
Flow rate	○											○	○	○	○		5
pH	○		○			○					○						4
ORP	○		$O_{\#2}$	○	○	○					○						7
DO	○							○			○						3
MLSS											○						1
SS														○			1
T-N	○					○					○					○	2 *)
T-P	○		○								○					○	2 *)
SV											○						1
Rr											○						1
Sludge level																○	1

*)、**) : Measuring in turn

Fig.1 Setting Points of Sensors and Schematic Flow of Experiment Plant

7. Results and Discussion

7. 1. Basic Characteristics of A 2 O Process

(1) Removal of nitrogen

The annual average of total nitrogen (T−N) in the influent to the bioreactor was 2 5 mg/l, while that in treated water was 5. 9 mg/l.

The removal ratio of T−N was fairly satisfactory. Figure 2 shows the behavior of nitrogen components (NH 4 −N, NO 3 −N, etc.) in individual tanks. As shown in the chart, the concentration of ammonia nitrogen decreases as one moves through the process. At the exit of the oxic tank, water was thoroughly nitrified, it contained ammonia nitrogen (NH 4 −N) at a level of less than 1 mg/l.

In autumn and winter when water temperatures were low, however, sometimes NH 4 −N levels were higher because the activity of the nitrifying bacteria was lowered.

On the other hand, in the denitrification process, recycled nitrate nitrogen (NO 3 −N) was almost completely removed in the anoxic tank, proving that denitrification reactions proceeded satisfactorily even in low temperature period. The concentration of NO 3 −N at the outlet of the oxic tank was often higher than that in effluent , suggesting denitrification reactions were also occurring in the secondary sedimentation tank.

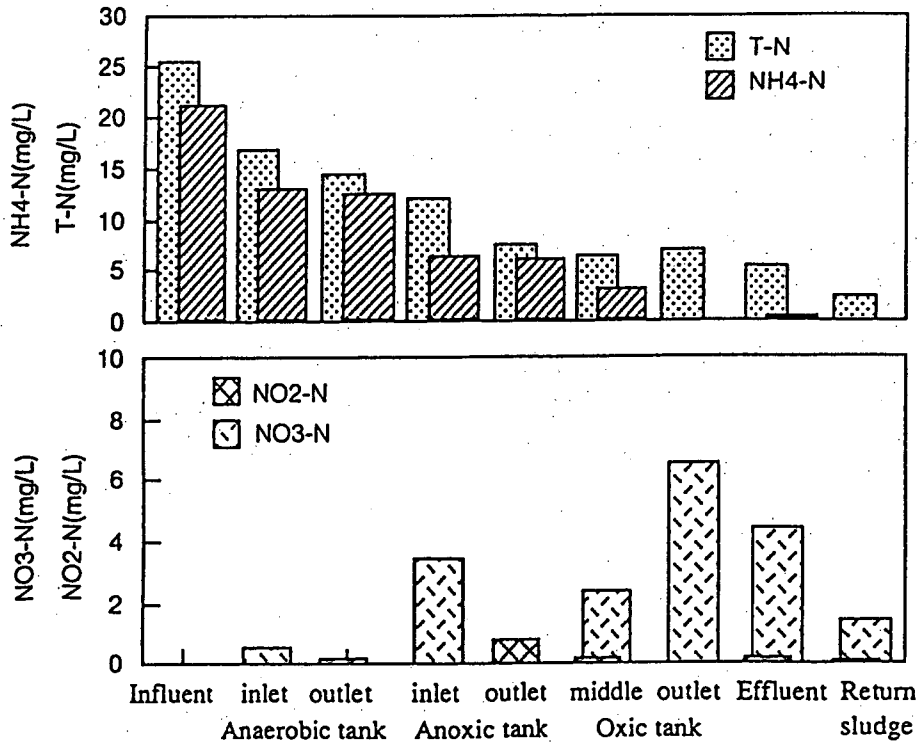


Fig. 2 Nitrogen Concentration Profile at Each Location in A 2 O process

(2) Removal of phosphorus

The annual average concentration of total phosphorus (T−P) in the influent was

3．5mg／l, while that in treated water was 0．3mg／l. The removal ratio of T－P was fairly satisfactory. Figure 3 shows the behavior of soluble phosphorus (s－P) in individual tanks. Phosphorus concentrations rose from about 2．5mg／l in the influent to about 6mg／l (about twice as much) in the anaerobic tank, showing that the bacteria released phosphorus.

The s－P concentration was less than 0．1mg／l in the oxic tank, which indicated excess uptake of phosphorus.

However, when it rained for several days in a row, phosphorus release mechanism did not function well, mainly because of a rise of DO in the influent, consequently the excess uptake dropped and so did the phosphorus removal ratio.

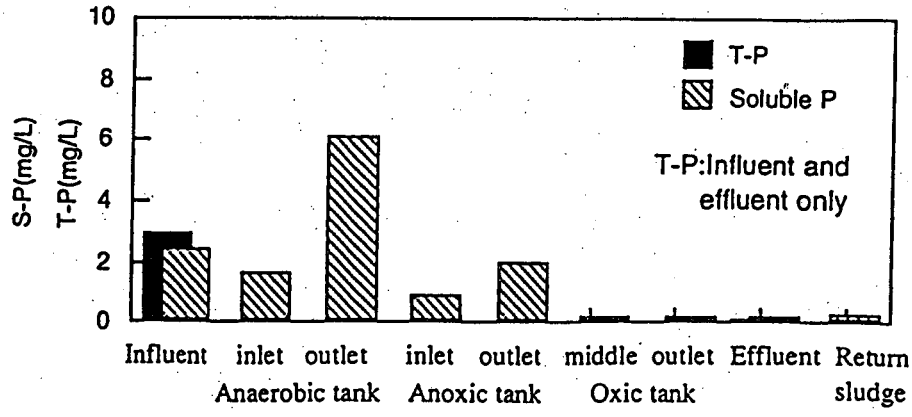


Fig. 3 Phosphate Concentration Profile at Each Location in A 2 O process

(3) Removal of organic matter

The annual average of the biochemical oxygen demand (BOD) in the influent was 1 3 2mg／l, while that in treated water was 2．7mg／l. The removal ratio of BOD was fairly satisfactory. Figure 4 shows the behavior of BOD in individual tanks.

As shown in the graph, BOD dropped drastically in the anaerobic tank. This is probably because organic matter in the influent was absorbed by bacteria in the activated sludge and remained there as accumulated organic matter.

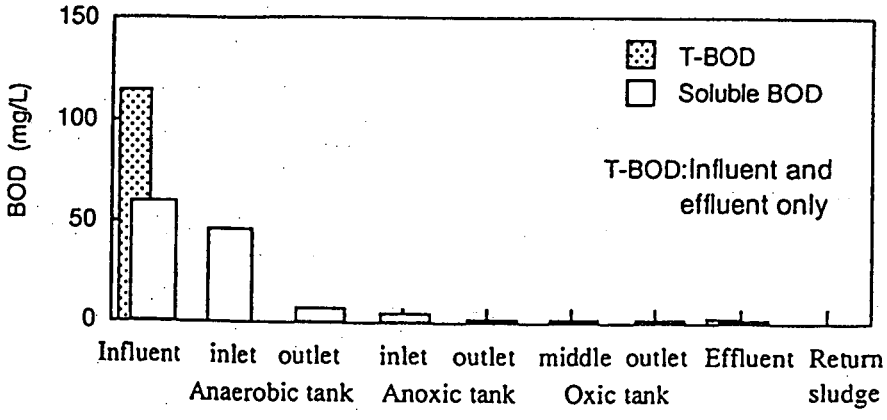


Fig. 4 BOD Concentration Profile at Each Location in A 2 O process

7．2．Operation Characteristics of A 2 O system

When working with on actual operating plant, it is difficult to determine the effect on nitrogen and phosphorus removal of major changes in operation conditions such as influent rate, mixed liquor recycling ratio, return sludge ratio etc. This is because such experiments may incur extreme quality deterioration of treated water.

Hence, we estimated removal characteristics under varying operation conditions by simulation.

(1) Verification of the dynamic bioreaction model equations

Caluculated simulation results agreed well with real water quality analysis data for BOD, soluble phosphorus, NH 4 −N, NO 3 −N, organic nitrogen, and pH at measurement points in the bioreactor, validating application of the model to the A 2 O process.

(2) Optimum values obtained by Simulated operation characteristics

1) Elongation of sludge retention time (SRT) improves T−N removal ratio but the s−P removal ratio deteriorates.
The appropriate SRT is between 12 and 15 days. (Shown in Fig. 5−1)

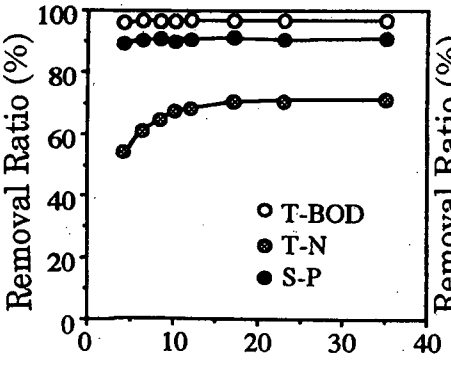
2) DO at the end of the oxic tank should be between 1.5 and 3.0 mg/l for higher removal ratios of both T−N and s−P. (Shown in Fig. 5−2)

3) Mixed liquor recycling ratio greatly affects the T−N removal ratio. At a mixed liquor recycling ratio of 150%, a T−N removal ratio of 80% is attained. (Shown in Fig. 5−3)

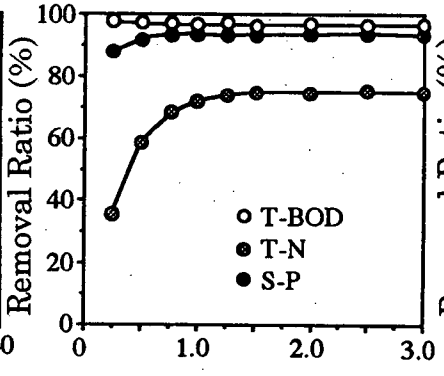
4) An appropriate return sludge ratio is about 50%, though it has little affect upon removal ratios.

5) Mixed Liquor Suspended Solid, between 1,500 and 3,000 mg/l.

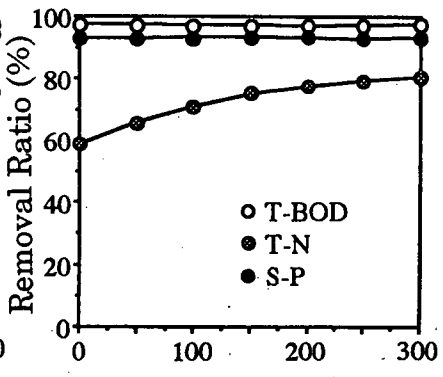
6) ORP at the anaerobic tank should be kept lower.



SRT (days)
Fig. 5−1



DO(mg/l) : oxic tank
Fig. 5−2



Recycling Ratio(%)
Fig. 5−3

7．3．Study on Operation Indices

As operation indices showing the status of reaction in the bioreactor, we selected readings of ORP, pH, and DO water quality meters.

(1) Operation indices for the anaerobic tank

Figure 6 shows the relation between oxidation−reduction potential (ORP) transition (exit−entry) and phosphorus release (exit−entry) in the anaerobic tank. As seen in the graph, when ORP at the exit becomes lower than that at the entry, phosphorus release occurs in the tank.

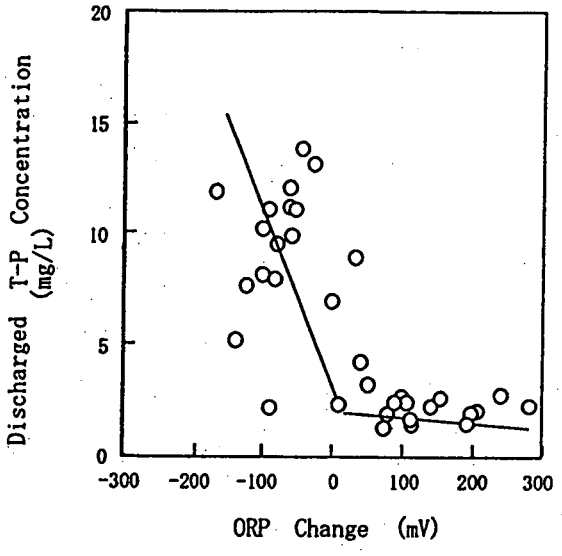


Fig.6 Relationship between ORP Change and Discharged T-P Concentration in Anaerobic Tank

(ORP Change = ORP in outlet of anaerobic tank−ORP in inlet of anaerobic tank)

(Discharged T-P = T-P in outlet of anaerobic tank−T-P in inlet of anaerobic tank)

Figure7 shows relation between DO in the influent and phosphorus release in an anaerobic tank. As seen in the graph, when DO in the influent to the anaerobic tank was about 0. 8 mg/l or lower, phosphorus release took place in the tank.

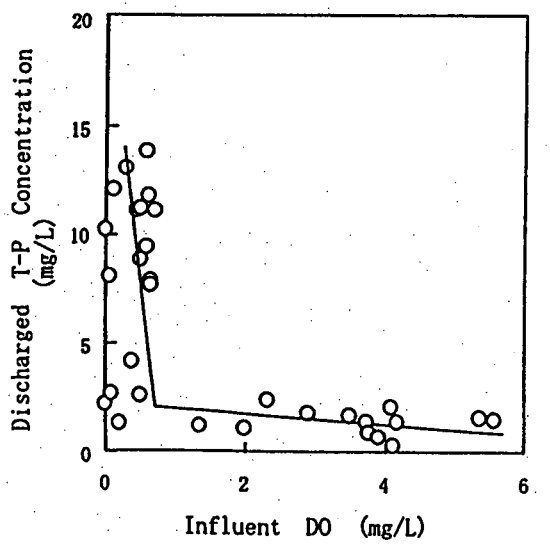


Fig.7 Relationship between Influent DO and Discharged T-P Concentration in Anaerobic Tank

Figure8 shows relation between the amount of released phosphorus in the anaerobic tank and bacterial uptake of phosphorus in the anoxic tank and the oxic tank. The phosphorus excess uptake after phosphorus release is shown in the graph.

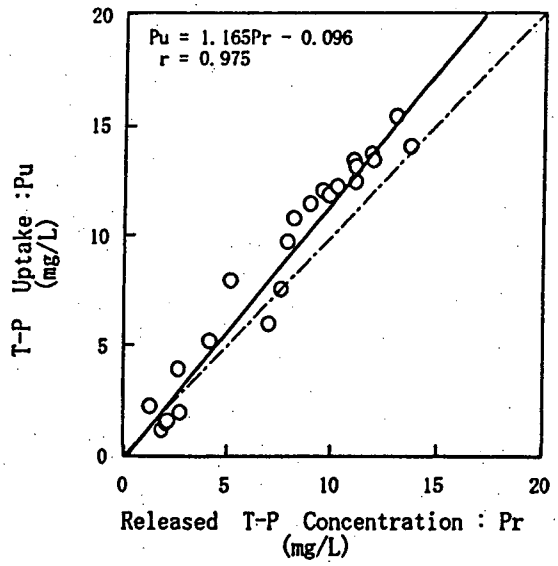


Fig.8 Relationship between Released T-P Concentration in Anaerobic Tank and T-P uptake

(T−P Uptake = removal T−P in anoxic tank + removal T−P in oxic tank)

(2) Operation indices for the anoxic and oxic tanks

Figure 9 shows the relation between pH transition (oxic tank exit−anoxic tank exit) and the degree of progress of nitrification in the oxic tank (NO 3 − N concentration). The chart indicates that as nitrification in the oxic tank proceeded, pH at the end of the tank fell. Keeping DO at a specified level or higher at the end of the oxic tank is essential to nitrification

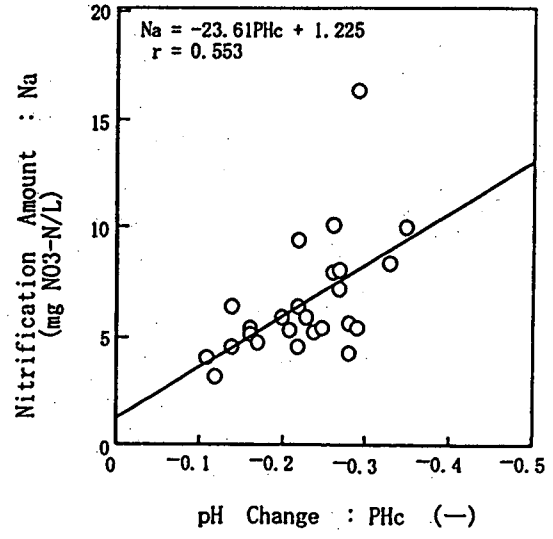


Fig.9 Relationship between pH Change and Nitrification Amount in Oxic Tank

(pH Change = pH in oxic tank − pH in anoxic tank)

8. The corrective action in case of rain

In this A2O treatment method, it is difficult to remove the phosphorus in a rain fall. When the accumulated amount of rainfall became more than 80mm, the total phosphorus values became higher than the target value 1.0 mg/l.

Figure 10 shows the deteriorating factor in removal of T−P. As shown in the graph, the efficiency of phosphorus removal is deteriorated after strong rainfall of more than 50 mm.

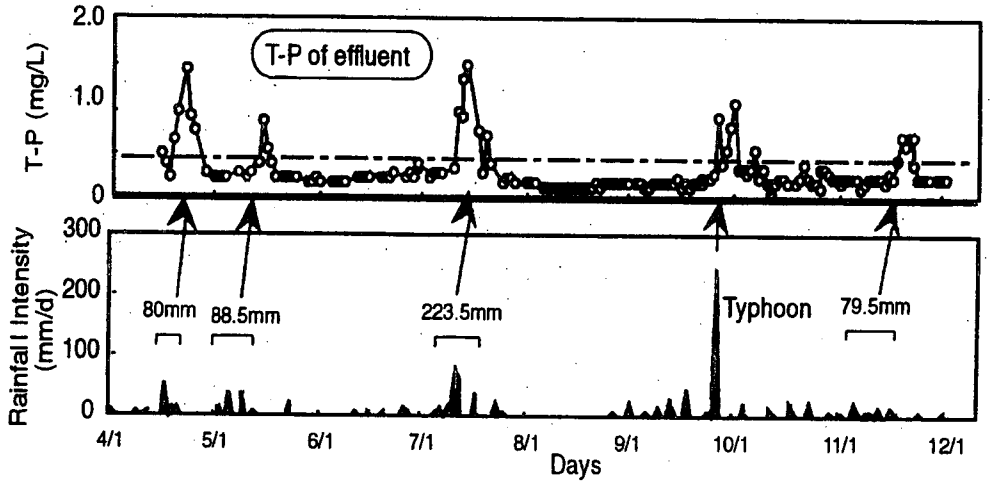


Fig. 10 The deteriorating factor in removal of T−P.

As for the corrective action, it is effective to add the coagulant temporarily for keeping the water quality of the effluent within a target value. In case of polyaluminium chloride (PAC) ,to decrease the T−P concentration in the effluent from 2.0 mg/l to 0.5 mg/l, we should inject the caugulant at the rate of 2mg/l−PAC. In another way, amount of polyaluminium chloride is required 1.33 mg for removal phosphorous of 1.0 mg. We can make the amount of coagulant the least, by starting injection and stopping it in exact timing, with the control indicaters such as DO value and ORP value.

9. Conclusion.

Results from the experiments at the A 2 O pilot plant were as follows.

(1) The optimum values of the typical operation indices
  (a) Sludge Retention Time, between 1 2 and 1 5 days.
  (b) Return Sludge Ratio, about 5 0 %.
  (c) Mixed Liquor Recycling Ratio, about 1 5 0 %.
  (d) Dissolved Oxygen at the outlet of the oxic tank, between 1.5 and 3.0 mg/l .
  (e) Mixed Liquor Suspended Solid, between 1,500 and 3,000 mg/l.
  (f) ORP at the anaerobic tank should be kept lower.

(2) T−N of effluent could meet the target value (1 0 mg/l) during all the

experiment period, but T−P could not meet it (0. 5 mg/l) in 5 rainy cases.

In case of rain, it is effective to add the coagulant temporarily for keeping the water quality of the effluent within a target value.

As for the necessary amount of coagulant, polyaluminium chloride is required 1.33 mg for removal phosphorus of 1.0 mg

(4) The simulator of A2O process was verified by water quality analysis, and found to be useful.

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Post-Denitrification at the Frankfurt-Niederrad Wastewater Treatment Plant by Fluidized-Bed Technology

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Abstract

At both two-stage activated sludge treatment plants of the city of Frankfurt an almost complete nitrification is achieved. Upgrading of the plants is required to ensure denitrification. As an alternative for implementing a solution according to the German ATV-Standard A 131 separate denitrification by an upflow fluidized-bed technology was thoroughly investigated on pilot plant scale. The results show, that a far-reaching denitrification can safely be obtained by this process. Equations for quantifying the volumetric denitrification capacity of the bed (kg $\Delta N/m^3 \cdot d$) and the effluent nitrate concentration are derived for process design. The denitrification efficiency of the system, its benefits and disadvantages are discussed together with economical aspects.

Keywords

upgrading of municipal treatment plants - advanced wastewater treatment - post-denitrification - fluidized-bed technology - application of methanol

1. Introduction

The wastewater of the City of Frankfurt am Main and from fourteen connected municipalities is treated in two major treatment plants, Frankfurt-Niederrad (1,300,000 PE) and Frankfurt-Sindlingen (470,000 PE). Both are two-stage activated sludge plants which went into operation 1985/1986. The two-stage concept resulted from thorough investigations and economical considerations. Already at that time it was clear, that two-stage plants operate very safely and have many advantages with respect to nitrification but that denitrification was very difficult to achieve. Moreover, the need for denitrification for water quality protection was not expected early in the eighties.

Both plants operate since commissioning extremely stable and produce almost complete degradation of organic matter and far-reaching nitrification. Upgrading of the plants is, however, re-

quired for denitrification and phosphorus removal in order to meet the present effluent requirements as from January 1, 1999. Plans according to the German ATV-Standard A 131 (ATV, 1991) have been finished to upgrade both plants to single step activated sludge treatment plants with pre-denitrification, enhanced biological phosphorus removal supplemented, if required, by chemical addition, resulting in total investment cost of some 500 million DM.

In view of maintaining the high process stability of the existing plants and of the possibility of notable savings on investment cost, the City of Frankfurt decided in 1993 to investigate the process of post-denitrification with methanol applying fluidized-bed technology on technical scale. As pilot plant a fluidized-bed reactor Oxitron of the Dorr-Oliver GmbH was applied and operated together with the company Lurgi Energie und Umwelt GmbH..

Based on the present knowledge on fluidized-bed technology, the following questions were to be answered by the research activities:

- performance and dependability of the process;
- determination of design parameters for the full-scale plant under the special local conditions;
- determination of the sludge production from methanol application;
- investigations into control measures and procedures with respect to methanol dosing and effluent control;
- economy of the process.

2. Pilot Plant and its Operation

Central part of the pilot plant is the bio-reactor (figure 1) with rectangular cross-sectional area ($0.9 \cdot 1.0$ m^2) and a height of 5.90 m, filled with a sand bed ($\approx$ 0.3 mm grain size) of 2.0 m. Via a special nozzle bottom the bed is expanded by some 100 % (4.0 m height) with the effluent of the secondary clarifiers of the Niederrad plant at filtration velocities of v_F = 20 to 30 m/h. In this state, a biofilm surface area of more the 3,000 m^2/m^3 of reactor volume is available giving rise to a very high concentration of fixed suspended solids of more than 25 kg/m^3.

Further important appurtenances (figure 1) are (a) the storage tank (2.5 m^3), receiving reactor effluent under conditions of recirculation for the reduction of the incoming nitrate concentration, (b) the methanol dosing pump and the feeding pump with a maximum capacity of 30 m^3/h, (c) the sand-washing equipment for separation of the biofilm from the sand grains, and (d) the sludge storage tank (2.0 m^3) connected to it.

The operational conditions of the pilot plant and its most important results are measured and controlled by an extensive data retrieval and control system. At six positions data are measured either on-line (concentrations of NO_3^--N and methanol, flow rate Q and temperature T), or via 24-hours-composite or grab samples (NO_2^--N, COD, suspended solids, volatile suspended solids). The excess sludge analysis comprises in addition total solids, TKN, total phosphorus, and calorific value. Details on the measurement and control system follow from figure 1.

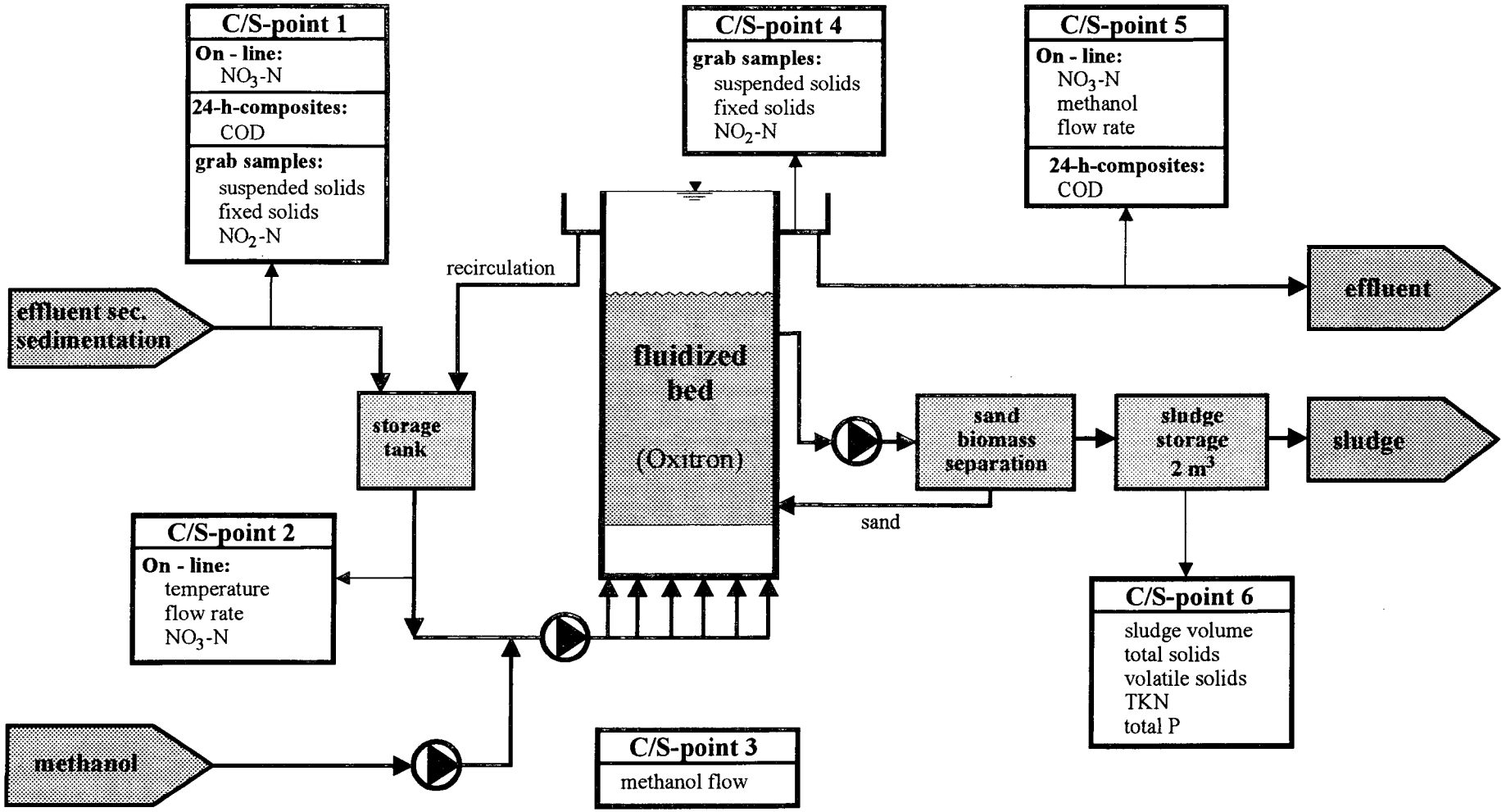


Figure 1: Schematic of pilot plant with control and sampling (C/S) points and program of analyses

The continuous removal of excess sludge from the sand grains is of utmost importance for proper functioning of the process. By growth of the biofilm the settling velocity of the particles is reduced and these particles accumulate in the upper part of the reactor, therefore. As soon as a set maximum expansion is reached, these particles are removed from the reactor and fed to the sand-biomass-separation equipment: a shear pump with a classifier. The removed excess sludge is pumped into the sludge storage tank for further treatment and analysis; the sand is recycled into the reactor.

3. Investigation Program and Basic Results

3.1 Investigation Program

The investigation program consisted of five phases with increasing **volumetric nitrate nitrogen loading rates** VNLR of the 4.0 m high expanded bed volume from 2,6 to 5,2 kg/m^3·d of NO_3^--N (see table 1). To achieve these relatively high VNLR-values, the concept of recirculation of effluent with very low nitrate content was abandoned after a short period of operation and the reactor was fed with clarifier effluent only at increasing hydraulic loading rates HLR (m^3/m^2·h = m/h) or filtration velocities v_F.

The methanol dosage (g/s) was adjusted to the influent nitrogen load (product of HLR and NO_3^--N-concentration) to give pre-set values of the **specific methanol dosage** SMD (g methanol per g of NO_3^--N). The theoretical specific methanol demand of 2,5 g/g and a **stoichiometric excess factor** of $\beta = 1.2$ (20 % excess dosage) were taken as an experimental basic value for the SMD. This would yield a SMD of 3.0 g methanol per g of NO_3^--N. Hence, the SMD was changed from 2.23 to 3.16 ($0.9 \leq \beta \leq 1.3$). The low SMD-values were chosen to find out whether at $\beta < 1$ any nitrite formation would occur. The table also contains the **specific methanol utilisation** SMU (g of methanol used per g of NO_3^--N denitrified), which is very close to the above SMD = 3.0 as average over all five phases: $SMU_{av} = 3.01$ g/gΔNO_3^--N.

Table 1: Operational data and basic results of five experimental phases

Parameter	Dimension	Phase 1	Phase 2	Phase 3	Phase 4	Phase 5
number of daily samples	-	15	20	22	15	6
volumetric N loading rate	kg/m^3·d	2,62	3,35	3,52	5,19	5,19
excess factor β	-	1,08	1,26	1,12	0,89	1,16
temperature	°C	17,4	21,3	20,0	20,0	19,3
filtration velocity	m/h	25,1	24,6	23,2	25,1	23,9
nitrate-N of influent	mg/l N	25,8	20,8	24,1	31,6	34,7
nitrate-N of effluent	mg/l N	2,3	1,1	1,7	6,0	0,5
percent denitrification	%	90,9	94,3	92,4	80,8	98,5
methanol in effluent	mg/l	0,34	0,41	0,48	0,40	0,54
specific methanol dosage	g/g NO_3^--N	2,69	3,16	2,80	2,23	2,90
specific methanol utilisation	g/g ΔNO_3^--N	2,95	3,36	3,03	2,76	2,95

Finally, nitrate nitrogen and methanol profiles were recorded over the bed height to get information on the course of denitrification during bed passage and on the required bed height as well as on the process reliability.

3.2 Basic Results

The basic denitrification results of the investigations are compiled in table 1. With respect to the different parameters, the results of the five phases can be characterised as follows. The **reactor temperature** was always in excess of 15°C and reached values of 22.5°C. With the exception of phase 1, the temperature was generally above 20°C. Despite of the low temperature range, its influence on the rate of denitrification will be investigated later. The **filtration velocity** was with (part of phase 1) and without recirculation relatively constant between 20 and 25 m/h. Hence the differences of the VNLR of 2.6 to 5.2 $kg/m^3 \cdot d$ were mainly caused by the variation of the influent nitrate nitrogen concentration (effluent of secondary clarifier).

The **nitrate nitrogen content** of the plant effluent Niederrad (influent to fluidized bed) varied over a considerable range from 21 to 35 mg/l. Within the phases, the daily averages ranged over 20 mg/l; the range of on-line data showed a daily variation of even 24 mg/l. The post-denitrification had to be adjusted to this strong variation. With the exception of the first part of phase 1 and the phases 3 and 4 with understoichiometric dosing, very low nitrate nitrogen concentrations were obtained at relatively high process stability. The all-over effluent average amounts to some 4 mg/l N with variations during the day of up to 10 mg/l. A still higher process stability can be achieved by a more precise control of methanol dosing. The **percent denitrification** was on the average (without phase 4 with $\beta = 0.89$) at least 90 % with daily variation from 75 to 99 %. The total nitrogen removal was therefore always in excess of 80 %, satisfying very high requirements.

The **effluent methanol content** was generally below 1 mg/l, in four of five phases even below 0.5 mg/l. This is a very low content, especially when taking into consideration, that the on-line measurement of methanol is very inaccurate at low concentrations and parallel analyses showed lower than on-line date, generally. Nevertheless, values as high as 5 mg/l were recorded now and then, which can be avoided by a more rigid methanol dosing control. The **specific methanol dosage** ranged in the phases without low dosing (1, 2 and 5) between 2.8 and 3.6 g/g NO_3^--N. During phase 3 with 15 % lower dosing it was within the range, also (2.8 g/g NO_3^--N). Only during phase 4 (30 % lower dosing) it was below this range (2.2 g/g NO_3^--N). The **specific methanol utilisation** (g methanol per g of denitrified nitrate nitrogen) is - as expected - much more stable and ranges between 2.8 to 3.4 g/g ΔNO_3^--N, only. Obviously, the bacteria adapt themselves to the methanol dosing and its variation. The highest constancy is reached during phases 3 and 4 with low specific methanol dosage.

3.3 COD Increase by Methanol Addition

The dosing of methanol together with the high filtration velocities can give rise to an increase of suspended solids (SS) and of COD in the reactor effluent. With respect to the SS the influent concentration (Niederrad plant effluent) varied from 1 to 14 mg/l, the reactor effluent, however, from 2 to 36 mg/l. The average increase amounted to 4.4 mg/l of suspended solids. The respective figures for COD are 15 to 47 mg/l reactor influent and 23 to 82 mg/l effluent concentration with an average addition of 13 mg/l. It can be shown by a further analysis that no solids hydrolysis can have occurred and that the COD increase can have been caused by the solids increase only.

3.4 Production of Excess Sludge and its Properties

A detailed analysis of the production of excess sludge by monitoring the excess sludge collection and taking into consideration the sludge losses by the reactor (effluent minus influent suspended solids) showed a gross production of 0.222 kg of solids per kg of methanol. Theoretical considerations lead to a growth of volatile solids of 0.212 kg/kg and hence of 0.212/0.863 = 0.246 kg/kg of total solids at the measured organic content of 86.3 %. This differs by 10 % only from the measured value. Of the produced solids 68 % is caught as sludge, 32 % leaves the reactor as suspended solids with the effluent. The moisture and ash free calorific value amounts to 20 MJ/kg, an important property with respect to practised sludge incineration.

4. Evaluation of the Experimental Results

4.1 Volumetric nitrate nitrogen removal rate of the fluidized bed

By evaluation of the experimental results, relations between the basic process parameters are to be developed which allow an optimum design of a large scale plant for post-denitrification. As most basic parameter the volumetric nitrate nitrogen removal rate (VNRR; kg $\Delta N/m^3 \cdot d$ was defined. Important factors influencing the VNRR are (a) the nitrate nitrogen content of the reactor influent N_i, (b) the reactor temperature T, (c) the filtration velocity v_F reducing the biofilm diffusion barrier, and (d) the methanol dosage, which is here expressed as methanol flux MF (kg methanol per m^2 reactor cross-sectional area per day). The experimental data were evaluated by linear regression according to the model

$$VNRR = k_o + k_1 \cdot MF + k_2 \cdot N_i + k_3 \cdot v_F + k_4 \cdot T \quad [kg\ \Delta N/m^3 \cdot d] \qquad (1)$$

The coefficients of equation 1 were determined by multiple regression according to the step-forward principle. The equations 2 through 5 show this step-wise approach, where the parameters methanol flux MF, influent NO_3^--N-concentration N_i, filtration velocity v_F, and the temperature T are added to the model in sequence of their relative importance.

$$VNRR = 0{,}092 \cdot MF \qquad r = 0{,}930 \qquad (2)$$

$$VNRR = 0{,}054 \cdot MF + 0{,}058 \cdot N_i \qquad r = 0{,}965 \qquad (3)$$

$$VNRR = -2{,}47 + 0{,}042 \cdot MF + 0{,}070 \cdot N_i + 0{,}109 \cdot v_F \qquad r = 0{,}978 \qquad (4)$$

$$VNRR = -1{,}59 + 0{,}042 \cdot MF + 0{,}101 \cdot N_i + 0{,}074 \cdot v_F - 0{,}038 \cdot T \qquad r = 0{,}980 \qquad (5)$$

By far the most important influence is caused by the methanol flux MF and the initial nitrogen content N_i. The influence of the filtration velocity is minor; reasons are probably its relatively large value around 25 m/h reducing the film diffusion barrier strong enough so that any further increase or decrease has little effect. Most striking is the - very small yet statistically significant - but negative regression coefficient for temperature. Surely, the bacterial denitrification activity will - like always - increase with increasing temperature proportional to the increase of the respiration rate r_o (kg O_2/kg TS·d). This influence is normally described by the exponential law $v_{o,T} = v_{o,R} \cdot \Theta^{(T-R)}$, with R as reference temperature. This temperature model takes into account only the bio-kinetic influence, not, however, the degree of process utilisation nor the type of reactor (complete-mix; plug flow or intermediate). These factors also govern the influence of temperature as has been shown earlier (Pöpel, 1971; Pöpel, 1994; Pöpel and Fischer, 1996). The low degree of process utilisation, which will be shown in detail later, is probably the reason for the insensitivity with respect to temperature. Altogether, the small influence of the filtration velocity and of temperature are neglected and equation 3 is further used as a model describing the main effects on the volumetric nitrogen removal rate with sufficient accuracy.

For purpose of illustration, equations 2 and 3 are depicted in figure 2, stating the VNRR as a function of the methanol flux. The influence of the influent NO_3^--N-content is shown for the three ranges of 8 to 18 mg/l, 18 to 28 mg/l, and 28 to 38 mg/l of N_i. It follows from figure 2 that even in the range of highest methanol flux and VNRR there is no drop in the bed capacity - otherwise many of the data points should lie below the regression line in this region. This "over capacity" causes the lack of any temperature influence.

4.2 Effluent concentration of nitrate nitrogen of the fluidized bed

Various models were tried out to find the most important factor(s) influence the effluent nitrate nitrogen concentration N_e (mg/l NO_3^--N). The following model showed a reasonable accuracy for all 5 experimental phases including those with understoichiometric methanol dosing. It relates the effluent NO_3^--N-content to the specific methanol dosage D_s (g methanol dosed per g NO_3^--N).

$$N_e = 16.5 - 5.07 \cdot D_s \quad (\text{mg/l } NO_3^-\text{-N}) \qquad r = 0{,}836 \qquad (6)$$

This means, that at 20 % excess dosing ($D_s = 3$) an effluent content of 1.3 mg/l could be reached. Recalculating the regression, equation 7 is derived allowing to find the required specific dosage

in order to reach a pre-set effluent concentration. For N_e = 8 mg/l NO_3^--N, a very typical value for normal denitrification operation, D_s = 2.03 g/g would be required.

$$D_s = 3.13 - 0.138 \cdot N_e \quad (g/g) \qquad r = 0{,}836 \qquad (7)$$

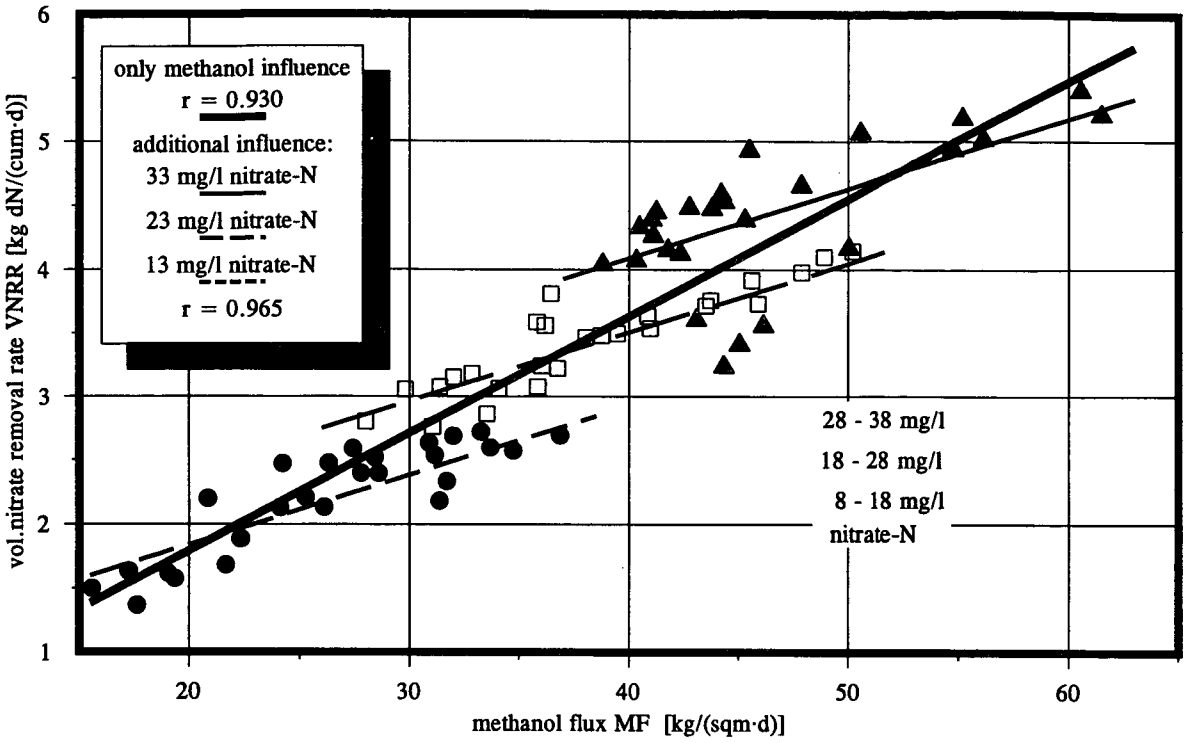


Figure 2. Volumetric NO_3^--N-removal rate as a function of methanol flux and influent NO_3^--N-content

5. Concentration Profiles

Five concentration profiles were taken in total during the experimental phase, which showed that methanol and nitrate are degraded already within the lower 1.3 to 2.5 m of the bed and that the remaining 2.7 to 1.5 m basically serve process safety and reliability. This is of great importance with respect to methanol and will prevent brake-through of methanol, especially at conditions of understoichiometric dosing. The formation of nitrite could never be observed, also not under these conditions.

Figure 3 contains two of the profiles for illustration purposes, left at understoichiometric dosing, right at very high volumetric loading rate (4.6 kg NO_3^--N/m^3·d). In the lower part of the bed, where most of the conversion takes place, very high denitrification rates of 7.6 and 8.6 kg ΔNO_3^--N/m^3·d are observed. Also, the profiles show that even higher loadings could be dealt with by the process. These, however, could be materialised only by strongly increasing the filtration velocity, which - on the other hand - would reduce the hydraulic stability of the process. A larger grain size could solve this problem but would lead to a lower specific surface area and hence to a

lower volumetric nitrate nitrogen removal rate. Grain material of higher density could solve this problem - if required at all. These reserves with respect to denitrification capacity cause also, that there is no temperature sensitivity to be observed. Any rate reduction by temperature decrease will be compensated by increase in activity in the upper part of the bed.

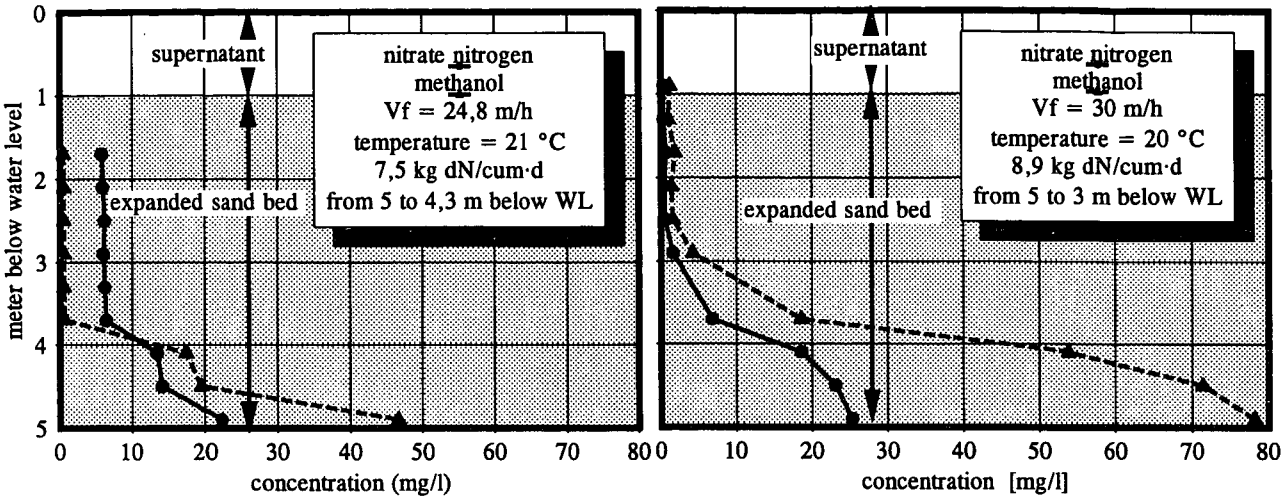


Figure 3. Concentration profiles with stoichiometric (right) and understoichiometric dosing

6. Process Economy of Fluidized-Bed Post-Denitrification

Based on the experimental results, process design for the Niederrad plant including total cost were worked out by a consulting company (GKW-Ingenieure, 1995). First cost including all extra cost amounted to DM 45,000,000. The operational cost are mainly determined by energy cost for pumping and chemical cost for methanol. Secondly, personnel cost and cost for repair and maintenance have to be added.

Taking all cost factors into account, a range of additional specific cost of DM 0.07 to DM 0.11 per m^3 of wastewater is calculated depending on energy and methanol cost. Hence, post-denitrification by fluidized-bed technology under the specific conditions of Frankfurt-Niederrad has shown to be feasible and more economic than the retro-fitting the two-stage plant.

With respect to operational and environmental considerations, there are important aspects in favour of this process compared to rebuilding the plant to a single- or two-stage activated sludge system:

- the plant can be extended without any influence on the existing part;
- the advantages of the existing two-stage process (process capacity and stability) are maintained;
- the time required for upgrading the plant is minimum;
- the degree of nitrate reduction can be controlled very flexibly;
- the modular construction of the plant allows a flexible increase of the capacity as may be required in the future.

Obviously, there is also a number of disadvantages:

- organic matter (methanol) must be constantly added, which actually is present in the incoming wastewater of the plant. There is an additional energy consumption of biological treatment of some 15 %;
- the excess sludge production is increased by some 3 %;
- the effluent suspended solids concentration is slightly increased;
- measurement and control of the process are fairly involved;
- a process failure will immediately lead to higher nitrate concentrations in the effluent;
- methanol belongs to the group of „hazardous matter" and its application requires observing special safety regulations.

7. Summary

Both two-stage wastewater treatment plants at Frankfurt (Niederrad with 1.30 million PE and Sindlingen with 0.47 million PE) produce excellent and very stable effluent results at present. However, in order to remove nitrogen, they have to be extended by the process of denitrification. The plans - including enhanced biological phosphorus removal - require total first cost of 500 million DM. For reasons of saving on investment and of maintaining process stability, the process of post-denitrification by means of a fluidized bed reactor with methanol was thoroughly investigated.

Within five experimental phases the volumetric nitrate nitrogen loading rate of the 4.0 m high and 100 % expanded sand bed was gradually increased by adjusting the filtration velocity to the NO_3^--N-concentration of the effluent of the secondary clarifier of the Niederrad plant from 2.6 to 5.2 kg NO_3^--N/m^3·d. The stoichiometric excess of methanol dosing was varied over a range from 0.89 to 1.26 giving rise to percent denitrification rates from 81 % to 98 % and effluent nitrate nitrogen concentrations from 6.0 to 0.5 mg/l.

The effluent methanol content was generally below 0.5 mg/l, whilst the COD and the suspended solids concentrations of the influent (clarifier effluent) was increased by 13 mg/l and 4.4 mg/l on the average, respectively. A careful analysis of the excess sludge production showed a specific value of 0.222 kg TS per kg of methanol added and at the volatile percentage of 86.3 % of 0.192 kg VS/kg. 32 % of the excess sludge left the process together with the effluent, 68 % were pumped to sludge treatment. With a lower calorific value (moisture and ash free) of 20 MJ/kg sludge incineration as practised in Frankfurt will cause no problems.

A thorough evaluation of the results showed that the volumetric NO_3^--N-removal rate (kg Δ NO_3^--N/m^3·d) depends (a) mainly of the dosed methanol flux (kg methanol per m^2 cross-sectional reactor area per day) and (b) on the incoming nitrate concentration (fig. 2 and equation 3). The effluent NO_3^--N-content is governed only by the specific methanol dosage (g methanol per g NO_3^--N). The derived equations 6 and 7 allow process design and control. Concentration profiles over the height of the reactor showed, that the biological conversion occurs mainly within the

lower 1.5 to 2.5 m of the fluidized bed. This „process safety" also explains that the overall removal rate and the effluent concentrations do not depend on temperature.

A process design by GKW-Ingenieure for the situation of Frankfurt-Niederrad including cost calculations resulted in investment cost of 45 million DM and - depending on the specific cost for electrical energy and methanol specific total costs of 0.07 to 0.11 DM per m^3 of denitrified wastewater.

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Session 11

Toxic Substance Removal

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NEW TECHNIQUES FOR REMOVAL OF SELENIUM FROM EFFLUENTS OF METAL REFINERIES

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Abstract

Three new methods to reduce selenate ion are investigated to develop the techniques for removal of selenium. On of them is homogeneous system where ferrous chloride is used as the reductant. In this system, almost selenium is reduced to amorphous selenium when the pH of the solution is near 0. There remains some selenite ion in the treated solution, but it can be precipitated in high pH solution easily. Therefore, total selenium concentration can be decreased by the following two step process. At first, selenate is reduced by ferrous chloride under low pH condition, next, pH of the solution is adjusted near 6 and remained selenite is coprecipitated with ferric hydroxide. We can decrease the total selenium concentration under 0.1 ppm by this process. The other two methods are heterogeneous system where TiO_2 is used as photocatalyst or cathode in galvanostatic electrolysis. In photocatalyst system, selenium is reduced to hydrogen selenide when the organic reductant exists in the solution whose pH is under 3, and removed from liquid phase. Total selenium concentration becomes under 0.1 ppm. In galvanostatic electrolysis system, selenium is reduced to amorphous selenium when the pH of the solution is under 3, and the total selenium concentration of the filtrate is under 1 ppm.

key words: reduction of selenate, ferrous ions, smelting waste water, Titanium dioxide, galvanostatic electrolysis

Introduction

Selenium in waste water from refineries exist mainly as selenite ion, but some of them exist as selenate ion. Selenite ion can be removed from the waste water easily with the traditional method [1], but selenate ion in aqueous solution is very stable and is difficult to remove it from the waste water. It is important to establish the actual method to remove selenate ion from the waste water. If selenate ion is reduced to selenite ion or more reduced form, they can be removed from waste water easily, so it is effective to develop the method to reduce selenate ion.

We have tried to reduce selenate ion with two methods. One of them is the chemical reduction method, in which ferrous salt, especially ferrous chloride is used as the reductant in low pH solution. The other is the photoelectrochemical method in which TiO_2 is used as photocatalyst or cathode in galvanostatic electrolysis. We can reduce selenate ion with both two method, and the total selenium concentration can be decreased under 0.1 ppm from 100 ppm.

1. Chemical reduction

Chemical reduction is a reduction process with chemical agents such as iron, ferrous ion, copper, zinc etc. Fig. 1 shows electrode potential of some kinds of ion/metal and ion/ion diagram which tell us the possibility in oxidation-reduction processes. Selenium has four valences of +6, +4, 0 and -2 in aqueous solution and stable ranges are shown in this figure. For example, if we use gold as reducing agents, selenate cannot be reduced to selenite or elemental selenium. When we use ferrous ions, selenate can be reduced to selenite. Elemental selenium can be obtained with copper.

Ferrous ion is used as a useful reducing agent in many metallurgical processes. The present study was conducted to obtain a fundamental understanding of the reaction kinetics of reduction of selenate with ferrous chloride in hydrochloric acid solution.

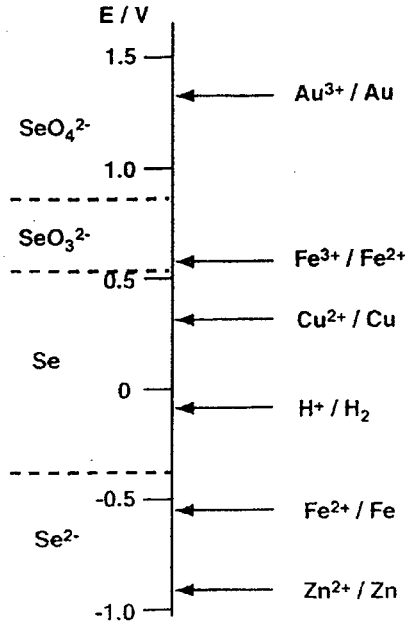


Fig.1 Electrode potential

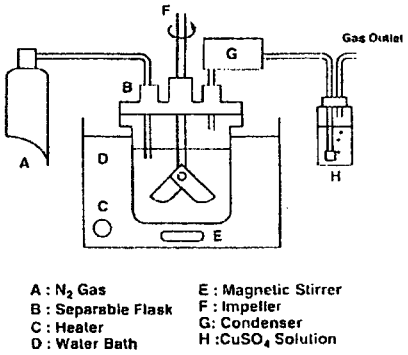


Fig.2 Schematic illustration of experimental apparatus.

Experimental

Fig. 2 shows a schematic illustration of experimental apparatus. A 500 cm^3 glass separable flask was used as a reaction vessel. The temperature of the water bath was controlled within ±0.2℃. Deoxygenated nitrogen gas was bubbled into solution throughout the experiment to prevent the oxidation of ferrous ions. Gas from the reaction vessel was put into an aqueous cupric sulfate solution to absorb hydrogen selenide gas. A 200 cm^3 of a ferrous chloride solution containing hydrochloric acid and a 200 cm^3 sodium selenate solution were separately prepared under oxygen-free conditions. The concentration of ferrous chloride ranged from 0.1 to 0.5 kmol m^{-3} and that of hydrochloric acid ranged from 0.1 to 2 kmol m^{-3}. Initial concentration of selenate was 100 g m^{-3}. After reaching to a predetermined temperature, these aqueous solutions were put into the separable flask and experiments were started. The solution was agitated at constant speed of 200 rpm with a impeller coating with Teflon.

Temperature of the solution ranged from 313K to 363K. A 5 cm^3 of aqueous solution was periodically sampled and the concentrations of selenite and selenate were determined with Inductively Coupled Plasma Atomic Emission Spectrometer (Seiko Inc., SPS4000). The use of a hydride generator enabled to determine the only selenite concentration. The selenate concentration was determined from the difference between the total selenium concentration selenium and selenite concentration.

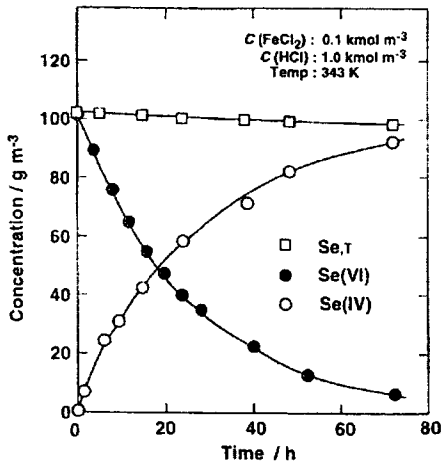


Fig.3 Time variation of the concentration of Se(IV), Se(VI) and Se_T. ($C(FeCl_2)$=0.1 kmol m^{-3}, C(HCl)=1.0 kmol m^{-3}, Temp.= 343K)

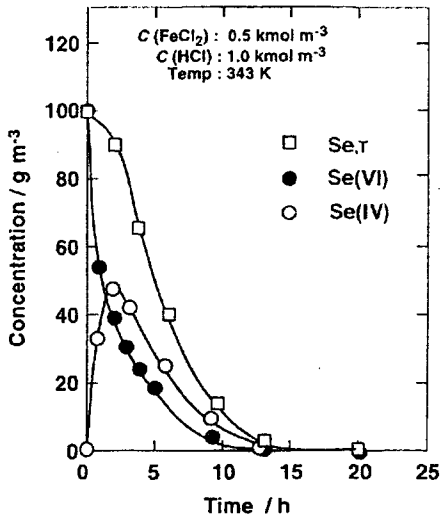


Fig.4 Time variation of the concentration of Se(IV), Se(VI) and Se_T. ($C(FeCl_2)$=0.5 kmol m^{-3}, C(HCl)=1.0 kmol m^{-3}, Temp.=343K)

Results and discussion

Fig. 3 and 4 show time variations of the concentration of selenite, selenate and total selenium in an aqueous solution at 343 K in 0.1 kmol m^{-3} $FeCl_2$ - 1.0 kmol m^{-3} HCl solution and in 0.5 kmol m^{-3} $FeCl_2$ - 1.0 kmol m^{-3} HCl solution, respectively. In 0.1 kmol m^{-3} $FeCl_2$ solution, total selenium concentration, which was the sum of the concentration of selenite and selenate, was nearly constant and selenate concentration decreased with time, which showed that selenite concentration increased with time. A slight amount of precipitates could be obtained during experiment. In 0.5 kmol m^{-3} $FeCl_2$ solution, selenate concentration decreased with time and reached 3.5 g m^{-3} after 9 hours reaction. On the other hand, selenite increased for approximately 2 hours , thereafter gradually decreased with time. Total selenium concentration in the solution decreased with time and amorphous selenium was precipitated. Selenate was found to be reduced to solid state following selenite by ferrous chloride. From these results, reaction rate was found to be of first order with respect to selenate concentration. Therefore, reaction rate may be written as

$$\frac{dC_{se(VI)}}{dt} = -kC_{se(VI)} \qquad (1)$$

where k is a rate constant with a dimension of s^{-1}. Rate constant, k, increased with increase in ferrous chloride concentration over the concentration range from 0.1 to 0.5 kmol m^{-3} and was found to be of a second order with respect to ferrous chloride concentration.

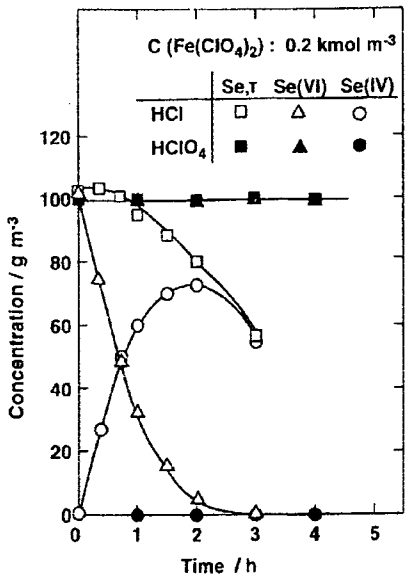


Fig.5 Time variation of the concentration of Se(IV), Se(VI) and Se_T. ($C(Fe(ClO_4)_2)$=0.2 kmol m^{-3}, C(HClO4)=1.0 kmol m^{-3}, Temp.=343K)

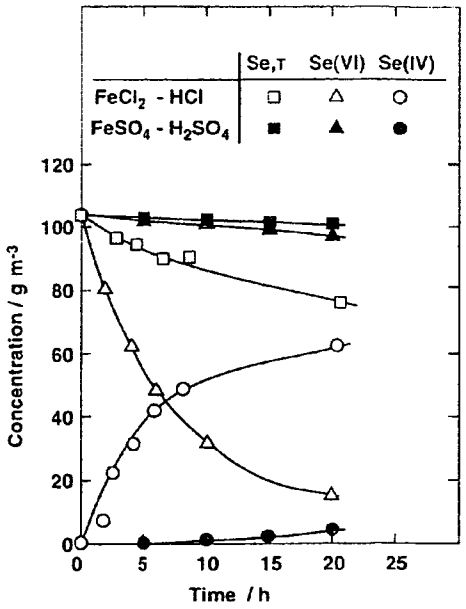


Fig.6 Time variation of the concentration of Se(IV), Se(VI) and Se_T. ($C(FeSO_4)$=0.2 kmol m^{-3}, $C(H_2SO_4)$=0.5 kmol m^{-3}, Temp.=343K)

It is well known that ferrous ions make chloro-complexes in aqueous chloride solutions. In order to study the effect of ferrous chloro-complexes on the reduction of selenate, reduction experiments in the ferrous perchlorate-perchloric acid solution were carried out. Fig. 5 shows time variations of the concentration of selenite, selenate and total selenium in an aqueous solution at 343 K in 0.2 kmol m^{-3} $Fe(ClO_4)_2$ - 2.0 kmol m^{-3} $HClO_4$ solution. In this figure, results in 0.2 kmol m^{-3} $FeCl_2$ -2.0 kmol m^{-3} HCl solution are also plotted. In $Fe(ClO_4)_2$ - $HClO_4$ solution, selenate concentration was constant and selenite concentration was below 1 g m^{-3} . Any precipitates were not obtained and total selenium concentration was also constant. Ferrous ions exist as aquo-complexes, $Fe^{2+}(aq)$, in this solution because perchlorate ions cannot make ferrous-perchloro complexes.

Fig. 6 shows time variations of concentration of selenite, selenate and total selenium in an aqueous solution at 343 K in 0.2 kmol m^{-3} $FeSO_4$ - 0.5 kmol m^{-3} H_2SO_4 solution. Selenate can be reduced to selenite or elemental selenium by ferrous sulfate. The reduction rate by $FeSO_4$ was smaller than that by $FeCl_2$. Ferrous ions make sulfato-complexes in aqueous sulfate solutions. Reduction ability of $FeSO_4$ is thought to be smaller than that of $FeCl_2$.

From these experiments it was found that reduction rate was effected by coexistence anion and the order was $kCl > kSO_4 > kClO_4$.

We tried removal test of selenium in aqueous solution. Initial concentration of selenate, HCl and $FeCl_2$ were 100 g m^{-3}, 1.0 kmol m^{-3} and 0.5 kmol m^{-3}, respectively. Table 1 shows the results of the test. selenate , selenite and total selenium concentration in aqueous solution became 0.06 , 0.07 and 0.13 g m^{-3} after 15 hours experiment. Then , after the reduction experiment, this solution was neutralized to pH of 6 by NaOH solution. selenate concentration was not changed , but selenite concentration became below 0.02 g m^{-3}. Therefore, total selenium concentration can be reduced to 0.08 g m^{-3}.

	343K 20 hrs	Adjust pH 6 with NaOH
Se(VI) g m^{-3}	0.06	0.06
Se(IV) g m^{-3}	0.07	<0.02
Total / g m^{-3}	0.13	0.08

Table 1 Removal test of Reduction-Neutralization method

Initial Solution

Se(VI) 100 g m^{-3} $FeCl_2$ 0.5 Kmol m^{-3}

Se(IV) 0 g m^{-3} HCl 1.0 Kmol m^{-3}

Temp.=343K

Conclusions

Reduction of selenate with ferrous chloride in hydrochloric acid solution was studied. Results indicates that reduction of selenate is an irreversible first order reaction with respect to its concentration and the reaction rate constant, k, is proportional to the second power of $FeCl_2$ concentration. Reduction rate is effected by coexistence anion and the order is $kCl > kSO_4 > kClO_4$. Selenium concentration can be reduced to below 0.1 g m^{-3} by chemical reduction with $FeCl_2$ - neutralization method.

2. Photoelectrochemical reduction

2-1. Photocatalyst reaction

It is well known that TiO_2 photocatalyst has strong activity to reduction and oxidation reaction [2,3]. We tried to use this to reduce selenate ion in aqueous solution and we succeeded to reduce selenate ion to hydrogen selenide.

Experimental

Sodium selenate aqueous solution whose concentration was 100 ppm, was used as model waste water. As photocatalyst, p25 (Ishihara Industry co. ltd.) was used, and 0.10-0.11 g of it was added to 100 ml of model waste water. Organic reductant and acid were also added to model waste water. This mixture was stirred to suspend the TiO_2 powder, bubbled by humid nitrogen gas to remove oxygen and other gases from the solution, and the emitted gas was bubbled through $CuSO_4$ aqueous solution. This suspension was irradiated directly by super high pressure Hg lamp (USHIO USH-500D). The change of the suspension and the $CuSO_4$ solution was observed with naked eyes.

Fig. 7 shows the illustration of the experimental apparatus. After irradiation, photocatalyst powder was removed by filtration. The total Selenium concentration in the filtrate was measured by using ICP as same as in chemical reduction experiment. When the concentration of selenium was larger than 1 ppm, we used normal nebulizer and when that was smaller than 1 ppm, we used ultrasonic nebulizer (CETAC Technologies Inc. U-5000AT+).

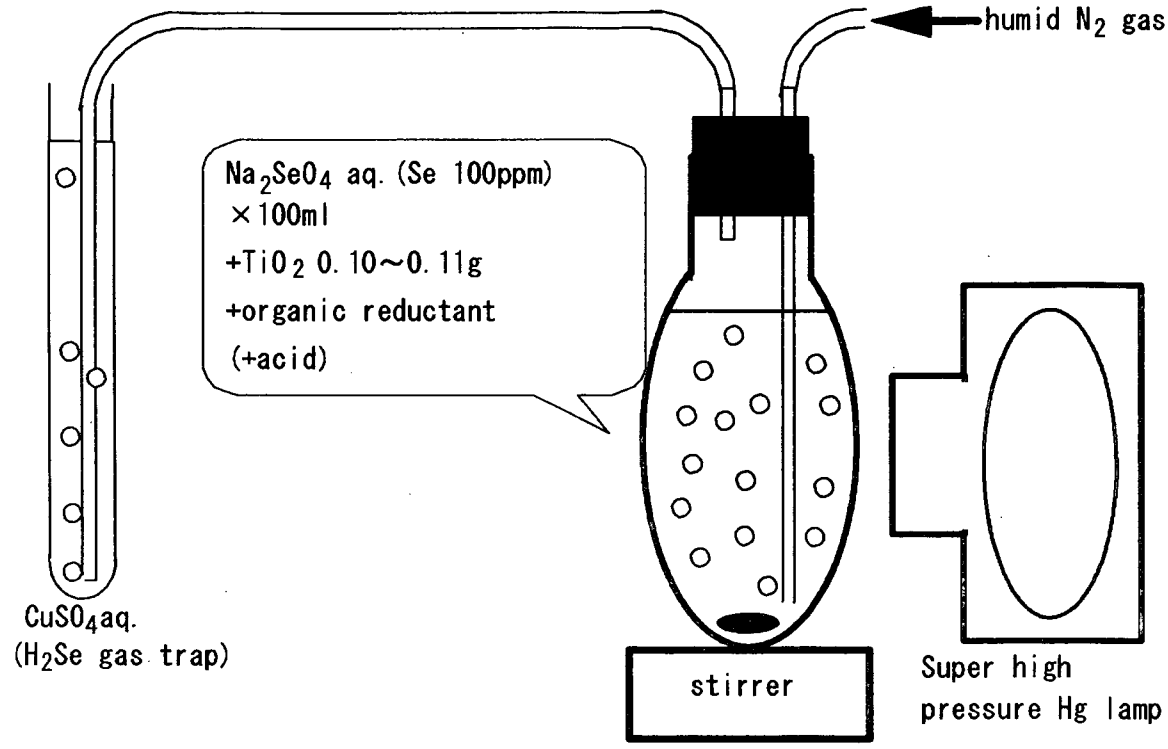


Fig. 7 experimental apparatus

Results

The color of the suspension, which was initially white, changed by irradiation when the some organic reductant was added. At first, it changed to reddish yellow. In the case of the pH of the suspension was low, black precipitation became generate in the $CuSO_4$ solution when the reddish yellow color became deepest. After that, the color of the suspension back to white. When the color of the suspension was reddish yellow, we analyzed the precipitation in the suspension with X-ray photoelectron spectroscopy, and found the elemental selenium was in it. The reddish yellow color was thought to be the color of amorphous selenium. The black precipitation in the $CuSO_4$ solution was identified as CuSe from XRD pattern. This shows that H_2Se generates from the suspension.

Experimental condition and the total selenium concentration are summarized in Table 2. The concentration of selenium in the filtrate was hardly reduced, when no reductant was added. On the contrary, when 1 mmol or more formic acid was added, or methanol was added with sulfuric acid, the remaining selenium concentration was under 1 ppm. In particular, the remaining total selenium concentration was under 0.1 ppm with 1 hour irradiation, when 2.5 mmol of formic acid was added.

When the selenium concentration in the filtrate was under 0.1 ppm, we measured the amount of total selenium in the precipitaion. The precipitation was oxidized and washed with nitric acid, TiO_2 powder was removed with filtration and the selenium concentration in the filtrate was measured with ICP. We found that there were 0.01-0.04 mg of selenium in it. This result shows that most of selenium was reduced to hydrogen selenide and removed from the model waste water.

Table 2. Total concentration of Se in the filtrate and the experimental conditions. Initial concentration of Se was 100 ppm, the amount of the test waste water was 100 ml and 0.10-0.11g of TiO_2 (p25) is added.

No.	Reductant/mmol	irradiation time	remained Se / ppm	coments
1	formic acid / 2.5	60 min	0.04	
2	formic acid / 2.5	230 min	0.03	
3	formic acid / 2.5	120 min	0.07	+Na_2SO_4 1.0mmol
4	formic acid / 1	75 min	0.11	
5	methanol / 2.5	300 min	0.18	+H_2SO_4 0.5 mmol
6	formic acid / 0.5	360 min	0.24	+H_2SO_4 0.5 mmol
7	formic acid / 0.5	80 min	24	it became colloidal solution, and measured after salting-out
8	none	420 min	92	+H_2SO_4 0.025 mmol
9	none	420 min	90	+H_2SO_4 0.5 mmol
10	methanol / 2.5	400 min	could not be measured	it became colloidal solution

Discussion

The reduction reaction of selenate ion is shown as follows.

$$SeO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SeO_3 + H_2O \quad (2)$$

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \quad (3)$$

$$Se + 2H^+ + 2e^- \rightarrow H_2Se \quad (4)$$

The standard redox potential of each reactions is as follows, (2) +1.15 V vs. NHE, (3) +0.74 V vs. NHE, (4) -0.4V vs. NHE. Potential of the conduction band edge of TiO_2 photocatalyst is near -0.2 V vs. NHE in the solution whose pH is 3. Then, reaction (2), (3) can be proceeded by the electron emitted from the conduction band of TiO_2. On the contrary, reaction (4) is thought to be impossible to be proceeded by TiO_2 photocatalyst. However, almost selenium is reduced to hydrogen selenide and removed form the model waste water. It can be explained by the accumulation of electron in the photocatalyst particle.

Dunn et. al. measured the electrophretic mobility of the TiO_2 particle under illumination, and found the electrons accumulate on the particle when there are no oxidant around the particles [4]. Sakata el. al. proposed the model in which the accumulated electrons shift up the conduction band

of the TiO_2 [5]. We think this model can explain the generation of hydrogen selenide. The conduction band edge of TiO_2 is shifted up by the accumulated electrons, and the TiO_2 photocatalyst becomes able to reduce amorphous selenium to hydrogen selenide. In our experiments, there were selenate, selenite and proton in the solution as oxidant. When almost selenate and selenite ion were reduced to amorphous selenium, there were no oxidant except proton. It is known that the reduction reaction of proton on the TiO_2 surface is very slow [5]. On the other hand, the oxidation reaction of organic reductant such as formic acid or methanol, can proceed rapidly. Electrons can accumulate in the TiO_2 photocatalyst particle when there are no oxidant except proton and there are sufficient formic acid or methanol. This model can also explain the color change of the suspension and the timing of the generation of hydrogen selenide. Electrons do not accumulate in the photocatalyst particles when there are sufficient selenate and selenite ion around the particles, and the TiO_2 photocatalyst cannot reduce amorphous selenium. In this step, amorphous selenium accumulate in the suspension, and the color of the suspension becomes deep. In the next step, almost selenate and selenite ion is reduced, and electrons begin to accumulate in the photocatalyst particles. The band edge of the photocatalyst is shifted up and amorphous selenium become able to be reduced to hydrogen selenide. Then the amount of amorphous selenium in the suspension begins to decrease and the color of the suspension becomes lighter.

When methanol was added without sulfuric acid, or 0.5 mmol of formic acid was added, the filtrate became reddish yellow and turbid just after the filtration. It looked like colloidal solution of amorphous selenium. We think that the hydrogen selenide remaining in the solution was oxidized by oxygen in air and amorphous selenium generated in the solution.

It needs eight electrons to reduce selenate ion to hydrogen selenide, and formic acid can emit two electrons. The amount of selenate ion in the 100 cm^3 of model waste water is ca. 0.127 mmol, so approximately 0.5 mmol of formic acid is needed to reduce selenate ion in 100 cm^3 of model waste water to hydrogen selenide. However, when 0.5 mmol of formic acid was added without any other acid, total selenium concentration in the filtrate after salting-out, was 24 ppm. When sulfuric acid was added with 0.5 mmol of formic acid, the filtrate was clear and the total selenium concentration in it was ca. 0.24 ppm. These results suggest the pH of the suspension needs to be kept low during irradiation to reduce selenate ion effectively. We think that low pH also has the acceleration effect to move hydrogen selenide to gas phase.

When sodium sulfate was added, the concentration of total selenium was larger than that of the case without sodium sulfate, but it is still under 0.1 ppm. This indicate sodium and sulfate have some effects to the reduction of selenate, but they do not inhibit this reaction strongly.

2-2. galvanostatic electrolysis

We also tried to reduce selenate ion by electrolysis. In the experiment with photocatalyst, TiO_2 can reduce selenate ion smoothly. We thought selenate could be reduced at TiO_2 surface, and we used TiO_2 thin film as cathode.

Experimental

TiO_2 thin film was deposited on SnO_2 coated glass with spray pyrolysis. The crystal structure of the TiO_2 film was anatase, and the thickness was several hundred nm. Platinum plate was used as anode (counter electrode), and Ag/AgCl electrode was used as reference electrode. The anode and the cathode were arranged parallel, and the distance between the electrodes was 5 mm. The area of the cathode and the anode was equal and were 9.0 cm^2. The cell was made air tight, and the volume of it was ca. 4.1 ml. Total amount of the selenium in the 4.1 ml of model waste water was ca. 5.2×10^{-6} mol. It needs 6 electrons to reduce selenate ion to elemental selenium. Therefor ca. 3.0 C is needed to reduce all selenate ion in the cell to elemental selenium. Humid nitrogen gas was bubbled into the cell, and the gas from the cell was exhausted through the copper sulfate aqueous solution. In the electrochemical experiments, potentiostat/galvanostat and function generator set (HA-501G and HB-105, HOKUTO DENKO) were used. After electrolysis, model waste water was filtered with HPLC filters whose pore size was 0.2 μ m (Gelman Science No.4192). Analytical condition was almost same as that in photocatalyst experiment, but ultrasonic nebulizer was not used because the amount of the filtrate was too small.

Results and discussion

Fig.8 shows the relation between the total selenium concentration in the filtrate and the electrolyzed time, when the current density was 0.5 mA/cm^3. It was needed 660 sec to flow 3.0 C of electricity in this condition, so the x-axis of Fig. 8 is scaled every 660 sec. In the case of the sulfuric acid concentration being larger than 2.5×10^{-3} mol/l, selenium concentration decreased almost exponentially until 2640 sec, and the selenium concentration became several ppm. After that,

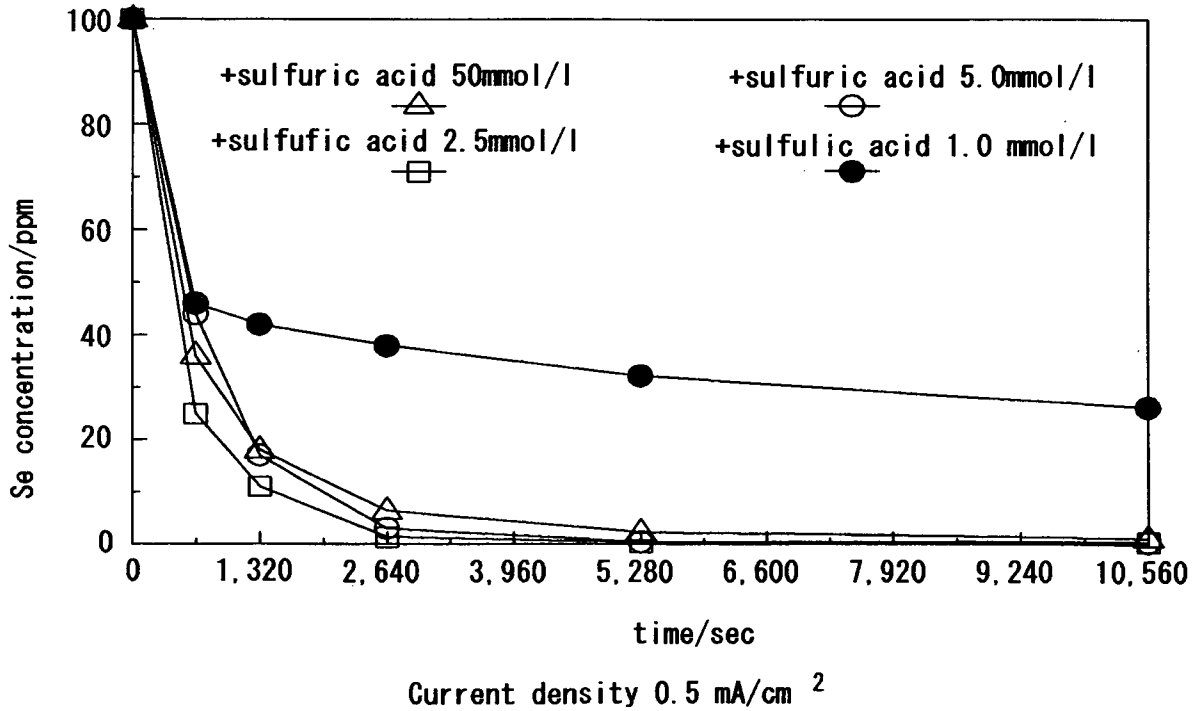


Fig.8 The relation between the electrolyzed time and the total selenium concentration in the filtrate

selenium concentration decreased slowly, and finally it became ca. 1 ppm or under. When the concentration of sulfuric acid was 1×10^{-3} mol/l, the speed of total selenium concentration decrease became low from 660 sec after the start of electrolysis. In these electrolysis, amorphous selenium precipitation generated in the cell. In some case, CuSe precipitation also generated in $CuSO_4$ aqueous solution gas trap, but almost selenium was remained as amorphous selenium.

The energy of the electrons emitted from TiO_2 cathode is constant without relation to the electrode potential, because TiO_2 is n-type semiconductor and the energy of the electron emitted from it is equal to the potential of its conduction band edge. Therefore, amorphous selenium is hardly reduced to hydrogen selenide. However, if the density of surface state of TiO_2 cathode is sufficiently high, electrons can be emitted via surface state and those electron can reduce amorphous selenium to hydrogen selenide. We think this is the reason why hydrogen selenide generation was observed in some cases.

With the reduction reaction proceeding, pH of the solution increases, because selenate and selenite ion is decomposed. If the concentration of sulfuric acid is not sufficient, pH of the solution becomes too high, and the reaction (1) and (2) do not proceed effectively. When the concentration of sulfuric acid was 1×10^{-3} mol/l, the concentration of sulfuric acid was not sufficient, and the reaction speed of selenate and selenite ion reduction became slow from 660 sec after the start of electrolysis.

Conclusion

Selenate ion in the aqueous solution can be reduced by chemical reduction with ferrous chloride, TiO_2 photocatalyst and galvanostatic electrolysis with TiO_2 cathode. Total selenium concentration can be decreased under 1 ppm with these methods, and especially by chemical reduction and TiO_2 photocatalyst, total selenium concentration can be decreased under 0.1 ppm.

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Application of the New Adsorber Polymer Lewatit EP 63 for the Treatment of Contaminated Water in Comparison to Activated Carbon

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1 Introduction

In the aquatic environment polar hydrophilic micropollutants like pesticides, drugs, surfactants and other industrial products, e.g. phenols and sulfonic acids, are widely distributed. These compounds are commonly well water-soluble substances and show high mobility in both aquatic media and soil. Due to their persistence against microbiological degradation numerous hydrophilic pollutants may be enriched in natural waters. In general these substances are of public health interest, because they are often not sufficiently removed by conventional water treatment techniques. Consequently, these polar pollutants of high persistence and mobility represent the most relevant class of organic compounds affecting drinking water resources and are regularly found in ground- and drinking water these days [1-9].

According to European Community Council Directives residues of single pesticides in drinking water must not be present at concentrations higher than 0.1 µg/L, and the concentration of total pesticides must not exceed 0.5 µg/L [10]. For the elimination of organic substances from aqueous solutions adsorption procedures are well-established techniques in drinking water, waste water and process stream purification [1-9, 11-18]. In general, the adsorption process using activated carbon is applied as the last purification step during conventional water treatment of contaminated surface water and groundwater.

Compared to unpolar compounds polar substances are substantially less adsorbed on activated carbon and therefore, these polar micropollutants determine the running times of fixed-bed adsorber plants. As a further disadvantage activated carbon is difficult to regenerate. The high-temperature reactivation causes loss of carbon and relative high costs for waste gas cleaning [4-9, 11]. In addition the application of granular activated carbon (GAC) normally leads to a reduction of adsorption capacity because of the carbon fouling effect which is caused by the preloading of the GAC with natural organic matter (humic substances).

Due to economic and ecological considerations, water purification by adsorption processes with polymeric adsorbents is supposed to be a promising technique that doesn't yield the deposition of high-loaded and toxic material e.g. on landfills. For this purpose regeneration procedures without any loss of capacity are indispensable.

2 Properties of the new adsorber polymer Lewatit EP 63

Lewatit EP 63 (formerly Wofatit) is a novel polymeric adsorbent manufactured by the Bayer Corporation (Leverkusen, Germany) which is widely used in adsorptive water treatment techniques [12-18]. It is a highly porous, weakly hydrophilic, crosslinked adsorbent (polystyrene-divinylbenzene structure) with a very large specific inner surface (1400 m^2/g) and a small pore size (0.5 - 10 nm). These excellent properties are the prerequisites for the high adsorption capacity for micropollutants. In comparison to conventional polymeric adsorbents like XAD resins, the specific surface of Lewatit EP 63 is two to three times higher and reaches values of activated carbons of high quality.

The adsorbing material Lichrolut EN which is produced by the Merck Corporation (Darmstadt, Germany) is equivalent to Lewatit EP 63 but differs in the particle size. Lichrolut EN is the fine-grained analytical material specially designed for solid phase extraction of polar substances [12].

A further particular advantage of Lewatit EP 63 is the feasibility of regeneration which may be performed by organic solvent elution, by oxidation with hydrogen peroxide followed by water elution or by ultrasonic treatment. In this context the similar adsorbent Wofatit EP 61, an unpolar material with an inner surface of 500 m^2/g, could be reused without any adsorption capacity loss after 10 loadings and subsequent regenerations [18].

3 Comparison of Lewatit EP 63 and activated carbon

3.1 Model substances

The intensive use of pesticides has led to their occurrence in both soil and natural waters like groundwater and surface water. In order to compare the adsorption capacities of Lewatit EP 63 and activated carbon (F 300) different polar model substances have been chosen which are known to be ubiquitous in the environment.

Especially atrazine has been one of the most widely used herbicides worldwide, but still it is detected in the aquatic and non-aquatic environment despite of the prohibition of its use in Germany since 1991. Apart from atrazine that has been replaced by terbuthylazine, the triazines generally are subject of various natural degradation processes which primarily lead to desalkylation reactions of the amine groups. Analogous to the triazine herbicides their desalkylated metabolites are very mobile and relatively resistant compounds [19].

Another important class of herbicides used worldwide in agriculture are chlorinated phenoxy acids, such as 2,4-dichlorophenoxyacetic acid (2,4-D). These polar compounds are degraded to phenolic metabolites, e.g. to 2,4-dichlorophenol in case of 2,4-D [20].

A topic of current interest in Germany is the occurrence and fate of drugs in the aquatic environment. For example, special hydrophilic agents are applied in medicine as physiologically active substances which are excreted after their application either unchanged

or metabolized and so reach the natural water cycle. For example, clofibric acid is a metabolite of a lipid-suppressor substance used in human medicine. Because of its high persistency and mobility, clofibric acid even reaches to groundwater and is regularly detected in the tap water of Berlin. In conclusion, drugs have to be considered as new ubiquitous environmental pollutants [21].

3.2 Adsorption equilibrium experiments

For the different model substances mentioned above adsorption isotherms were obtained by batch operated experiments (bottle-point isotherm technique). Different quantities of the adsorbing polymer have been added to several bottles containing a distinct volume of the adsorbate solution. The adsorption equilibrium for both powdered activated carbon (PAC), type F 300, and Lichrolut EN was established after a running time of two days. For the coarse-grained Lewatit EP 63 a time period of two weeks was proved to be sufficient to assure adsorption equilibrium. After equilibration the adsorbent was filtrated and the liquid phase concentration of the adsorbate was analyzed either by absorption measurement or by gas chromatography. The concentration of the solid phase was calculated from a mass balance. Finally, the adsorption isotherms were evaluated by fitting the Freundlich or the Langmuir-Freundlich equation against the experimental data.

All adsorption isotherms were measured both in a high (mg/L) and in a low (µg/L or ng/L) concentration range to compare the different adsorbents PAC, Lichrolut EN and Lewatit EP 63 using atrazine and 2,4-dichlorophenol as model substances. *Figure 1* shows exemplarily the results obtained for atrazine and the isotherms which have been calculated for the polymeric adsorbents. In case of Lichrolut EN the measured values could be represented by the Freundlich equation. The evaluation for Lewatit EP 63 is based on a combination of the Freundlich and the Langmuir-Freundlich isotherm indicating different adsorption mechanisms at low and high concentrations.

According to *figure 1* the values for activated carbon lie above the isotherms for the polymeric adsorbents in the high concentration range, whereas in the low concentration range the isotherms of Lichrolut EN and Lewatit EP 63 are higher than of activated carbon. Thus, in particular for atrazine the adsorption capacity of Lewatit EP 63 is substantially higher than of activated carbon. In case of 2,4-dichlorophenol only marginal differences between the isotherms could be found for the µg/L-range. Generally, the resins possess a stronger adsorbability at smaller concentrations.

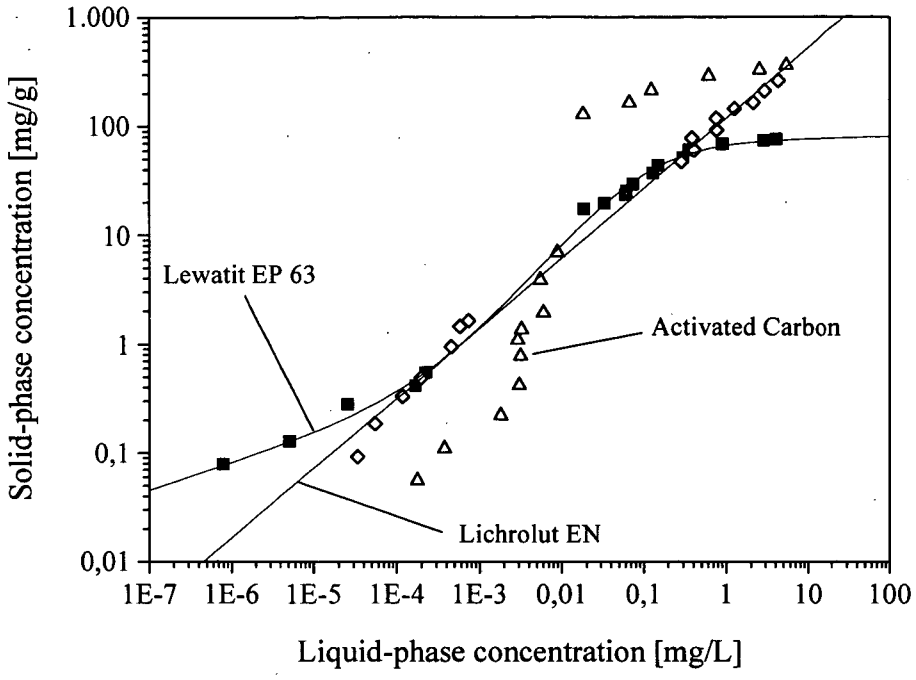


Figure 1 *Logarithmic adsorption isotherms for atrazine.*

3.3 Column breakthrough experiments

Dynamic adsorption experiments have been carried out with two different column sizes. On the one hand laboratory scale columns with an i.d. of 25 mm and a length of 40 cm were packed with 35 g Lewatit EP 63 corresponding to a layer depth of 15 cm. On the other hand a pilot scale adsorption plant with a column i.d. of 15 cm and a height of 2 m was filled with 10.4 kg Lewatit EP 63 which is equivalent to a layer depth of 1 m. Breakthrough curves for the triazine herbicides atrazine and terbuthylazine and their metabolites desethylatrazine, desisopropylatrazine and desethylterbuthylazine were measured. The characterization of the compounds in the effluent has been performed every day by solid phase extraction and by GC/MS. The total amount of triazines in the influent was 50 µg/L, i.e. 10 µg/L for each of the five compounds. The volume flow of the small column was adjusted to 2 L/h corresponding to a filter velocity of 4 m/h. The pilot scale adsorption plant was operated with a volume flow of 200 L/h, which is adequate to a filter velocity of 10 m/h. Within a total operation time of 3 months, 30000 bed-volumes or 2.3 m^3 of triazine-contaminated water have been pumped through the small column. In case of the pilot scale plant a breakthrough occurred after a running time of 8 weeks, i.e. 13000 bed-volumes or 230 m^3 contaminated water.

The breakthrough curves of the small column for the five triazines are shown in *figure 2*. After 10000 bed-volumes a marginal breakthrough could be observed for the more polar metabolites desethylatrazine, desisopropylatrazine and desethylterbuthylazine, whereas the

retardation is stronger for atrazine and terbuthylazine showing a breakthrough after 20000 bed-volumes.

In order to compare different column adsorption experiments with different adsorber materials, the conventional method has been used which comprises the measurement of the effluent concentration up to a distinct threshold limit and the calculation of the specific throughput in m^3/kg, i.e. cubicmeters water needed divided by the mass of adsorbent applied. This parameter depends on the initial pollutant concentration as well as on the content of dissolved organic carbon (DOC) in the raw water. Based on the threshold limit of 0.1 µg/L for pesticides in drinking water and an influent concentration of approximately 10 µg/L, the specific throughput for pesticide removal with GAC adsorbers typically is in the range of 30 - 40 m^3/kg [4-5].

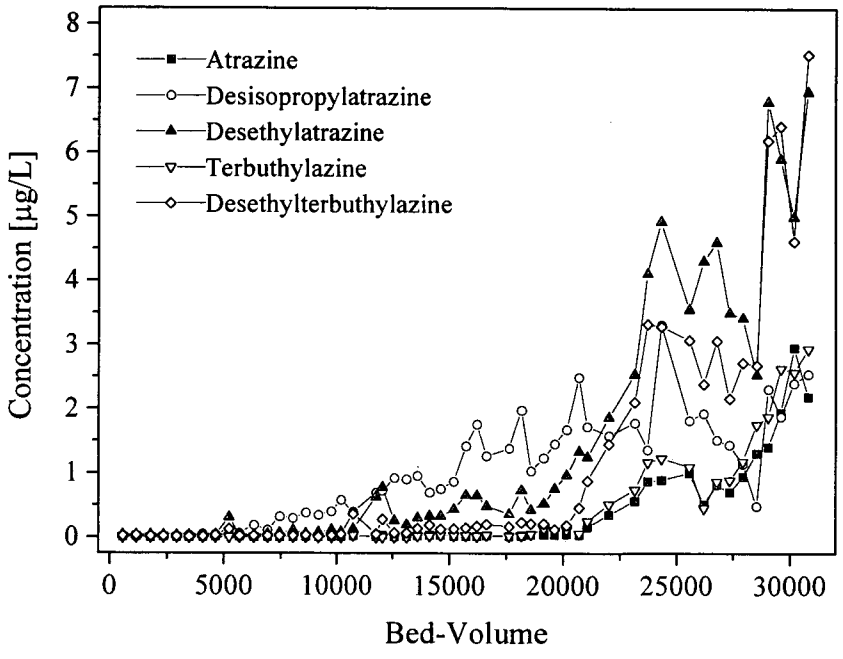


Figure 2 *Breakthrough curves for triazine herbicides with Lewatit EP 63 filters.*

In comparison to this value the measured specific throughputs for the Lewatit EP 63 adsorption columns are listed in *table 1*. The different values for atrazine and terbuthylazine for the two columns are due to the different column packing conditions and the different filter velocities. Considering the fact that the influent concentrations of the pesticides in this experiments were 5 times higher than that from the literature with GAC adsorbers, the new adsorber polymer Lewatit EP 63 is a very promising material for an effective adsorption technique. These investigations confirm the high adsorption capacity of Lewatit EP 63 which is equivalent to that of activated carbon.

Table 1 Specific throughputs in m^3/kg for the Lewatit EP 63 adsorption filters, if the drinking water threshold of 0.1 µg/L is taken into account.

Triazine	Laboratory scale column	Pilot scale plant
Desisopropylatrazine	13.3	12.1
Desethylatrazine	20.5	12.1
Desethylterbuthylazine	28.6	7.9
Terbuthylazine	40.2	7.5
Atrazine	44.2	8.4

3.4 Regeneration of Lewatit EP 63

The triazine-loaded laboratory scale column was taken to test the reliability of organic solvents for the regeneration of the adsorbing material Lewatit EP 63 after a total operation time of 3 months. First experiments have been performed with isopropanol as regenerating solvent that was circulated for several hours through the column to assure a sufficient contact time between the solid and the liquid phase. According to *figure 3* approximately 87 % of the triazines have been successfully eluted from the column after 16 bed-volumes, while the remaining 13 % are supposed to be degraded.

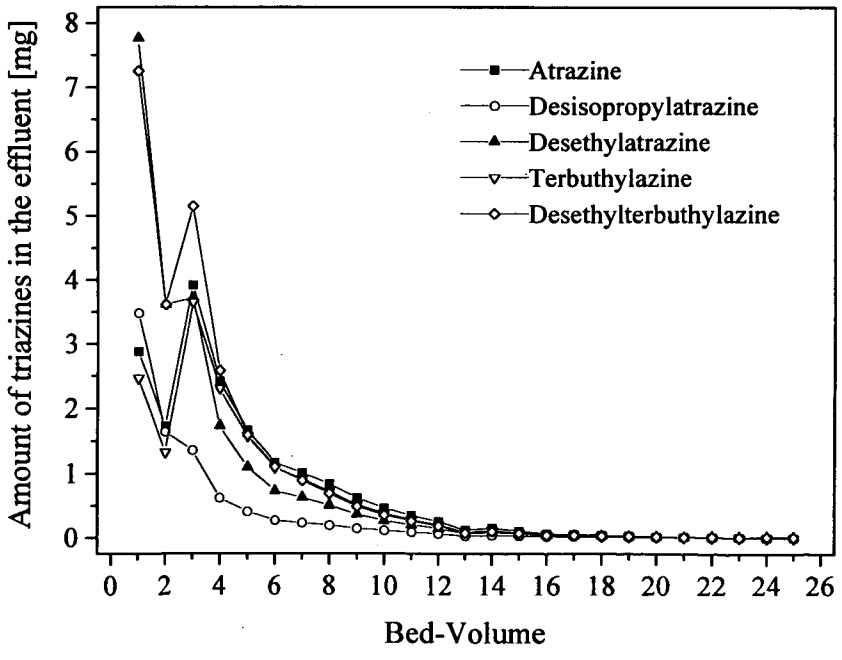


Figure 3 Regeneration of a Lewatit EP 63 filter with isopropanol.

3.5 Adsorption of humic substances

In contrast to activated carbon natural organic matter, in particular humic substances, are practically not adsorbed onto Lewatit EP 63. The adsorption behaviour of humic substances has been investigated extensively by the cooperation partners of the current project. This outstanding property of Lewatit EP 63 is certainly regarded to be of great advantage, because the adsorption capacity for micropollutants may not be reduced by preloading with natural organic matter. In contrast to this fact, the adsorption of humic substances is known to cause grave problems in waterworks working with granular activated carbon.

4 Conclusions

Resulting from the adsorption isotherms for atrazine and 2,4-dichlorophenol the new adsorber polymer Lewatit EP 63 shows advantageous adsorptive properties, predominantly for the low concentration range. For example, the adsorption capacity of Lewatit EP 63 for atrazine was found to be higher than that of activated carbon, whereas more polar compounds like carbonic or sulfonic acids are better adsorbed onto activated carbon. A further advantage results from the fact that humic substances are practically not adsorbed by the polymeric adsorbents.

The results of the column adsorption experiments show that triazine herbicides and their metabolites could be efficiently adsorbed by Lewatit EP 63 and thus, an appropriate removal of these pesticides from contaminated water seems to be feasible even on large scale.

The outstanding feature of Lewatit EP 63 compared to activated carbon is its easy regeneration ability. The effective regeneration of triazine loaded Lewatit EP 63 was successfully performed by elution with isopropanol.

Because of the increasing demand for the purification and detoxification of surface waters in the field of drinking water production, the adsorption technique with polymeric adsorbents such as Lewatit EP 63 are supposed to be a very promising tool to reach higher efficiency. The application of these adsorptive processes for the removal of toxines and undesirable odorous substances which result from algae growth in surface water will therefore be an advisable approach for a cooperation project with a Japanese researche group.

5 Acknowledgements

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PHOTOCATALYTIC DEGRADATION OF HERBICIDE ASULAM IN AQUEOUS TiO_2

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ABSTRACT

Disappearance and mineralization rates for the photocatalytic degradation of asulam were measured and some of its intermediates were identified with regard to aromatic and aliphatic compounds. The results indicated the degradation process of asulam. Whereas photocatalytic degradation of humic acid was monitored by the measurements of TOC and absorbance. Its organic acid intermediates and mineralization products were analyzed, and transformation of chemical structure in the course of degradation was studied by FTIR and GPC. Mainly oxidative cleavage were suggested from these measurement. In the presence of the two compounds the photocatalytic degradation of asulam was retarded by humic acid. However it was suggested that humic acid can also accelerate the degradation of asulam at lower pH.

KEYWORD

Titanium dioxide, Humic acid, Degradation. Intermediate compound, Mineralization. Photocatalyst

INTRODUCTION

Photocatalytic method for environmental protection has been widely studied recently, and it was shown that many organic pollutants could be degraded by this method [1-6]. However most studies were carried out on the solution of single component, and the interaction of two pollutants coexisiting in the solution has been rarely studied in the photocatalytic

process [4].

The present work describes the effect of humic acid on the photocatalytic degradation of asulam. Humic acid is one of major pollutants in natural water such as river and lake. Neverthless there have been very few studies on its photocatalytic degradation [7]. Whereas asulam is a herbicide commonly used for vegetable, fruit and lawn. Pollution by this agrochemical was reported especially at golf courses in Japan [8]. In our previous paper [9] we reported the rate of its photocatalytic degradation and tentatively identified several aromatic intermediates. To study the infleuence of humic acid on the photocatalytic degradation we chose asulam, because its degradation rate is moderate, some of intermediate products in the oxidation process have been reported by us [9] and it is often found in natural water where humic acid is likely to occur.

EXPERIMENTAL

Chemical : TiO_2 used throughout the experiments was TP-2 (anatase, 17.3 $cm^2 g^{-1}$ of specific gravity) supplied by Fujititan Co., unless otherwise mentioned. Its photocatalytic activity was reported in our previous paper [10].

Asulam (methylsulfanilylcarbamate, $NH_2C_6H_4SO_2NHCOOCH_3$) is an analytical grade reagent. Humic acid was purchased from Wako Pure Chemical Industry LTD and was treated by NaOH to make it water - soluble by the fillowing procedure. Humic acid was dissolved in NaOH solution (pH 11.8). After evaporating the solution, the precipitate was washed by methanol and then dried.

Degradation : Seventy five mg of TiO_2 was suspended in 25 ml of sample solution in a Pyrex glass vial by stirring magnetically. This concentration of TiO_2 was constant throughout the experiments. The vial was illuminated by a 500 W super-high pressure mercury lamp though water filter. After specific times small quantities of the suspension were withdrawn and filtered off by a Millipore membrane filter and the filtrate was subjected to analyses.

Analysis : Disappearance of asulam and the formation of aromatic

intermediate were monitored by a JASCO HPLC with a MD - 910 multiwavelength detector. TOC elimination was measured by a Shimadzu TOC - 500.

Organic acid intermediates were analyzed by a Yokokawa IC-7000. Aldehyde and ketone were detected by a Shimadzu HPLC 10 A with a UV detector after coloring with 2,4-dinitrophenylhydrazone [11,12].

Molecular weight distributions of humic acid before and after degradation were measured by a Shimadzu 10A HPLC with a UV detector and a GPC column of Shodex OHpak.

FTIR spectrum of humic acid was meaured by a Horiba FT-200 in KBr pellet.

RESULTS AND DISCUSSION

Asulam

Asulam at the initial concentration of 1.45×10^{-4} mol l^{-1} disappeared within 30 min by photocatalytic degradation. Pseudo-first order rate constant (k_1) for the disappearance was 0.17 min^{-1}. In the absence of TiO_2 (photolysis), k_1 was 0.010 min^{-1} and it is 16.4 times smaller than

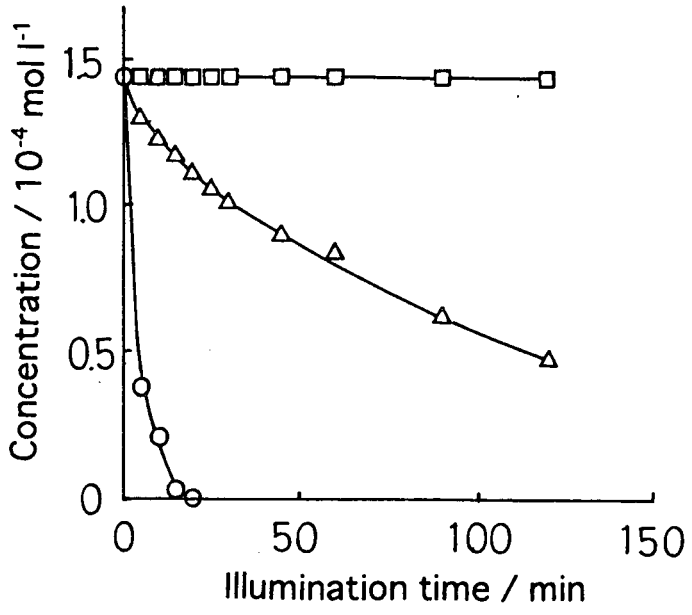


Fig. 1. Photocatalytic degradation of asulam.
○ TiO_2+UV, △ UV, □ Dark

photocatalytic degradation (Fig. 1). pH of the solution did not affect the disappearance rate in the pH range of 3.8 to 7.2. However at pH 2.4 the rate dropped to k_1 = 0.113 min^{-1}. Whereas TOC elimination rate (k_1 = 0.07min^{-1}) was 2.4 times smaller than the disappearance rate.

Four aromatic compounds, namely 4-aminophenol, hydroquinone, sulfanilic acid and hydroxyhydroquinone were found as intermediates, which confirmed the tentative identifications in our previous paper [9]. Their maximum formations were observed at 5 to 10 minutes, although the exact quantification of hydroxyhydroquinone was not possible because of the overlapping with unidentified peak. All of these aromatic intermediates disappeared within 30 min.

As aliphatic intermediates several organic acids, formaldehyde and acetone were detected from the beginning of the degradation and their maximum formations were observed after the disappearance of asulam. Among them formic acid and formaldehyde were formed in the largest concentration. The detection of these intermediates suggests the photocatalytic degradation process of asulam. The degradation is initiated by the hydroxylation of aromatic ring, and further hydroxylation (polyhydroxylation) leads to the openning of aromatic ring [13]. The scheme for the hydroxylation process of aromatic moiety was proposed in our previous paper [9]. The subsequent oxidation forms oxygenated aliphatic compounds such as organic acid, ketone and aldehyde.

Mineralization products were NH_4^+, SO_4^{2-}, NO_3^-, NO_2^- and CO_2. The pH variation of the solution during the degradation reflected the formation of these ions : sharp drop of pH in the beginning is due to the rapid formation of SO_4^{2-}, then the pH rose by the formation of NH_4^+ and after the completion of those ions it remained constant.

Humic acid

TOC elimination was measured to estimate the degradation of humic acid. Its degradation curve consists of three distinct parts (Fig. 2). The first sharp drop is due to the adsorption of humic acid to TiO_2. The following slow decrease may be due to the combination of degradation and desorption. Absorbances at 250 and 300 nm were also measured to

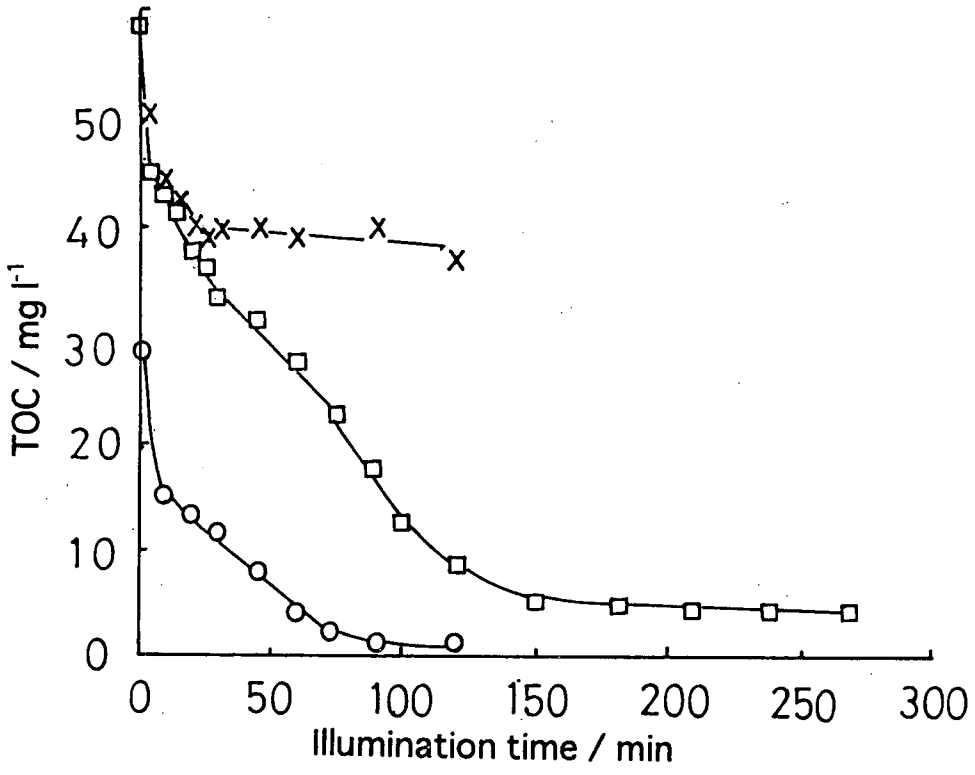


Fig. 2. Photocatalytic degradation of humic acid.
○, □ TiO_2+UV, × Dark

monitor the degradation. The results were similar to TOC elimination. This suggests that the openning of aromatic ring and the subsequent mineralization reactions proceed at the same time. Molecular weight distributions were shown in Fig. 3. The peak before illumination evaluated from polyethyleneglycohol as a standard reference corresponds to the molecular weight of 1,500 and the majority of the molecules are distributed in the lower molecular weight. The peak shifted toward the higher molecular weight after 2 hour illumination. This unexpected result may be explained by the polymerization as observed in the case of UV irradiation and UV + H_2O_2 [14].

Several organic acids (formic, acetic and oxalic acids) were detected as intermediates. Other acids are in smaller quantity and their identifications were not confirmed. Formic acid was formed more rapidly and in larger concentration than acetic acid.

larger wave number. This shift might be attributed to the formations of alcohol and ketone, and the hydroxylation of aromatics. This result suggests that hydroxylation and / or carboxylation take place by illumination.

Mineralization products were NH_4^+, SO_4^{2-}, NO_3^- and CO_2. The amounts of these ions give the elementary composition of humic acid. The weight percentages of C, S, and N in the humic acid caculated from the concentrations of these ions and initial TOC were 47.6, 1.6 and 3.2, respetively which are within the range of values reported for different humic acids [16].

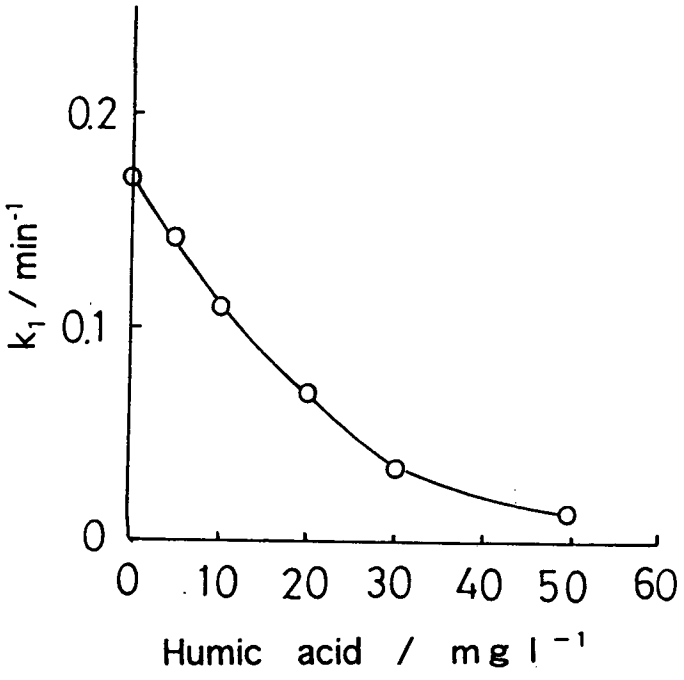


Fig. 5. Effect of the concentration of humic acid on the disappearance of asulam.
Asulam : 1.4×10^{-4} mol l^{-1}

Degradation of asulam in the presence of humic acid

Humic acid at the concentration larger than 5 mg l^{-1} retarded the degradation of asulam (at its initial concentration of 1.45×10^{-4} mol l^{-1} or 33.4 mg l^{-1}) (Fig. 5). The disappearance rate increased with lowering pH. This appears contradictory to the result shown in the previous section. Because humic acid adsorbs to TiO_2 more strongly and degrades faster at lower pH, and hence should retard the degradation of asulam

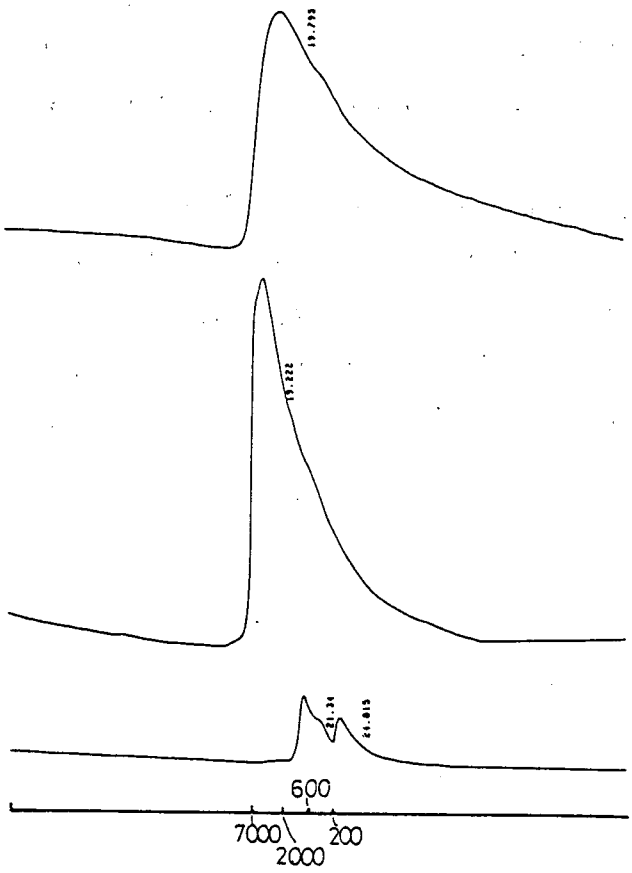


Fig. 3. GPC chromatogram of humic acid before and after illumination.
a. Before illumination
b. 2 hr illumination
c. 10 hr illumination

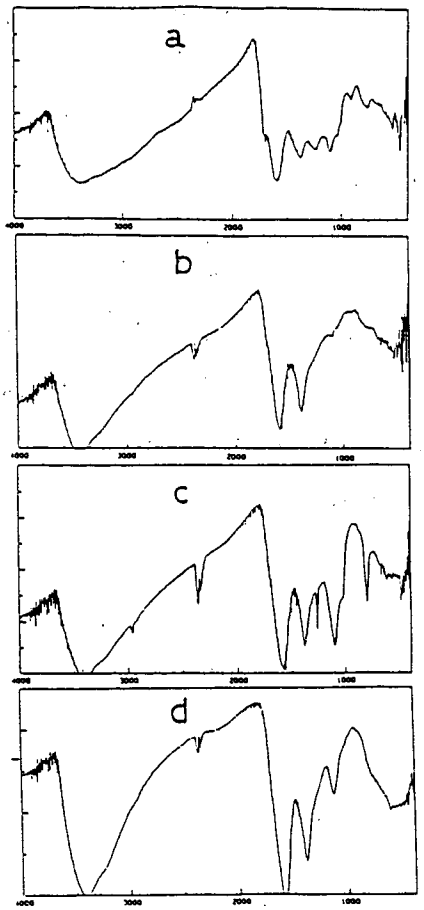


Fig. 4. FTIR spectra of humic acid before and after illumination.
a. Non-treated
b. NaOH-treated
c. 1 hr illumination
d. 3 hr illumination

Fig. 4 shows FTIR spectra of humic acid before and after illumination. Major bands are observed at 3900, 1600 and 1450 cm^{-1} before illumination(Fig.4b). They are due to OH stretching, aromatic C = C combined with carbonyl C = O and / or COO^-, and bending vibration of aliphatic C - H, respectively. For nontreated sample (before NaOH treatment)(Fig.4a) there are additional bands at 1750, 1250 and 1100 cm^{-1}. Thy are assigned to C = O stretching vibration due to carboxyl groups, C - O stretching vibration combined with OH bending deformation [15] and OH of polysaccharide, respectively. Those bands appeared again by illumination(Fig.4c), though the band at 1750 cm^{-1} is not clear because of overlapping with a strong band at 1600 cm^{-1}. Band at 1100 shifted to

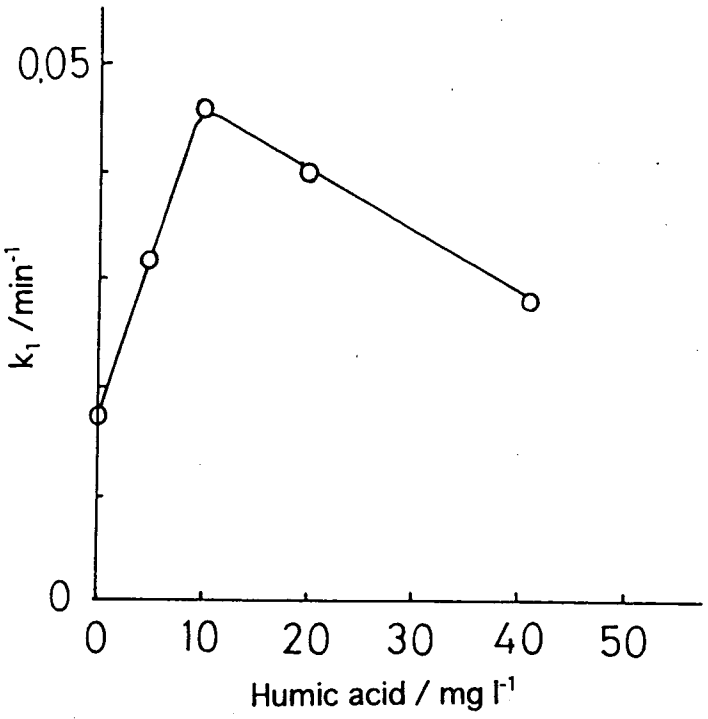


Fig. 6. Effect of the concentration of humic acid on the disappearance of asulam on rutile TiO_2 (Fujititan TM-1).

more effectively as pH lowers. This contradictory result leads us to assume that humic acid promotes the degradation of asulam as well as suppress it. To evaluate the role of humic acid in the photocatalytic process, experiments were carried out with rutile (Fujititan TM - 1) as photocatalyst instead of TP - 2, considering that less photocatalytic activity of rutile helps to show the effect of humic acid more clearly. Fig. 6 shows that humic acid accelerates the degradation of asulam and there is an optimum concentration for the acceleration.

In conclusion humic acid adsorbs to TiO_2 strongly, and thus detards the degradation of asulam. But at the same time somehow it can promote the oxidation of asulam.

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