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**PAPERS PRESENTED
AT THE SIXTH U.S.-JAPAN CONFERENCE
ON SEWAGE TREATMENT TECHNOLOGY**

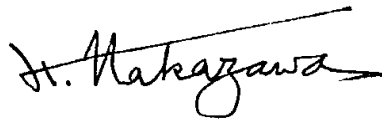
JANUARY, 1979

**WATER QUALITY CONTROL DIVISION
PUBLIC WORKS RESEARCH INSTITUTE
MINISTRY OF CONSTRUCTION,
JAPAN**

FOREWORD

Japan and the United States of America share a common concern for development of the sewage treatment technology. In the past eight years, both countries have made a cooperative effort on problems of mutual concern through the five earlier successful conferences. This publication includes eleven technical papers written by our researchers, which were submitted to the sixth U.S.-Japan Conference on Sewage Treatment Technology, held in Cincinnati, Ohio in October 1978. The Institute hopes that this publication will be of value to the future efforts in this field.

January, 1979.

A handwritten signature in dark ink, reading "K. Nakazawa" with a stylized flourish at the end.

Kazuto Nakazawa
Director General
Public Works Research Institute
Ministry of Construction

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CHAPTER 1 BIOLOGICAL NITROGEN CONTROL

I. BIOLOGICAL NITROGEN CONTROL IN ACTIVATED SLUDGE PLANT (LABORATORY STUDY)

The objectives of the study are: 1) to determine physical, chemical and biological operational conditions for effective nitrification in the conventional activated sludge process. 2) to define optimum operational variables to maintain effective nitrification and organic removal at existing sewage treatment plants with the least modification of the facilities. 3) to develop recovery techniques of organic carbon from anaerobic digester supernatant, for carbon source of denitrification process.

Effect of pH and sludge retention time (SRT) on nitrification has been studied by the laboratory scale plug flow type aerators under the temperature of 20°C, using synthetic sewage with the substrate of dextrin, meat extract, yeast extract, peptone, ammonium sulfate and other inorganic components.

Effects of seawater, Mg, anions and phosphate buffer on the activities of the nitrifiers in activated sludge have been studied separately by a shaking culture method and an aeration method. Synthetic seawater used here was the one developed by Lyman et al. (1949). Determination of the nitrifiers was followed by IBP (1968).

1. SUMMARY

Nitrification in activated sludge process: 1) Result of the field survey showed that numbers of nitrifiers were in the range of 10^3 to 10^4 N/m (Dec. 1975) and Nitrobacter was more than Nitrosomonas. 2) Analysis of "Annual Sewage Treatment Plants' Report" indicated: i) Highest degree of nitrification under the temperature of 18 ~ 23°C. ii) Minimum effluent dissolved oxygen level of 28% of saturation value for effective nitrification. 3) Generation time of the each organisms at the temperature of 20°C in mixed culture system was; ammonium oxidizers 7.4 hours, nitrite oxidizers 11.6 hours, activated sludge ciliata 2.5 days, Rotifera 3.5 days and Sarcodina 13.6 days. 4) More than 10^4 N/ml of nitrifiers would be necessary to obtain nitrate in the effluent. 5) Nitrification activity of the biomass was not likely to be interfered with a shock load of 2 hours when pH was kept within 4 to 11. 6) Above nitrification activity is affected by organic loadings. When pH of the system goes down from 8, which is an optimum pH level of nitrification, to the lower, effect of organic loadings become severe. The long SRT is necessary to obtain the same extent of nitrification.

7) As for the biological fauna, activated sludge ciliata and Rotifera were dominant when pH was within the range of 7 to 8 and Sarcodina was easily to appear when it goes down to 6. This tendency was much clearer when STR of the system was kept longer. 8) Rotifera and Sarcodina could be used as index organisms to determine whether nitrification could be expected or not in the system. 9) Optimum pH for nitrification was 8. To achieve substantial nitrification, SRT of

the system should be kept more than 3, 6, 11 days when pH is 8, 7, 6 respectively under the temperature of 20°C. 10) Removal efficiency of soluble organics was more than 97% in all the experimental runs regardless to the pH and SRT. High solid removal efficiency was obtained when SRT was maintained between 5 and 10 days. However, when SRT was less than 3 days, solid removal was deteriorated due to the bulking of the sludge and when SRT was more than 10 days, solid washout was observed due to the deflocculation and floatation of the denitrified sludge.

Effect of trace inorganics: 1) Growth of fresh water nitrifiers were inhibited when cultured with more than 40% of sea water, while maximum growth rate was obtained when no sea water was added at all.

2) Under the case that both sea water and fresh water nitrifiers were co-inhabited, maximum growth rate were obtained when cultured just in sea water. However, lag phase was shortest when sea water was added 40 to 60%. This may indicate that changes in "environment" of the nitrifying bacterias is related to the length of the lag phase.

3) Results of shaking culture tests indicated that addition of sea water provides buffer capacity to the system rather than accelerating nitrification by the effects of trace materials in sea water. In all cases of the run, degree of nitrification was preceded by the addition of sea water. As pH in the system has kept relatively high due to the buffur action of sea water, activities of Nitrobacter seemed to be restrained and nitrite nitrogen be readily to exist in the system.

4) Growth rate on Nitrosomonas in 40% mixture of sea water under the existence of Tris-buffer was about 1.34 times as much as that in 20% mixture. This was probably due to the favorable effect of Mg in sea water. However, ammonium oxidation rate per Nitrosomonas was more in 20% mixture than that in 40%. 5) In a system in which culture time was less than nitrifiers' generation time, phosphate was effective to accelerate nitrification. Optimum dose was 13mM for ammonium oxidation. 6) High dose of anions deteriorates the rate of nitrification under the existence of phosphate. Deterioration effect of anions is summarized as follows: NO_3^- (29mM) > F^- (48mM) > SO_4^{2-} (76mM) > I^- (80mM) > Br^- (140mM) > Cl^- (170mM). Numbers in parenthesis are the critical concentrations which deteriorate the rate of nitrification down to 50%.

Bacteria culture procedure: 1) Dispersion technique of activated sludge for bacteria determination applied here was ultrasonic shredding. Selected power for the apparatus was 25 W and 2.5 minutes for shredding. Those are recommended values. 2) Recommended procedures for bacteria determination for counting are 10 day incubation for heterotrophs in 20°C with Trypton media and for nitrifiers 20 – 40-day when IBP method is applied.

2. SUCCESSION OF MICROORGANISMS IN ACTIVATED SLUDGE IN NITRIFICATION

It is a well known fact that microorganisms contained in activated sludge differ in types and compositions with influent quality, organic loads, return sludge rate and dissolved oxygen and so on.

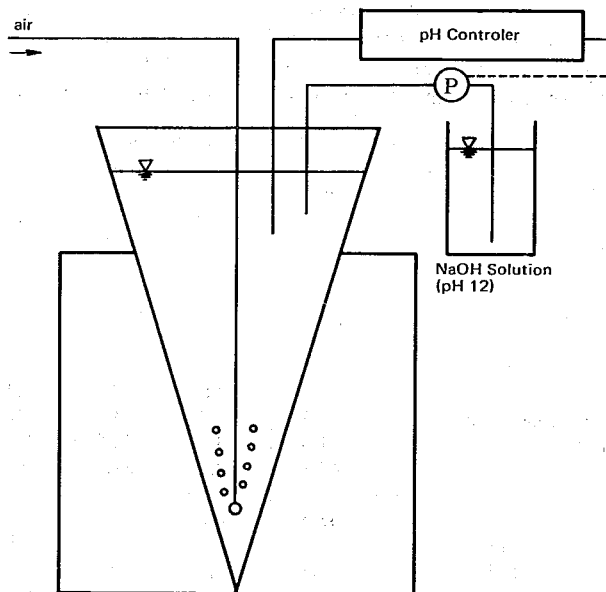
This particular study was conducted to determine operating conditions that would promote nitrification at activated sludge treatment facilities by conducting examinations of the changes of heterotrophs, nitrification bacteria, protozoa and metazoa besides studying organic removal and nitrification rate of the mixed culture system based on SRT as an indicator of activated sludge. SRT is one of the factors that is detrimental in dominating the types and compositions of micro organisms and is an indicator for the generation time of microorganisms.

Studies were also made on the influence of sudden change of the pH against nitrification.

2.1 EXPERIMENT METHOD

Five Inhoff type cones were used for the experiment. (Fig. 2.1).

Fig.-2.1 Batch Type Testing Apparatus



The synthetic sewage mainly composed of protein such as meat extract, peptone was fed to the aerators by batch method with aeration time being 22 hours and sedimentation time 2 hours. Activated sludge obtained from domestic sewage treatment plant was seeded to the each aerator. The experiment was conducted in a 20°C constant temperature room. pH was controlled at a range between 7 and 8 continuously by automatic regulator, and the SRT was set by controlling MLSS in the aerators. Namely, influent organic load was kept constant while the MLSS was adjusted each aerator at 500, 1,000, 1,500, 3,000 and 6,000 mg/l.

Nutrient bacteria, nitrite bacteria, nitrate bacteria, protozoa and metazoa in mixed liquor were determined beside water quality analysis.

The trypton glucose culture medium was used for determination of heterotrophs, culturing at 20°C for 10 days. All colonies emerging from the culture were counted. The nitrification bacteria determination was followed by the IBP.

2.2 TEST RESULTS AND DISCUSSION

The summary of the results is shown in Table 1. The shortest SRT was about 4 days while the longest 60 days. As to the sludge characteristic, when the F/M ratio was high, SVI became 125 and growth of filamentous bacteria was observed resulting in bad sedimentation condition. However, when the F/M ratio maintained lower, or in the longer SRT condition, protozoa in the sludge became affluent. And the SVI was easy to be maintained less than 100.

The organic load was estimated to be between 0.2 and 1.5 g/ss.g/day from the following: TOC-SS load 0.06 – 0.58 g/ss.g/day; and BOD-SS load based on the relationship between TOC and BOD (observed ratio: BOD = 2.78 TOC).

Table-2.1 Average Values of Analytical Results

Phase	A	B	C	D	E
SRT (day)	3.65	5.82	9.60	18.01	59.3
MLSS (mg/l)	670	1,202	1,626	3,083	5,979
MLVSS (mg/l)	647	1,089	1,465	2,585	4,618
MLVSS/MLSS	0.966	0.906	0.901	0.839	0.772
TOC Load (mg/ss.g/day)	538	308	213	115	58.6
Removed TOC (mg/ss.g/day)	489	288	198	107	54.6
Removal Rate (%)	91.0	93.5	92.5	93.0	93.1
SS (mg/l)	49.1	32.4	31.4	39.2	22.2
Removal Rate K-N	43.6	50.8	59.4	92.1	93.6
(%) Org-N	91.9	95.4	91.3	91.2	91.5
T-N	35.1	25.7	20.4	3.8	-0.1
Nitrification Rate (%)	11.6	36.5	55.8	97.1	99.0

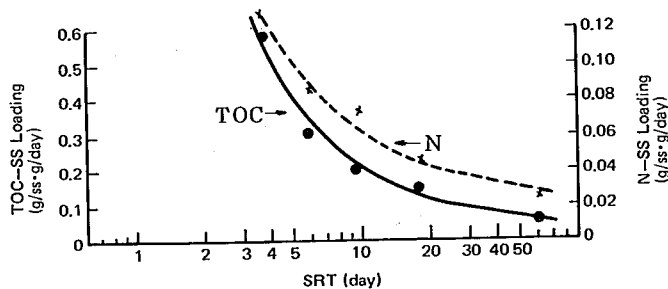
The SRT in this paper is defined as below.

$$\text{SRT (days)} = \frac{V \times S}{\Delta s + \text{ss} \cdot q}$$

V: Aerator capacity (liter), S: MLSS (mg/l),
 s: Excess activated sludge (mg), ss: effluent SS (mg),
 q: flow (l/d).

SRT expresses the retention rate of activated sludge within the system. At normal condition, the SRT is subjected to sludge production which depends upon the volume of removed organic matters to be converted into sludge. The conversion rate to sludge differs according to sewage strength and for the municipal sewage the rate is about 0.7 while the synthetic sewage used in this test was about 0.21 which means the sewage is easily degradable. The relation between organic load and SRT in this study is shown in Fig. 2-2. The longer the SRT the smaller the F/M ratio.

Fig.-2.2 SRT vs Loading

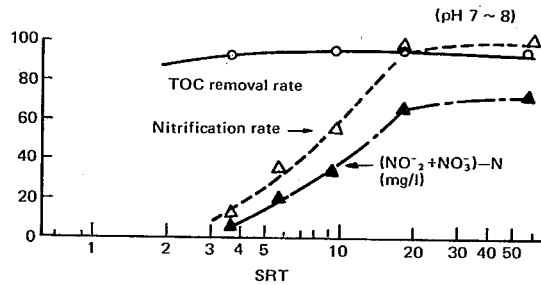


2.2.1 SRT and Removal Rate

The removal rate of organic substances under each run is in the range of 91 to 93.5 percent, and there was little difference in removal rate.

The removal rate of nitrogen in terms of TKN increased in proportion to SRT and reached 90% when SRT exceeded 18 days. In each run, organic nitrogen was removed mostly and removal rate was more than 91%. Total nitrogen removal rate was 35% at about four days of SRT. The removal rate decreased in proportion to the increase in SRT while nitrification rate increased. (Fig. 2.3). When SRT is kept over 18 days, mostly all nitrogen were converted to nitrate. When SRT increased, self oxidation in the sludge resulted in the release of ammonium to increase the total amount of nitrogen in effluent. The nitrate concentration, up until the 18 days of SRT, followed a straight ascending line. And beyond the 18 days, amount of TKN in the influent served as the limiting factor of nitrification. Since the amount of nitrite was extremely low in this SRT range, there was a possibility that the nitrification rate was hindered by nitrite in system.

Fig.-2.3 TOC Removal Rate, Nitrification Rate and SRT



2.2.2 Bacteria Population and SRT

The bacteria growth rate can be described as follows:

$$\frac{dN}{dt} = \mu N \quad (1)$$

or

$$\ln \frac{N}{N_0} = \mu(t_2 - t_1) \quad (2)$$

N_0 : Number of bacteria at t_1

N : Number of bacteria at t_2

μ : Specific growth rate (1/t)

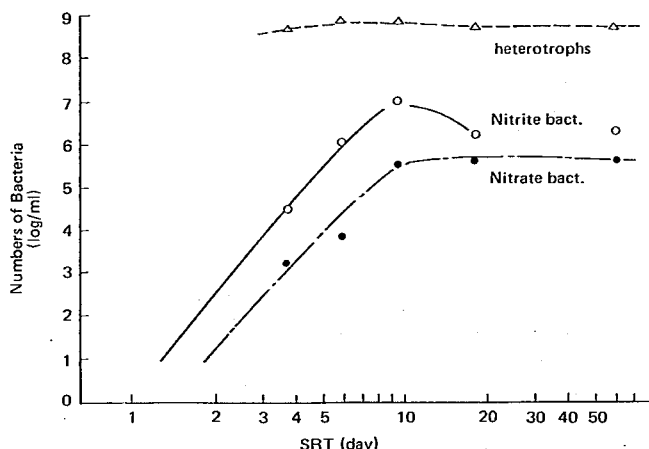
t_g : Average Generation Time (t)

$$t_g = \frac{\ln 2}{\mu} = \frac{0.693}{\mu} \quad (3)$$

Generally, the growth rate of nitrification bacteria is known to be between 10 and 12 hours, although some species require 20 or 40 hours. When compared to the growth of heterotrophs, the growth rates of autotrophs are slower owing to energy efficiency. The numbers of nitrification bacteria in activate sludge also changes in proportion to the length of SRT.

The relationship between bacteria number and SRT obtained is as shown in Fig. 2.4. With regards heterotrophs, constant number was maintained between 10^8 and 10^9 in this SRT range and thus the substrate in the system was regarded as the ruling factor. Furthermore, the value was close to the one obtained from the activated sludge at an existing plant. The nitrite bacteria increased in proportion to the SRT and reached the maximum value of 10^7 in number when SRT was 7 days while the nitrate bacteria were between 10^5 and 10^7 . The existed number of nitrate bacteria was less than nitrite bacteria.

Fig.-2.4 Relation between SRT and Bacteria Number



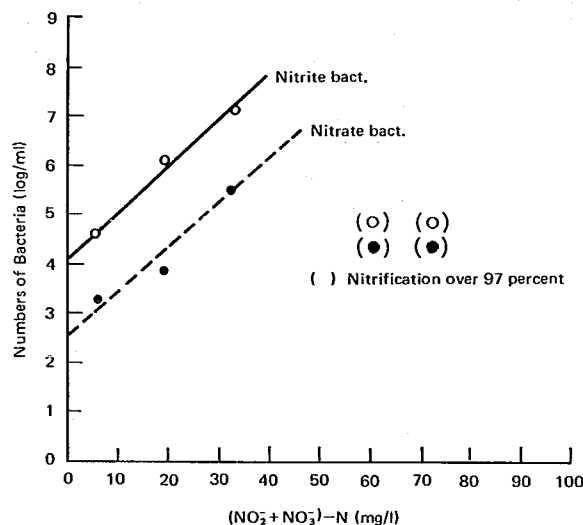
This fact also was confirmed by the water quality analysis that resulted in low concentration of NO_2^- in effluent. This indicates that the NO_2^- have acted as the ruling factor against the growth of nitrate bacteria.

When nitrification bacteria are to be maintained in maximum concentration with the substrates being the ruling factors similar to heterotrophs, the system requires SRT of over 10 days. At existing plants, although it is affected by operational factors, it is considered possible to designate operating SRT by estimating the maximum yield of nitrification bacteria by TKN concentration.

Since it is possible to consider that the maximum yield of nitrification bacteria is maintained at each designated SRT, from the relationship as shown in Fig. 2.4, the growth rate of nitrification bacteria (μ , 1/day) and generation time (tg.h) are calculated as follows: for nitrite bacteria $\mu = 2.26$, tg = 7.4h and for nitrate bacteria $\mu = 1.44$, tg = 11.6h respectively. Based on this generation time, from the relationship between nitrite bacteria and nitrate bacteria (Fig. 2-5), the minimum

culture time or SRT can be obtained from Equation (2) (3) on bacteria multiplication rate after obtaining the nitrification bacterial number based on the assumption that the nitrification of TKN attained 100 percent.

Fig.-2.5 Nitrification Bacteria and Amount of Nitrification



2.2.3 Protozoa and Metazoa in the System

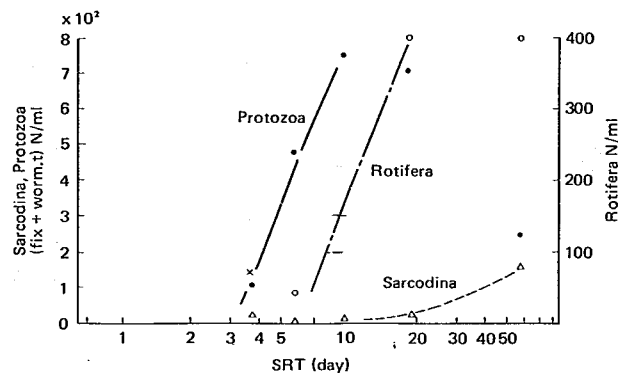
Table 2.2 shows the microscopic test results. From these results, the growth condition can be grasped to a certain degree. When organic load is high, the number of swim type microorganisms is great. And when the load decreases, the population of swim type diminishes accordingly. In this case, the *Pleuromonas* is quoted as the index. When settlability of activated sludge sedimentation is good, it is generally regarded that the fix type and worm type microorganisms increase in number. And similar tendency was observed in this study. In the condition of aerobic digestion or extended aeration system, *Rotifera*, *Arcella* and *Euglypha* were frequently observed. In this case, they were observed when load was low. Also filamentous bacterium, related microorganisms to bulking, appeared in proportion to the load. The filamentous bacteria that appeared here included those in divided and shredded forms. Zoogloes also were detected as *Z-ramigera* and *Z-filpendula* coexisting.

The observation of the relationship of organic load and biological fauna indicated that the organic load and SRT are also in relationship and that the species of fast multiplying rate become dominant when SRT is short and those of slow growth rate appeared when SRT become longer to increase in variety. The relationship between SRT and biological fauna is shown in Fig. 2.6. Protozoa of fix type and worm type appeared when SRT was over 3 days, *Rotifera* over 6 days, and *Sarcodina* much longer. Similar to bacteria, the growth rate and generation time are calculated from Fig. 2.6 as follows: for Protozoa $\mu = 0.28$ 1/day, $t_g = 25$ days; for

Rotifera $\mu = 0.20$ 1/day, $t_g = 35$ days; and for Sarcodina $\mu = 0.05$ 1/day, $t_g = 13.6$ days. Rotifera rank at the top of food chain and are polyphagia thus showing such t_g level.

With regards loricate amoeba, it is often observed when organic loading is maintained low like in extended aeration or in aerobic digestion processes.

Fig.-2.6 Relation Between SRT and Protozoa Sarcodina, Protozoa



Being loricate, the percentage of such amoeba being preyed upon is low and their generation time being to the short category.

The microscopic studies of protozoa and metazoa revealed that the organisms that were identifiable also maintained intimate relationship with SRT in activated sludge. Furthermore, concerning the Flagellate organisms observed when organic loading was high, as the substrate became the ruling factor when organic substrate became low in concentration because they utilize soluble ingredients, they were handicapped in the race to consume energy. The swim type ciliata appeared were few when TOC-SS load were in the range of 0.2 – 0.3 mg/ss.g/day, and they were detected when the load was either higher or lower than this range.

2.2.4 Organism Index Predicting Nitrification Activity

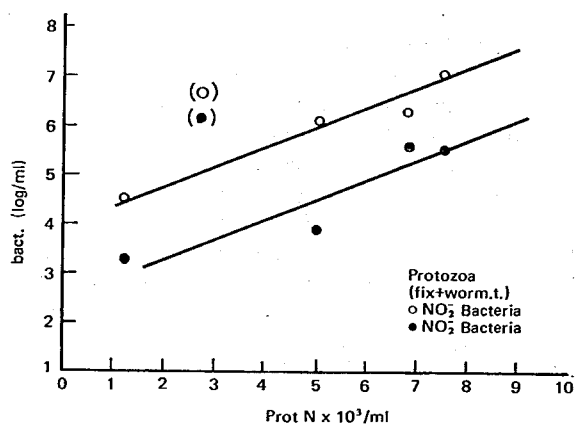
The attempt to grasp activated sludge condition by microscopic study results is one of the important procedures to maintain and control biological treatment.

To assume nitrification conditions from the results of microscopic studies, the relationship between nitrification bacteria concentration and protozoa (fix type plus worm type) shown in Fig. 2.4, Fig. 2.6 and Table 2.2 was used to develop Fig. 2.7. There is a clear correlation between nitrifier number and protozoa. It is possible to expect nitrification when protozoa of fix and worm type with comparatively long t_g exist in quantity. This figure shows just an example, and it is necessary to accumulate data at actual existing plants. With regards Rotifera, Arcelia and Euglypha, they were often observed in existing treatment plants thus can be considered an effective index to predict nitrification activity.

Table-2.2 Organisms Survey Result

Phase	A	B	C	D	E
Sarcodina	243	29	29	200	1,622
Amoeba	243	29			
Arcella			29	171	371
Euglypha				29	1,257
Flagellate					
Pleuromonas	30,800	1,409	428	200	171
Ciliata					
Swim. type	1,267	0	324	1,200	1,000
Litonotus	1,170	0	324	1,200	1,000
Unknown g.	97				
Worm. type	0	340	1,228	1,114	486
Aspidisca		291	1,142	1,000	457
Euplates		49	96	114	29
Fix. type	1,215	4,672	6,285	5,877	1,771
Vorticella	389	1,321	571	620	257
Epistylis	729	1,268	1,714	571	200
Cpercuraria	97	437	829	143	200
Unknown g.		1,651	3,171	4,543	1,114
Rotifera	0	49	0	400	400
Filamentous bact. (%)	50	30	5	2	
SRT (day)	3.63	5.82	9.60	18.01	59.3

Fig.-2.7 Relationship between Nitrification Bacteria and Protozoa



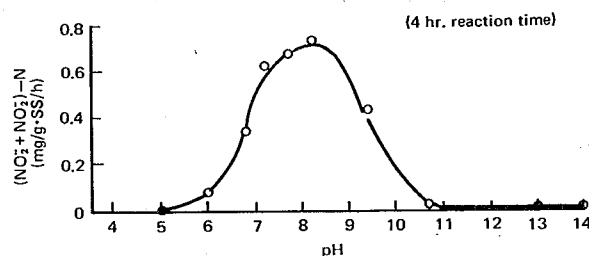
2.2.5 The Influence of pH on Nitrification Activity

Experiments were conducted to see the effect of pH change on the nitrification activity. Two procedures were chosen for the experiment. One is that four hour reaction time aerators were used for each pH condition between 4 and 14. The other is that after two hours of reaction at a set pH, the pH was adjusted to 7 for further reaction of four hours.

Concerning the optimum pH for nitrification bacterial activity, although researchers differ in opinion with regards the optimum pH range, it is generally regarded best between 7 and 8.5.

The reaction time for these experiments was too short for multiplication of nitrification bacteria, and the tests were to simply compare the pH effects against enzyme reaction. Fig. 2.8 shows the relationship between pH and nitrification rate.

Fig.-2.8 Relation between pH and Nitrification



Maximum rate was obtained in the neighborhood of pH 8. It was 0.7 mg. (NO₂⁻ + NO₃⁻) - N/g.ss/d. The Optimum pH range was 8 ± 0.5. The forms of pH and nitrogen were as shown in Fig. 2.9. On the acidic side, more ammonium residue was found, while on the alkaline side, more organic nitrogen was detected. In terms of total nitrogen amount, it was found increasing on the alkaline side perhaps due to elution of decomposing inert organisms and cells when pH was above 11.

Fig. 2.10 shows that, the inhibition occurred when contacted with fixed pH for a short time and then adjusting the pH to 7. Within the range of pH 4 and 11, even when contact was made with each pH for two hours, little inhibition was observed against nitrification activity when adjusted to neutral later on. It also became obvious that there are strong resistance against sudden change in pH shock load deriving from the inflow of industrial waste water.

Fig.-2.9 pH and Form of Nitrogen

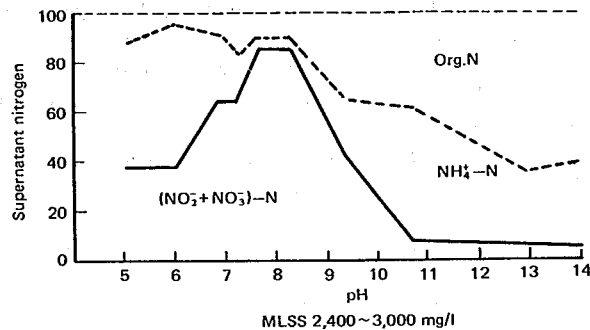
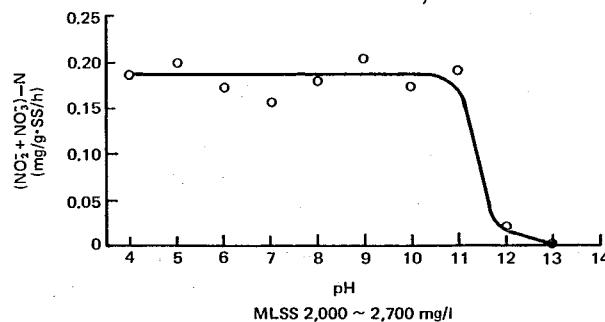


Fig.2.10 Influence on Nitrification Rate when Adjusted to pH 7 after 2 Hours Contact with Set pH



2.3 SUMMARY

It became clear that the biological fauna in activated sludge was subjected to SRT. The amount of nitrification bacteria for sufficient nitrification was over 10^4 N/ml. The generation time of the biological fauna in mixed culture was as follows: Nitrite bacteria 7.4 hours; Nitrate bacteria 11.6 hours; Flagellate of fix and worm type 2.5 days; Rotifera 3.5 days and Loricata Ameoba 13.6 days. It is also effective to expect substantial nitrification by the control of treatment facilities with SRT required to maintain nitrification bacteria based on generation time. It is also possible to grasp the nitrification condition of plants by indexing Rotifera and Loricata Ameoba by microscopic examinations.

Maximum rate of nitrification in short time reaction was obtained at around pH 8. There were no changes observed in total nitrogen at pH 5 to 9, and the balance of nitrogen forms was affected by nitrification activity. As organic nitrogen increased on the alkali side, total nitrogen also increased. In the range of pH 4 to 11, even when contact was made with each pH for two hours, it was possible to continue nitrification activity after being neutralized.

3. NITRIFICATION STUDY BY CONTINUOUS OPERATION

In this study, a continuous testing apparatus of plug flow type aerators were used to control SRT and pH to determine their influence on nitrification.

3.1 TEST METHOD

In this test, four sets of continuous testing apparatus (A, B, C, D) of 60 liter aeration tanks and 30 liter sedimentation basins were employed. As shown in Fig. 3-1, the tests were conducted by continuously feeding synthetic sewage in constant temperature room of 20° Centigrade. The tests were broken up in three stages as follows:

I) The pH was set at 8 and SRT was varied in each unit. II) at pH 7, III) and at pH 6. Furthermore, the air flow was thoroughly controlled to prevent the DO from becoming a ruling factor in this experiment.

The pH control was done by Automatic pH Regulating Units at 2 points. The chemicals for pH control were NaOH and HCl diluted by tap water. SRT was indirectly controlled by introducing the following method. The concentration and flow rate of influent to all units were fixed at the same amount. And the MLSS concentration in each unit was maintained in different level. By this manner, each unit was fixed to have different organic loadings. SRT was controlled by extracting the set amount of waste activated sludge. The MLSS in the aeration tank of Unit A was set at 500 mg/l, B 1,000 mg/l, C 1,500 mg/l, and D 3,000 mg/l.

In the operation care was placed on controlling MLSS because it was necessary to maintain as constant as possible the organic loadings. Therefore, efforts were exerted to sludge withdrawal. Further, periodic checks were conducted on the flow rates of pumps. The daily sampling was made by the 24-hour composite sampling by analyzing the Transparency, pH, SV_{30} , MLSS, MLVSS, SS, BOD, COD, TKN, ammonia, nitrite and nitrate. A once weekly determination was conducted of heterotrophs, nitrification bacteria, protozoa, and metazoa. The counting method based on plane culture was employed for heterotrophs determination while the MPN Method was introduced to count nitrification bacteria after 100 days of culture. With regards counting of protozoa and metazoa, the microscopic method was incorporated. The culture media used for counting the bacteria were as follows:

Heterotrophs: Trypton glucose culture medium (pH 7)

Trypton: 20g, glucose 10g, and agar 9g are dissolved in one liter of water.

Bacteria infection: 115°C, 30 minutes.

Nitrification Bacteria Quantitative Culture Medium:

A Solution: KH_2PO_4 100 mg., $MgSO_4$ 50 mg, $CaCl_2$ 20 mg.,
 $NaHCO_3$ 200 mg, EDTA-Fe 6 μ g, $CaCO_3$, SiO_2 trace
 dissolved in one liter of ion exchange distilled water.

Nitrite Bacteria: A Solution plus $(NH_4)_2SO_4$ 30 mg

Nitrate Bacteria: A Solution plus KNO_3 30 mg

(filtered by 0.2 μ membrane filter.)

Fig.-3.1 Outline of Testing Apparatus

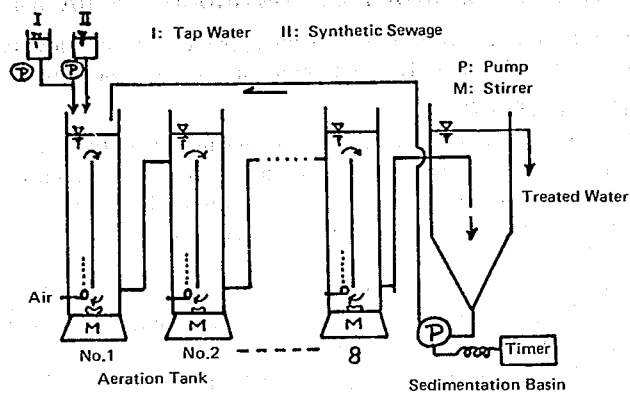


Table-3.1 Synthetic Sewage (BOD = 150 mg/l)

Substrate	mg/l	Substrate	mg/l
Dextrin	23	NaCl	5
Meat extract	49	MgSO ₄	3
Yeast extract	56	KH ₂ PO ₄	14
Peptone	49	KCl	10

3.2 RESULTS AND DISCUSSION

Table 3.2 shows the summary of the results. The values represent each respective testing condition that are considered stable.

The organic load was within the range of BOD-SS Load $0.07 - 0.51$ g/ss.g/day and COD-SS load $0.07 - 0.51$ g/ss.g/day. And SRT was within the range between 2.7 and 22.4 days. The pH was successfully controlled in the range neighboring the set value. The SVI has shown a tendency to be in proportion to the organic load and marked a maximum 2,350 at high load. This was due to the growth of two or three species of filamentous bacteria.

3.2.1 Relationship between Organic Load, Removal Rate and SRT

With regards soluble (S) BOD, COD and T-N, Fig. 3.2 shows each relationship between the organic load per sludge unit and removal rate. The removal rate within this load range was: BOD, about 98 percent and virtually unaffected by load changes; and removal rate of total nitrogen increased in proportion to load-increase and remained virtually unaffected from pH. Similarly, Fig. 3.3 shows the relationship between loadings and the removed amount for each item. Each has shown that the removal rate per solid had the tendency to increase in proportion to the load applied loadings, and the gradients were: BOD, 0,984, COD, 0,853 and T-N, 0,447. These values express the removal rate per solid.

Fig.-3.2 Load and Removal Rate

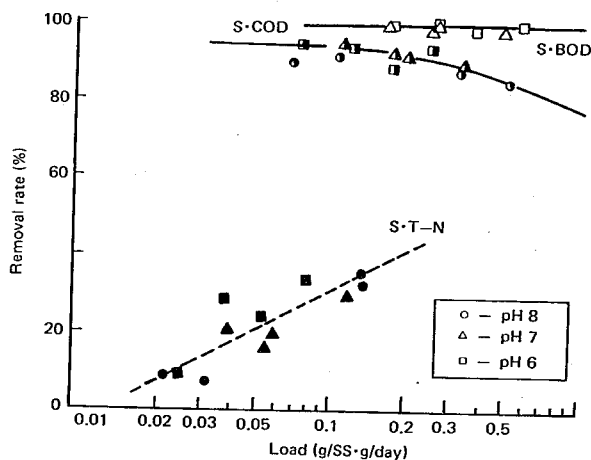


Fig.-3.3 Load and Removal Per Unit Sludge

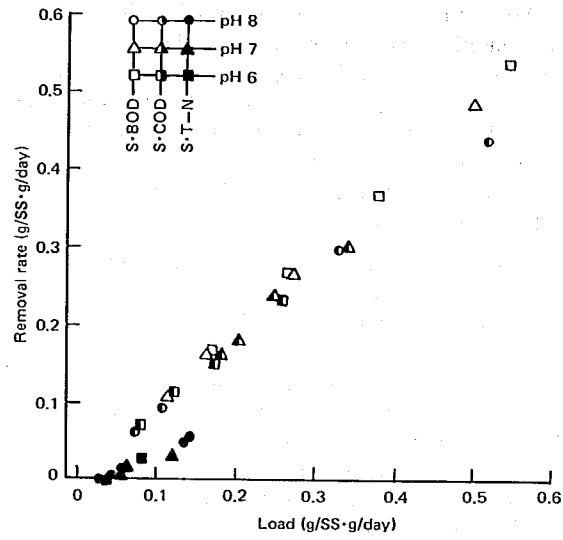
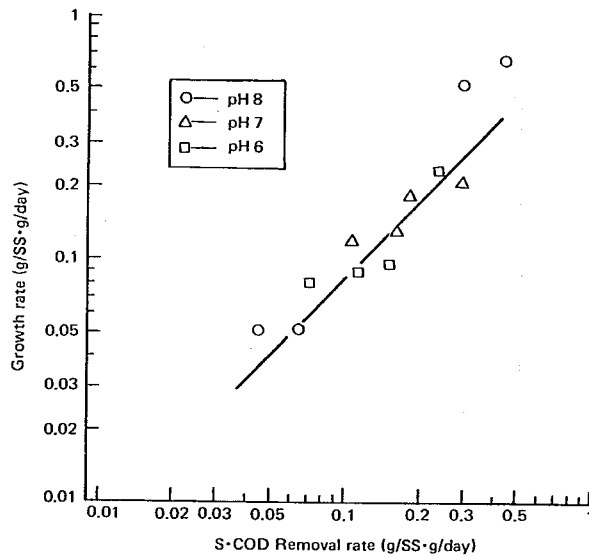


Fig.-3.4 Removal Rate and Multiplying Rate Per Unit Sludge



When examining the relationship between the removal rate of soluble COD per sludge unit and the amount of sludge production per solid, a positive primary interrelation as shown in Fig. 3.4 was obtained. If the relation between load and generating amount can be given, SRT to a certain degree can be predicted. The SRT can be expressed in the following:

$$\text{SRT} = \frac{\Sigma \text{SS}}{\Delta S} \quad (1)$$

$$= \frac{(1 + \alpha) \text{MLSS} \cdot V_0}{S} \quad (2)$$

$$= (1 + \alpha) \cdot F(R)^{-1} \quad (3)$$

$$= (1 + \alpha) \cdot F(L)^{-1} \quad (4)$$

SRT: Sludge Retention Time (T)

ΣSS : Total Solid in the system (M)

ΔS : Multiplying Rate of Activated Sludge ($\text{M} \cdot \text{T}^{-1}$)

MLSS: Activated Sludge Concentration in Aeration Tank (ML^{-3})

V_0 : Aeration Tank Capacity (L^3)

α : Coefficient when Total Solid in the system is expressed in MLSS.

$F(R)$, $F(L)$: Multiplying Rate (Function of Amount per Solid (R) and Load (L)) (T^{-1})

Equation (1) is the fundamental equation of SRT which can be expressed in Equation (2). Also Equation (2) can be expressed as a function by the inverse number of the multiplying rate. When the relation between the multiplying rate and the removal rate per sludge unit and load can be given, SRT can be predicted by Equations (3) and (4).

$F(R)$ and $F(L)$ are obtained as follows by applying soluble COD.

$$F(R) = K_0 \cdot \text{RCOD} C_0 + (K_0 = 0.864, C_0 = -0.002) \text{ and}$$

$$F(L) = K_0 \cdot K_1 \cdot \text{LCOD} + K_0 C_1 + C_0 \quad (K_1 = 0.853, C_1 = 0.009)$$

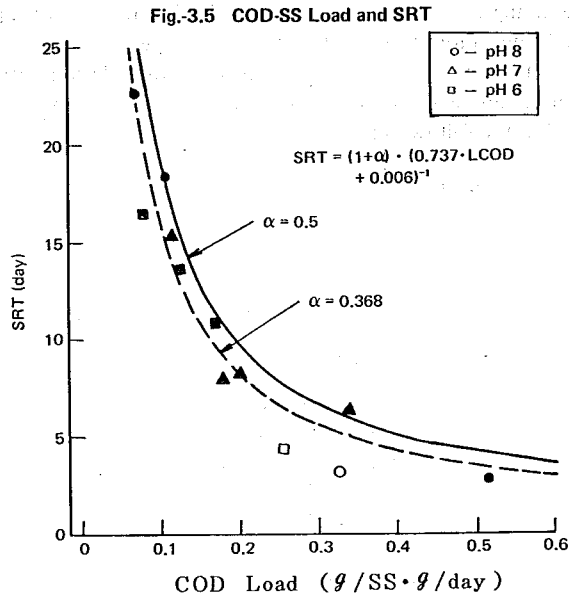
$$\text{SRT} = (1 + \alpha) \cdot (0.737 \cdot \text{LCOD} + 0.006)^{-1} \quad (5)$$

Thus the SRT was obtained as follows:

$$\text{SRT} = (1 + \alpha) \cdot (0.737 \cdot \text{LCOD} + 0.006)^{-1} \quad (5)$$

When α is approximated by the settler capacity of this testing apparatus, α is 0.5. Fig. 3.5 compares the results of SRT calculated by Equation (5) and the observed value. Fig. 3.5 shows that the values differed slightly. But if $\alpha = 0.368$ is used, it coincides with the observed values.

In this test, the effect of pH within the range of 6 – 8 was not clear on the relationship between organic load and SRT (Fig. 3.5). Perhaps, the pH range was so close to the optimum range of microorganisms like heterotrophs and protozoa in the activated sludge.



3.2.2 SRT and Effluent Quality

Fig. 3.6.1, 2, 3 and 4 are the relationship between SRT and effluent quality in terms of BOD, COD, SS and Transparency. There is a tendency to deteriorate in effluent quality when SRT is either kept longer or shorter. As is seen in Fig. 3.6.1 and 2, the soluble BOD and COD were comparatively constant and low in any SRT. Effluent quality is influenced by effluent solids. Effluent solids increase by the bulking of filamentous bacteria when SRT is short, and increase of floatable solids due to denitrification in final settler or micronization of activated sludge when SRT was long. From this result, the optimum SRT range is to be between 5 and 10 days.

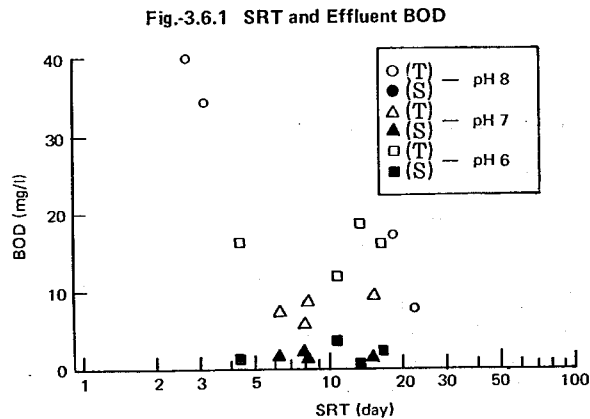


Fig.3.6.2 SRT and Effluent COD

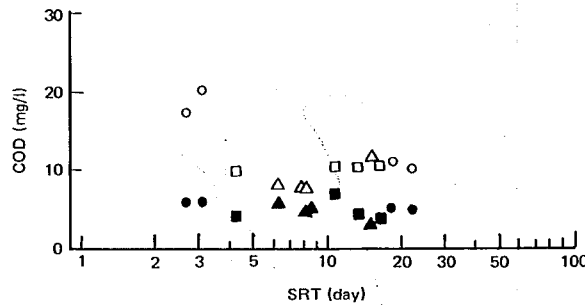


Fig.3.6.3 SRT and Effluent SS

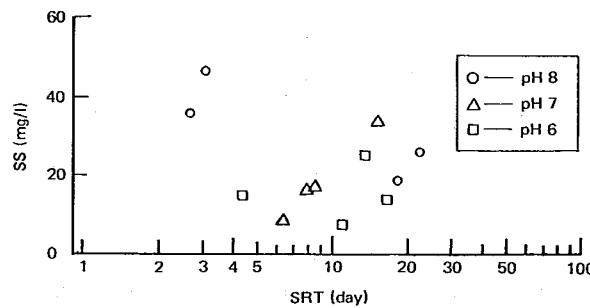
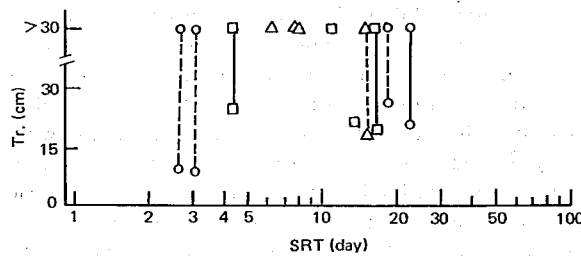


Fig.3.6.4 SRT and Effluent Tr



3.2.3 SRT and Nitrification

Fig. 3.7 and 8 show the relation between SRT and nitrite and nitrate in the effluent, of each pH condition. From Fig. 3.7, the tendency is that the longer the SRT, the easier the nitrification. Also the pH greatly affects the whole process. Required SRT that nitrification start are; the SRT at pH 8 is 3 days; at pH 7, 6 days; and at pH 6, 11 days. This shows that within the range of these pH, when SRT is short or when organic loading is high, it is possible to maintain substantial nitrification by controlling the pH at around 8. When the SRT is maintained at over 15 days, the affects of pH are negligible, thus sufficient nitrification is expected.

Fig.-3.7 SRT and Nitrification

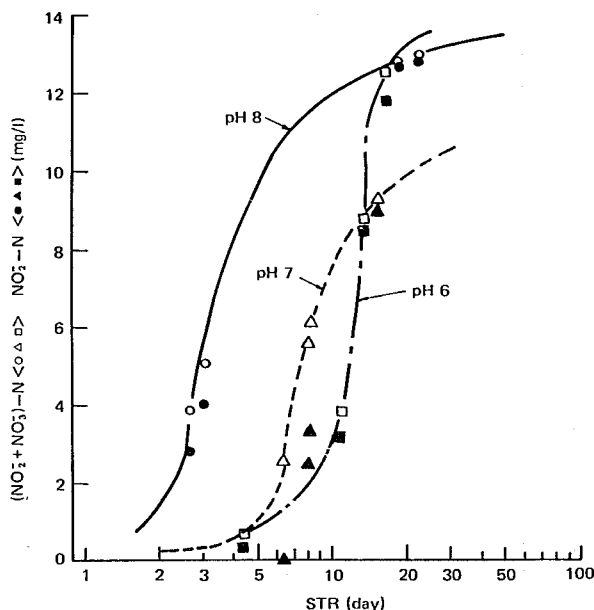


Fig. 3.8 shows the relation between SRT and nitrification rate. Of the nitrified nitrogen, the ratio of existing nitrite and nitrate is reported to change with the pH in the reaction tank. The condition allowing predominance of nitrate is pH 6 – 7 while at pH 8.0 – 8.6 there will be more nitrite existing. This explains that the activity of nitrite bacteria and that of nitrate bacteria change with pH. In this study, the existing ratio of nitrite of nitrified nitrogen was highest at pH 7 and at SRT 7 – 8 days, and at pH 8 the abovementioned pattern was not observed. In comparing the existing ratio of nitrite with SRT, when SRT was short or nitrification rate low, the existence rate was slightly high; and when the SRT was long the majority existed as nitrate. This tendency was also observed in the two other experiments. The multiplying rates of nitrite and nitrate bacteria from the two tests were 7 hours and 12 hours respectively. Accordingly, in a condition when nitrification rate was low or SRT short, as the existing amount of nitrite bacteria could not catch up with that of the nitrite bacteria, nitrite increased in amount. And when the nitrification rate was high or SRT long, the activities of both bacteria reached the same level allowing nitrified nitrogen to remain more in the form of nitrate.

Fig. 3.9 shows the relation between the pH and nitrification rate with SRT. When expecting more than 80 percent of nitrification at pH 6 – 7, the SRT should be more than 15 days. And it shows that in the neighborhood of pH 8, a reasonably sufficient nitrification can be expected by setting SRT at around 6 or 7 days.

Fig.-3.8 SRT and Nitrification Rate

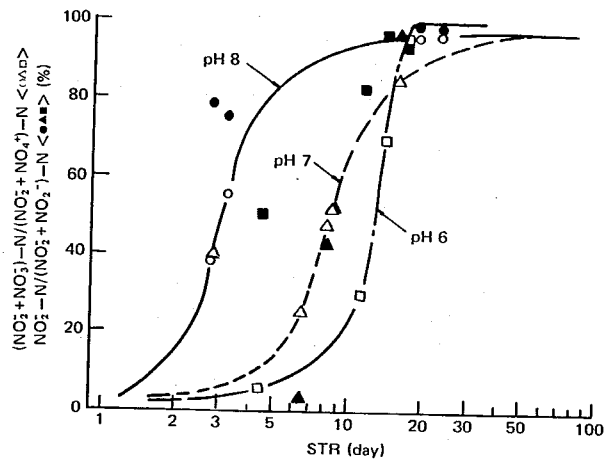


Fig.-3.9 pH and Nitrification Rate and SRT

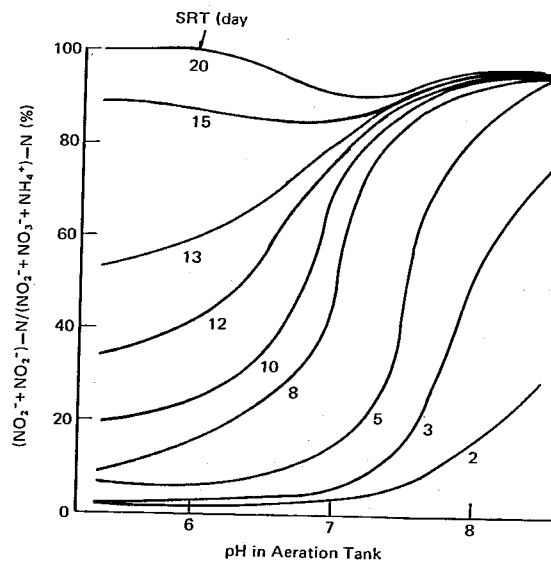


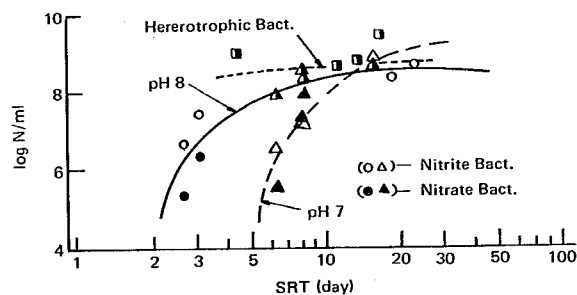
Table-3.2 Average Water Quality

	I pH 8				II pH 7				III pH 6				
	A	B	C	D	A	B	C	D	A	B	C	D	
SRT (day)	2.68	3.06	18.27	22.4	6.31	8.18	7.96	15.25	4.33	10.86	13.47	16.43	
Δ S (g/day)	14.04	17.13	7.74	8.96	8.42	11.13	9.32	13.09	12.81	7.41	10.35	12.91	
pH	7.81	7.67	7.91	8.19	7.33	7.20	7.06	7.00	6.10	6.38	6.13	6.11	
	7.65 ~ 8.15	7.44 ~ 7.93	7.80 ~ 8.02	7.94 ~ 8.31	7.10 ~ 7.52	6.95 ~ 7.34	6.95 ~ 7.20	6.81 ~ 7.12	5.63 ~ 6.99	5.97 ~ 6.84	5.84 ~ 6.47	5.72 ~ 6.57	
SV ₃₀ (%)	85.4	85.0	70.7	45.0	72.0	78.3	91.8	93.5	19.6	28.3	20.5	41.8	
MLSS (mg/l)	366	565	1,967	2,920	688	1,031	1,205	1,831	939	1,307	1,954	2,730	
MLVSS (mg/l)	324	508	1,751	2,540	635	926	1,079	1,662	831	1,194	1,790	2,500	
MLVSS/MLSS (%)	88.5	86.7	89.0	87.2	91.6	89.8	89.6	91.1	87.6	91.7	91.7	93.1	
SVI	2,350	1,770	345	146	1,123	791	791	542	209	217	105	146	
BOD (mg/l)					70.7	87.8	71.3	71.0	116.4	117.8	126.3	111.7	
COD (mg/l)	48.4	48.9	51.2	49.9	49.1	47.4	49.3	49.4	54.5	53.5	36.6	51.3	
K-N (mg/l)	15.42	15.57	16.29	15.90	15.80	14.90	16.10	15.54	17.33	16.79	17.80	16.40	
KH ₄ -N (mg/l)	9.41	9.41	9.07	8.81	10.20	9.84	10.27	10.24	4.38	4.52	5.09	4.00	
Tr (cm)	(9.30) ~ 30 < ^{1/2}	(8.81) ~ 30 < ^{1/2}	(26.0) ~ 30 < ^{1/2}	20.5 ~ 30 < ^{1/2}	30 <	30 <	30 <	(17.6) ~ 30 < ^{1/2}	24.5 ~ 30 < ^{1/2}	30 <	20.8	19.4 ~ 30 < ^{1/2}	
SS (mg/l)	35.7	46.2	18.7	25.1	8.3	16.8	16.0	33.6	14.7	7.1	24.9	13.6	
BOD (mg/l)	Total	39.9	34.2	17.13	7.70	7.18	8.42	5.68	9.17	16.13	11.78	18.48	15.87
	Soluble					1.62	1.00	2.03	1.34	1.21	3.56	0.52	2.01
COD (mg/l)	Total	17.19	20.0	10.83	9.85	7.87	7.43	7.41	11.10	9.81	10.33	10.03	10.36
	Soluble	5.81	5.81	4.98	4.58	5.60	4.39	4.22	2.86	3.93	6.71	4.02	3.63
K-N (mg/l)	Total	7.97	10.48	3.10	3.17	9.36	6.75	8.49	3.45	12.58	10.04	6.27	3.87
	Soluble	6.55	5.30	1.10	1.10	8.07	6.10	7.11	7.60	10.74	8.96	3.92	2.18
NH ₄ -N (mg/l)	6.25	5.56	0.31	0.51	7.77	5.47	6.38	1.61	10.73	8.96	3.88	0.53	
NO ₂ -N (mg/l)	1.05	1.02	0.06	0.16	2.58	2.77	3.13	0.30	0.30	0.64	0.29	0.75	
NO ₃ -N (mg/l)	2.82	4.04	12.73	12.75	0.01	3.32	2.45	8.94	0.32	3.17	8.47	11.79	
BOD					0.496	0.270	0.247	0.1668	0.540	0.378	0.267	0.1696	
COD	0.513	0.327	0.1065	0.0705	0.338	0.1996	0.1775	0.1147	0.252	0.1720	0.1214	0.0776	
T-N	0.1376	0.1343	0.0320	0.0218	0.1180	0.0557	0.0597	0.0386	0.0801	0.0538	0.0375	0.0249	
BOD	Total				89.8	87.0	96.6	87.1	85.9	90.3	85.6	85.6	
	Soluble				97.6	98.5	97.1	98.1	98.9	97.1	99.6	98.1	
COD	Total	52.3	40.5	76.0	78.8	83.8	83.4	84.7	76.2	81.8	80.5	82.2	79.4
	Soluble	84.9	86.5	90.7	89.0	88.5	90.5	91.0	93.9	92.7	87.4	92.9	92.8
T-N	Total	27.6	4.82	9.96	-5.57	17.60	11.01	10.88	1.13	22.4	17.36	13.18	-0.92
	Soluble	32.4	34.7	6.99	7.43	29.2	16.01	19.69	20.7	33.3	23.9	28.6	9.49
BOD	Total				0.446	0.235	0.225	0.1451	0.466	0.340	0.228	0.1380	
	Soluble				0.484	0.266	0.239	0.1636	0.535	0.367	0.266	0.1664	
COD	Total	0.293	0.1596	0.0843	0.0566	0.284	0.1680	0.1518	0.0855	0.207	0.1396	0.0997	0.0614
	Soluble	0.436	0.297	0.0963	0.0641	0.300	0.1815	0.1637	0.1076	0.234	0.1508	0.1127	0.0720
T-N	Total	0.0501	-261 × 10 ⁻³	4.46 × 10 ⁻³	-0.888 × 10 ⁻³	27.4 × 10 ⁻³	6.25 × 10 ⁻³	10.93 × 10 ⁻³	-0.949 × 10 ⁻³	19.88 × 10 ⁻³	9.59 × 10 ⁻³	4.92 × 10 ⁻³	-0.633 × 10 ⁻³
	Soluble	0.0574	0.0508	2.30 × 10 ⁻³	2.01 × 10 ⁻³	35.7 × 10 ⁻³	8.79 × 10 ⁻³	17.57 × 10 ⁻³	8.23 × 10 ⁻³	28.2 × 10 ⁻³	12.89 × 10 ⁻³	10.88 × 10 ⁻³	2.14 × 10 ⁻³

Table-3.2 (continued)

		I pH 8				II pH 7				III pH 6			
		A	B	C	D	A	B	C	D	A	B	C	D
Nitrification rate (%)	$\text{NO}_3^- - \text{N}$ ($\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$) - N	9.97	18.25	0.75	0.99	20.1	24.3	25.5	2.80	2.73	5.20	2.40	5.80
	$\text{NO}_2^- - \text{N}$ ($\text{NO}_2^- + \text{NO}_3^- + \text{NH}_4^+$) - N	28.2	37.1	95.6	95.3	5.04	27.2	22.1	82.2	2.88	24.7	67.2	90.3
	$(\text{NO}_2^- + \text{NO}_3^-) - \text{N}$ ($\text{NO}_2^- + \text{NO}_3^- + \text{NH}_4^+$) - N	38.2	55.4	96.3	96.3	25.1	51.5	47.6	85.0	5.61	29.9	69.6	96.1
	$\text{NO}_3^- - \text{N}$ ($\text{NO}_2^- + \text{NO}_3^-$) - N	78.6	75.4	99.2	98.7	0.31	51.2	42.6	96.7	50.3	82.6	96.6	94.0
Inflow and Outflow (%)	$\text{NO}_3^- - \text{N}$	7.87	6.24	0.38	1.01	16.19	15.1	15.88	1.76	1.83	3.92	1.72	4.58
	$\text{NO}_2^- - \text{N}$	17.49	26.7	74.2	82.4	0.08	21.9	18.93	62.9	1.88	18.83	47.7	72.5
	$\text{NH}_4^+ - \text{N}$	38.9	31.8	1.79	3.16	48.5	41.1	38.7	7.61	62.9	53.4	21.7	3.29
	Soluble Org-N	3.13	0.40	6.61	3.79	7.55	5.80	6.87	7.08	0.08	0.00	0.29	10.15
	Total Org-N	7.88	24.9	15.19	16.72	19.09	10.80	15.67	26.6	10.98	6.51	14.42	20.6
	Nitrite Bacteria (/ml)	4.9×10^4	2.8×10^5	2.4×10^6	4.9×10^6	3.3×10^7	1.7×10^7	1.7×10^7	7.0×10^8				
		2.4×10^4	2.4×10^4	2.4×10^4	2.4×10^4	3.3×10^4	7.9×10^5	7.2×10^7					
						7.6×10^7	2.4×10^8	3.2×10^8	5.3×10^8	1.0×10^9	4.3×10^8	6.4×10^8	2.6×10^9

Fig.-3.10 SRT and Bacteria Population



3.2.4 SRT and Microorganisms

Fig. 3.10 shows the relation between SRT and the numbers of heterotrophs and nitrification bacteria. The number of heterotrophs was somewhere around 10^8 N/ml, and no drastic change was observed by change in SRT. This value was close to the one in the activated sludge in the actual sewage treatment plant. The number of nitrification bacteria amounted to between 10^5 and 10^8 per milliliter and it was subjected to change to both SRT and pH in the aeration tank. It is considered that this is due to the difference in the activities of nitrification bacteria as against the organic load and pH. Considering the fact that the optimum pH of nitrification bacteria is in the neighborhood of 8 when high, they become formidable against inhibition caused by organic load, leading to maintenance of higher activity and multiplying rate than other pH. When comparing nitrate and nitrite bacteria from Fig. 3.10, at low SRT range, the existing patterns of both bacteria closely resembled with each other. In this test, as the influent did not

contain any nitrite nitrogen, the existing quantity of nitrite bacteria or the amount of nitrite was considered to have accelerated the growth of nitrate bacteria.

Fig.-3.11.1 SRT and Metazoa

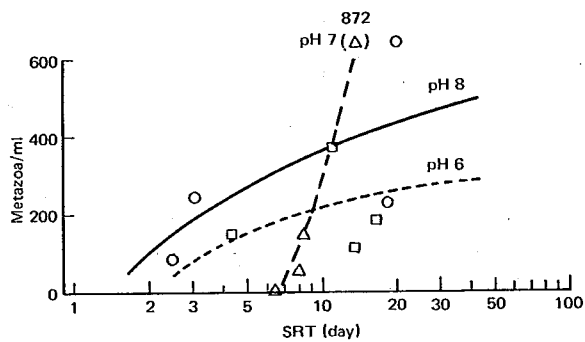


Fig.-3.11.2 SRT and Amoeba

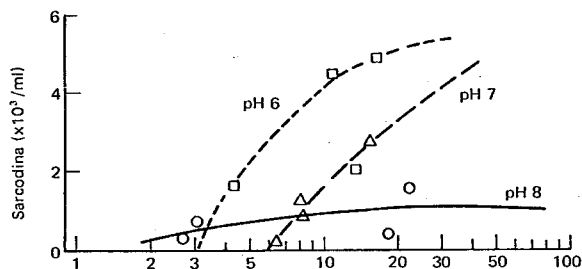


Fig.-3.11.3 SRT and Amoeba

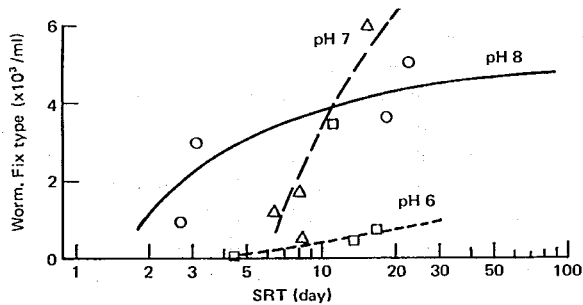


Table-3.3.1 Microscopic Test Results (pH 8 N/ml)

Phase	A	B	C	D
Sarcodina	240	657	400	1,510
Flagellata	4,305	3,430	147	783
Ciliata	1,146	3,199	3,906	6,270
Swim. type	200	226	306	1,266
Worm. t.	360	1,143	2,680	3,744
Fix. t.	586	1,830	920	1,260
Rotifera	67	244	227	444
Nematoda	27	0	0	167
	Pleuromonas	Arcella Euglypha Aspidisca Vorticella	Arcella Aspidisca	Euglypha Aspidisca
SRT (d)	27	3.1	18.3	22.4

By classifying the biological fauna in the activated sludge into Metazoa, Rhizapoda and activated sludge ciliata, Fig. 3.11.1, 2 and 3 show the relationship between each group and SRT. Table 3.3.1, 2 and 3 show the population of the main organisms that appeared. Each biological fauna has shown a tendency to increase in number on the high SRT side. Also when comparing this with pH, Rotifera increased in number at pH 7. In contrast to other biological fauna, Rotifera remained formidable against pH influence and proved highly adaptable to pH. In this pH range, it was amoeba galore in the lower pH area and showed a tendency to decrease in the higher pH zone. In this study Euglypha, Arcella and other loricate amoeba observed in extended aeration or long SRT system were found in abundant. Loricata amoeba is one of Protozoas upon which Rotifera find them difficult to prey and this is why they still exist in this low pH 6.

The activated sludge ciliata, on the other hand, unlike amoeba, were found in less quantity in the lower pH range.

Table-3.3.2 Microscopic Test Results (pH 7 N/ml)

Phase	A	B	C	D
Sarcodina				
Euglypha	50	286	457	1,357
Arcella	86	407	422	793
Amoeba	43	157	343	607
Flagellata (Pleuromonas)	50,840	22,293	2,382	893
Ciliata				
Swim. type	436	3,607	3,979	750
Litonotus	129	2,400	514	43
	307	1,207	3,465	707

Table-3.3.2 Microscopic Test Results (pH 7 N/ml) (continued)

Phase	A	B	C	D
Worm. type	222	244	1,365	5,579
Aspidisca	214	222	1,179	4,300
	8	22	186	1,279
Fix. type	916	257	300	386
Vorticella	522	50	43	86
Zoothamnium	300			
Carchesium	72	107	43	
Tokophrya		14	50	
	22	86	164	300
Rotifera	0	108	43	872
Nematoda	0	36	8	0
SRT (d)	6.3	8.2	8.0	15.3

Table-3.3.3 Microscopic Test Results (pH 6 N/ml)

Phase	A	B	C	D
Sarcodina				
Euglypha	930	3,180	1,100	2,960
Arcella	0	30	190	240
Amoeba	550	900	720	1,570
	150	380	30	120
Flagellata (Pleuromonas)	21,780	3,060	10,870	3,050
Ciliata				
Swim. type	10	0	300	200
Litonotus	10	0	100	50
			200	50
Worm. type	40	0	340	100
Aspidisca	40	0	340	100
Fix. type	20	3,460	130	630
Vorticella	20	1,960	70	200
Epistylis	0	1,350	0	100
Tokophrya		50	20	10
		100	40	320
Rotifera	150	370	110	180
Nematoda				
SRT (d)	4.3	10.9	13.5	16.4

3.3 SUMMARY

(1) Load and SRT.

The relation between load and SRT was proved to be described by Equation (5). It is recommended that the coefficient α be the ratio of the settler capacity to the aerator capacity.

(2) SRT and Nitrification.

The study results revealed that at pH 8, nitrification can be expected in only half of SRT than at pH 7. When applying this to existing conventional treatment plant operation, either the load should be kept low to maintain long SRT or the pH in the aeration tank should be kept high. The application of the former to the existing treatment methods is difficult because capacity is limited at the most plants. Also the employment of the latter requires installation of the pH adjustment facilities.

(3) SRT and Microorganisms.

The number of Heterotrophs was 10^8 per milliliter, and the amount remained unaffected by SRT changes. The number of nitrification bacteria was between 10^5 and 10^8 per milliliter and was strongly affected by the length of SRT and also by pH. When SRT was fixed, the amount of nitrification bacteria increased in the order of pH 8, 7 and 6.

In this study, on the slightly alkaline side of the pH, protozoa and activated sludge ciliata were detected in galore, while on the acidic side more amoeba were found. On the other hand, under long SRT condition, both had shown a tendency of increasing. Rogifera and Sarcodina are regarded as useful index organisms of nitrification condition.

(4) SRT and Effluent Quality.

The optimum SRT was 5 – 10 days. When SRT was kept short, it induced a bulking condition. When SRT was long, outflow of minute floc and floating of sludge from settlers perhaps due to denitrification occurred, at the final sedimentation basins.

4. EXPERIMENTS CONCERNING EFFECTS OF TRACE ELEMENTS ON NITRIFICATION

There are two procedures to determine effects of trace elements on nitrification acceleration.

1) Short terms culture method; to determine effects of trace element addition on nitrification rate within a short period (4 – 5 hrs) in which growth of nitrifiers is negligible. Namely, this method is to determine the effect of trace element addition on the enzyme reaction.

2) Long term culture method; to determine effects of trace elements on growth of nitrifiers and nitrification activity of nitrifiers by measuring amount of nitrifiers and nitrified nitrogen in effluent.

In this study, long term contact method has been adopted.

4.1 TEST METHOD

The activated sludge at sewage treatment plants, (chlorine concentration of 40 – 50 mg/l as Cl) where substantial nitrification achieved was used as nitrification bacteria. Ultrasonic treatment (50Hz, 25 watt 5 ~ 10 minute) was conducted to kill protozoa to prevent them to prey on nitrifiers. The sludge was washed two or three times with ion exchange distilled water to release soluble metals.

To alleviate the influence of buffer solution and sea water, the analysis was conducted by diluting samples of 10 to 20 times.

Test 1) The Effects of Sea Water under the Existence of Tris Buffer

Effect of sea water on nitrification was tested adding sea water of 0, 20, 40, 60, 80, and 100% to the influent.

As buffer solution, 50mM Tris buffer (tris hydroxymethyl aminomethane) was used as it was considered comparatively low in physiological influence. $(\text{NH}_4)_2\text{SO}_4$ and NaNO_2 were added at the concentration of 30 mg.N/l as sources of ammonia and nitrite respectively. Under the existence of 50mM Tris-buffer, activated sludge collected at sewage treatment plant was used after one week of aeration. The sea water was prepared according to the Lyman and Fleming Synthetic Seawater Composition List.

In 3-liter vessels, sea water, Tris-buffer, washed activated sludge (MLSS adjusted to 520 mg/l) and substrate were added in that order to total 3 liters each and to reach the designated concentrations respectively. Then the mixtures were separated in 500 ml flasks by 100 ml transfer pipers, and the flasks were attached to shaking culture units. The shaking culture was conducted at an amplitude of 50 mm, and shaking frequency of 10 times per minute.

Test 2) Effects of Phosphate Buffer

From the results of Test 1) Tris-buffer, that inhibit nitrification bacteria, was found inappropriate for use in the nitrification tests. To examine the effects of phosphate ($\text{Na}_2\text{HPO}_4 + \text{NaH}_2\text{PO}_4$) which is the alternative buffer solution against nitrification, the short incubation method was introduced.

To reach the designated concentrations, one-liter cylinders were filled with phosphate (When NH_4^+ substrate: 10^{-4} , 5×10^{-4} , 10^{-3} , 10^{-2} , 25×10^{-2} , 5×10^{-2} , 10^{-1} M phosphate. When NO_2^- substrate: 10^{-6} , 10^{-5} , 10^{-4} , 10^{-3} , 10^{-2} , 10^{-1} M phosphate), 2000 mgN/l $(\text{NH}_4)_2\text{SO}_4$ or NaNO_2 ... 25 ml, and washed activated sludge collected at sewage treatment plant (When NH_4^+ substrate) 21800 mg/l ... 100 ml or activated sludge (When NO_2^- substrate) 24800 mg/l ... 150 ml in that order to total 1 liter each. Then the mixtures were aerated and the pH adjusted between 7.5 and 8.0 of NaOH. And finally the amount of nitrite bacteria contained in 0, 0.5, 5, 10 and 20mM solutions of NH_4^+ substrate 24 hours later were measured.

Test 3) The Effect of Mg^{2+} on Nitrification under the Existence of Phosphate

Phosphate of 2mM was added to the solution of MgSO_4 (0.02, 0.2, 2, 50mM), MgCl_2 ... 50mM, and $(\text{MgCO}_3)_4 \text{Mg}(\text{OH})_2$... 0.04mM ($\text{Mg} = 0.2\text{mM}$) to determine the effects of Mg in short period incubation.

In 1-liter cylinder, 40 ml of 0.5M Phosphate was added. Then Mg compounds were added to reach the designated concentration. This was followed by the annexing of 100 ml of washed activated sludge (MLSS 19400 mg/l) and 25 ml of $(\text{NH}_4)_2\text{SO}_4$ 2000 (mg/l as N). The mixtures were aerated and five minutes later amount of ordinary bacteria were measured.

Test 4) Effect of Anion under the Existence of Phosphate

Under the existence of phosphate, NaF, NaCl, NaBr, NaI, Na_2SO_4 and NaNO_2 of 10^{-4}M , 10^{-3}M , 10^{-2}M and 10^{-1}M were added respectively to examine the effects of anion against nitrification.

4.2 TEST RESULTS

Prior to the buffer addition study, tests to determine the effects of sea water on nitrification was conducted.

The results are shown in Figs. 4.1, 4.2 to 4.4. Since these tests were conducted by adjusting the pH only once every day, when the sea water addition rate was low or the buffer capacity low, the pH also decreased, making it impossible to maintain optimum pH. The more the pH was lower than the optimum pH, the apparent nitrification rate decreased. In short, it is assumed that the actual nitrification rate will increase to the extent of the concentration of sea water as shown in Figs. 4.1 and 4.2: This indicated that the optimum pH must be maintained in this manner to make comparisons of nitrification rates. Then, the experiments were extended to be done under the addition of buffer solution to remove the effect of pH change.

Fig. 4.1 Effect of Sea Water on Nitrification Rate (fresh water nitrifiers CL = 50 mg/l)

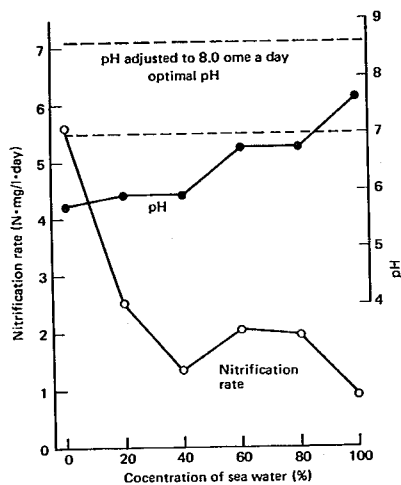


Fig. 4.2 Effect of Sea Water on Nitrification Rate (Activated Sludge of 6000 - 7000 CL plant)

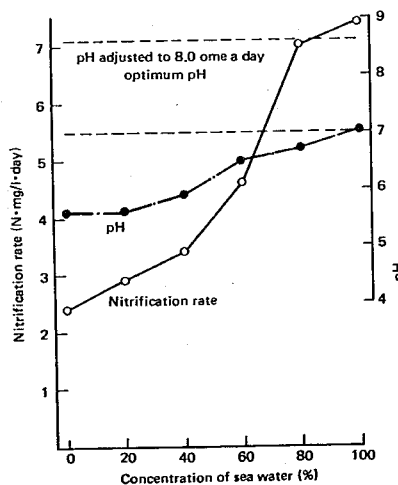


Fig.-4.3 pH and Nitrification

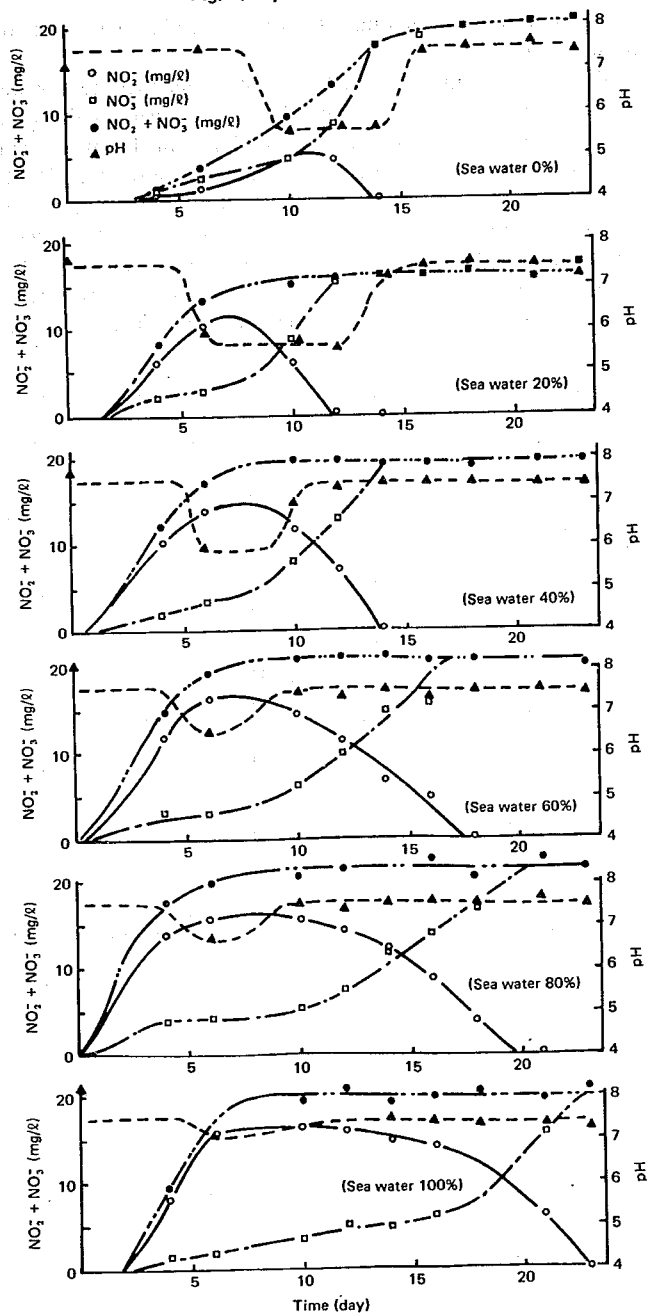


Fig.-4.4 Sea Water vs. Percentage of Nitrite

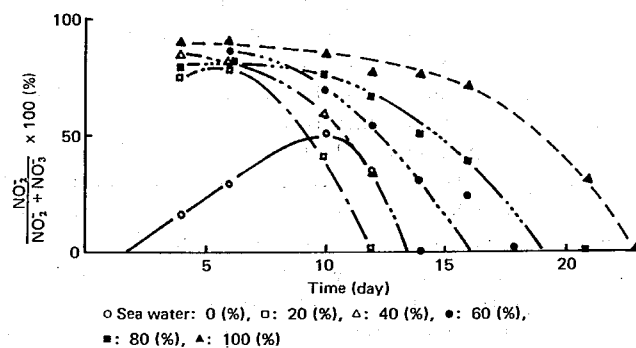
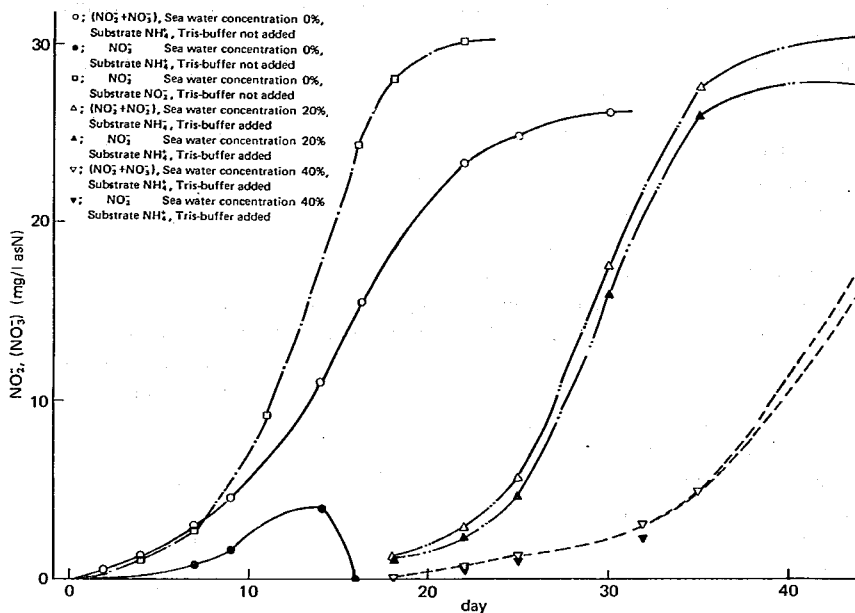


Fig.-4.5 Nitrification in Different Substrat. and Sea Water Conditions



Test 1) Influence of Sea Water under the Existence of Tris Buffer

Figure 4.5 shows the relation between nitrified nitrogen (NO_2^- , $\text{NO}_2^- + \text{NO}_3^-$) in effluents and reaction time (days), under the different sea water concentration, fed forms of substrate nitrogen (NH_4^+ or NO_2^-).

Similar to the result shown in Fig. 4.1, the inclination was that the nitrification declined when sea water concentration increased. The rates were 2.38 (mg/l.day) in 20 percent sea water concentration and 1.21 (mg/l.day) in 40 percent sea water concentration. These values relate that the nitrification rate in 40 percent sea water was only about 1/2 of that of 20 percent, indicating the fact of sea water inhibition.

Inversely, the growth rate of nitrite bacteria as shown in Fig. 4.6 was higher in 40 percent than in 20 percent sea water with the values being 0.126 (generation number) and 0.0941 respectively. This means that the growth rate in 40 percent sea water solution was about 1.34 times faster than in 20 percent. The generation time, on the other hand, was 2.4 days in 20 percent sea water and 5.5 days in 40 percent.

Test 2) Effect of Phosphate Buffer

The ratios of nitrification rate of phosphate addition and without addition under the nitrogen substrate of NH_4^+ and NO_2^- are shown in Fig. 4.7. It shows that the phosphate added as pH buffer had accelerated ammonia oxidation with the optimum concentration being about 13mM. The rate at this point was about twice the rate of that phosphate was not added (Control). However, when phosphate concentration was below 0.1mM, there was no action observed to accelerate ammonia oxidation. Also over 13 mM in concentration, the rate suddenly dropped. And when 100mM, the rate dropped about 45 percent against Control. The nitrite bacteria count in 0 ÷ 10mM concentration, 24 hours later, roughly maintained the same population of 1.5×10^8 N/ml. However, the count in 25mM concentration dropped to about one third of the original level and was 4.9×10^7 N/ml.

Test 3) Effect of Mg on Nitrification under the Existence of Phosphate

To see the effect of Mg^{+2} addition, ratios of nitrification rate of Mg^{+2} level against control rate are shown in Fig. 4.8. The figure shows that even in MgSO_4 50mM solution (Mg^{+2} concentration in 96 percent sea water) the effect to nitrification rate was hardly seen, and also $(\text{MgCO}_3)_4$ $\text{Mg}(\text{OH})_2$ was similar to MgSO_4 . Although there was about 10 mg/l of ammonia oxydation, there was no pH drop demonstrating strong buffer strength. Table 4.1 shows the population of bacteria after five minutes of each chemical addition.

Test 4) Effect of Anion under the Existence of Phosphate

Fig. 4.9 (a) and (b) show the ammonia oxidation rate of halogen concentration against control. The Figures show that the concentrations that decreased rate to 50 percent were NO_3^- (29mM) > F^- (48mM) > SO_4^{2-} (76mM) > I^- (80mM) > Cl^- (170mM) in that order. Cl^{6-} had shown the least effect.

Fig.-4.6 Change in Population of Nitrifiers

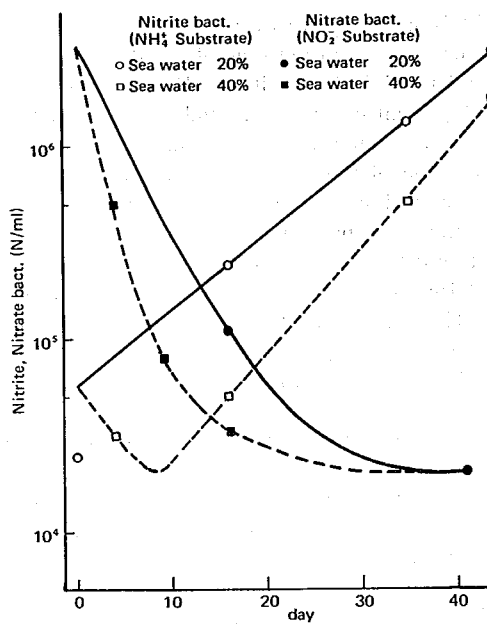
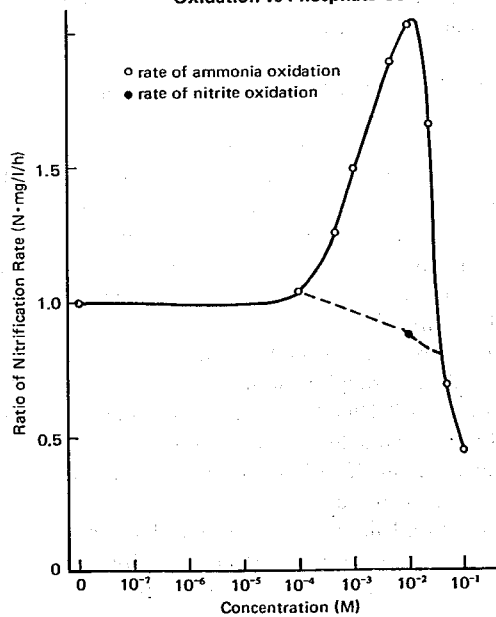


Fig.-4.7 Rate of Ammonia Oxidation, Nitrite Oxidation vs Phosphate Concentration



4.3 DISCUSSION

The Influence of Tris-buffer on Nitrification:

Despite the fact that the generation time of Nitrite bacteria by pure culture is known to be between 10 and 12 hours, it was 10.6 days in 20 percent sea water addition, 7.9 days in 40 percent solution or 23 and 17 times respectively longer than pure culture. Furthermore, from Figures 4.3(a) and 4.5, when comparing the lag phase of sea water addition of 0 percent and 20 percent, the former showed no difference, but the latter had shown an excessive difference of 14 days between 0 percent sea water (without Tris-buffer), perhaps, owing to the fact that Tris-buffer had caused inhibition to nitrite bacteria growth.

By addition of Tris-buffer, as is seen from Fig. 4.3(b), nitrite concentration increase significantly. The population of nitrate bacteria with NO_2^- as substrate in Fig. 4.6, diminished with the passing of days. From these facts, it is concluded that Tris-buffer acted to inhibit activity of nitrate bacteria.

Addition of higher sea water had higher bacteria growth rate, and this phenomenon is reasoned as follows: Either substances contained in the sea water acted as catalyst to stimulate growth or metal enzyme, engulfed in bacteria, had been formulated to promote growth. According to Loveless Report (1968), by addition of MgCl_2 , the nitrite bacteria heightened in growth. So, this fact in this study was considered to be due to Mg contained in sea water.

It is regarded that anions such as Cl^- and SO_4^{2-} affected to causing the acceleration of lag phase and nitrification rate in proportion to the increase in sea water addition. From the fact that the amount of nitrification per nitrite bacterium was smaller in 40 percent sea water solution, it is necessary to check whether the amount of nitrification per nitrite bacterium will increase by grafting and acclimatization.

With regards oxidation of ammonia to nitrite, phosphate proved effective as accelerators.

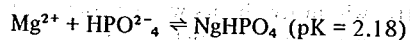
The forms when phosphate is pH 7.5 and pH 8.0 are as follows: pH 8 ... H_2PO_4^- 13.8 percent, and HPO_4^{2-} 86.2 percent. pH 7.5 ... H_2PO_4^- 33.9 percent and HPO_4^{2-} 66.5 percent (at 25 degrees centigrade). If H_2PO_4^- is an accelerator to promote nitrification, it should increase 2.5 times between pH 7.5 and pH 8, and HPO_4^{2-} should decrease more than 20 percent. With this in mind the subject rests were conducted by setting the pH at about 7.75, a high concentration phosphorous acid solution in which pH drop is scarce.

By the addition of more than 13mM of phosphate, the activity to convert to NO_2^- suddenly decreased. But despite the fact an equal amount of nitrite bacteria inhabited in the solution until 10mM, the bacterial population decreased to about 1/3 in 25mM phosphorous acid solution. From these facts, it was considered that even though the apparent nitrification dropped suddenly, the per bacterium nitrification inhibition also slightly decreased.

Characteristics of Cation Under the Existence of Phosphate:

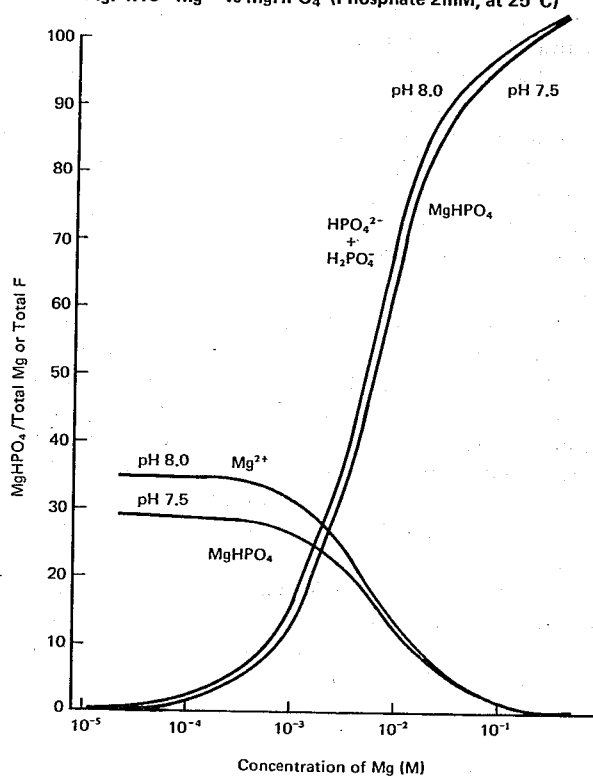
It was proved that phosphate is an effective nitrification accelerator. But it bears a characteristic to form complex or sediments with cation. As an example, the

characteristics of phosphate with Mg^{2+} are as shown in Fig. 4.10. The figure shows the existing form ratio of Mg^{2+} in 2mM of phosphate. The reaction of phosphate and Mg^{2+} is expressed in the following equation:



From this equation, the complex formation is influenced by the concentration of phosphate. If phosphate concentration is maintained constant level, by increasing Mg^{2+} , the amount of complex increases. In this case, however, MgHPO_4 / Total Mg ratio will decrease.

Fig.-4.10 Mg^{2+} vs MgHPO_4 (Phosphate 2mM, at 25°C)



When studying the effects of additives such as cation, the addition of buffer solutions should be with care. Addition of the buffer solutions is held down to the minimum. For example, in case of phosphate, it should be controlled to about $0.1 \mu\text{M}$. In this case, the nitrogen as substrate, too, must be similarly controlled.

However, it is impossible to conduct the aforementioned studies by using activated sludge. When activated sludge is cultured, NH_4^+ will liberate from the sludge. And the release rate of NH_4^+ is affected by the composition and

concentration of the culture solution, the condition of the collected activated sludge (collected time & place), the preservation method of the collected sludge, and so on. In this study irrelevant to the concentration of phosphate, the increase in T-N due to the release of NH_4^+ within five hours was not observed. But 24 hours later, the soluble T-N, when compared to the initial T-N, increased about 5 (mg/l as N). Release of NH_4^+ was observed until about four hours in other case. But after that (between 4 and 6 hours) no release was observed. The initial release rate without any chemical addition was about 1.9 to 2.9 (mg.N/liter/h). Also, in proportion to the increase in anion addition the release of NH_4^+ showed an inclination to decrease. In this way, the cause of the large amount of NH_4^+ release in the initial stage is attributed to the preservation method of activated sludge. In other words, as the collected activated sludge (MLSS: 10,000 – 20,000 mg/l) was preserved under an aeration, the released NH_4^+ has nitrified and caused pH to drop. It should be noted if pH adjustment is conducted only once or twice every day, the nitrification bacteria will exist in the solution at around pH 5 most of the time. However, in this test as pH was maintained highly between 7.5 and 8.0, it was concluded that the release was not triggered by sudden pH changes.

From these results, in the nitrification tests using activated sludge, it is recommended that a reasonably large amount of nitrogen as substrate be needed.

4.4 SUMMARY

1) Under the existence of Tris-buffer, the population of nitrite bacteria contained in 20% sea water solution and 40% solution were counted and the growth rate in 40% solution was about 1.34 times faster than in 20% solution. This was, perhaps, caused by Mg^{2+} in the sea water. However, the amount of nitrification amount per nitrite bacterium was higher in the 20% sea water solution.

2) In short period incubation (under the existence of 2mM phosphate), no Mg^{2+} nitrification acceleration activity was observed.

3) In short period incubation, nitrification to nitrite was accelerated by phosphate addition and the optimum concentration was about 13mM.

4) Under the existence of 11mM phosphate, when expressing the 50% nitrification decrease in terms of concentration due to the influence of anion, it can be as in the following order: NO_3^- (29 mM) > F^- (48 mM) > SO_4^{2-} (76 mM) > I^- (80 mM) > Br^- (140 mM) > Cl^- (170 mM).

5. DETERMINATION OF NITRIFICATION BACTERIA AND HETEROTROPHS IN ACTIVATED SLUDGE

The biological composition of activated sludge is: bacteria, protozoa and metazoa or microorganisms. And bacteria exist in the form of autorotrophs such as nitrite bacteria, nitrate bacteria. Then there are the heterotrophs. Counting of protozoa and metazoa population is possible by the microscopic method. On the other hand, although there are no established measurement methods for bacteria, Sakurai (1967) and Chida et. al (1971) reported several types of culture media for the measurement of heterotrophs. With regards the measurement of autorotrophs, especially nitrite and nitrate bacteria, the plate culture method and the liquid culture medium are suggested. But concerning the development of the plate culture method incorporating silica gel, it takes up considerable time in the preparation of the culture medium and the colony is little too small for counting. Therefore, the method is considered inconvenient for practical use.

Incubation of nitrification bacteria is generally conducted by the MPN Method introducing the liquid culture medium. But this medium, too, has many problems yet to be cleared such as determination of the incubation period, etc.

In this study to bring to light the succession of nitrifiers and heterotrophs in the biological treatment system, considerations were made on the dispersing method, incubation period and culture medium of specimens that were considered fundamental to measure the actual population of existing microorganisms.

5.1 TESTING PROCEDURE

The specimen sludge was activated sludge produced by the indoor experiments boosting a comparatively high nitrification activity.

The TOMY SEIKO UP200P Ultrasonic Shredding Unit was introduced to disperse the specimen. The selected power for the apparatus was 25 watts with the maximum shredding time being 3 minutes. The specimen was a mixed solution of 5 ml in quantity. The cultured temperature was maintained at 20°C and the incubation periods for heterotrophs maximum 30 days and nitrifiers maximum 130 days.

Considerations of the culture medium were made only on heterotrophs. And concerning nitrification bacteria, there were no discussions conducted pertaining to the culture medium incorporating the IBP Method.

The culture media for heterotrophs were: Medium A ... ordinary agar medium. Medium B ... ordinary agar medium diluted 10 times. Medium C ... Sakurai Culture Medium. Medium D ... Trypton Glucose. Medium E ... ASE Culture Medium. And Medium F ... PWRI (Public Works Research Institute) Culture Medium. There were six types in all. As PWRI culture medium employs synthetic sewage produced by the indoor experiments, 15 grams of agar was added to the synthetic sewage to have the concentration of influent. The population of heterotrophs was measured by counting all colonies formulated in the medium. With regards measurement of nitrification bacteria, the counting of nitrite and nitrate was done to measure nitrite bacteria; while the number of nitrate was counted and plus and minus judged to measure nitrate bacteria. The measurements

of nitrite and nitrate were conducted by introducing the Technicon Auto Analyzer based on the Cd-Cu Reduction Method.

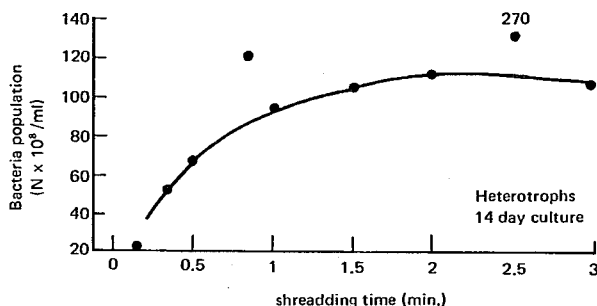
5.2 RESULT AND DISCUSSION

5.2.1 Dispersion of Specimen Sludge

Various types of microorganisms are adhered to the activated sludge. Especially, as nitrification bacteria are microorganisms with a sticking tendency (fixed type), special methods must be incorporated to disperse them to make way for easy measurement. And there are many methods developed.

Since the specimen contains live microorganisms, this gives rise to the problem of dispersion force. Therefore, it is important to confirm the optimum conditions of each specimen with regards dispersion method and force before implementing dispersion. Here, the ultrasonic shredding method was implemented and the relation between shredding time and the number of microorganisms was searched. The results are shown in Figs. 5.1 and 5.2.

Fig.-5.1 Living Microorganisms and Ultrasonic Shredding Time



Until around two minutes of shredding, the number of bacteria continued to increase and reached a fixed quantity, (two or three minutes.) Similar tendency was observed of nitrification bacteria. When this apparatus is used, the shredding time would be about 2.5 minutes. According to Chida (1971), with homogenizers, the appropriate time was 10 minutes. However, when coping with a number of specimens, the ultrasonic shredding unit is instrumental to shorten time. When conducting microscopic observation of specimens subjected to ultrasonic shredding, protozoa were shredded between 1.5 and 2 minutes leaving no trace of the original form. With regards shredding of Rotifera, only traces of shells were barely recognizable. From these observations, it is assumed that shredding can cause the mortality rate of the microorganisms to increase. Therefore, comparison with other dispersion methods is necessary. Here the shredding time was set at 2.5 minutes for activated sludge.

5.2.2 Incubation Period

The growth rate of bacteria is easily subjected to physico-chemical conditions such as temperature, pH, nutrient source and inhibitors. The growth rate is further

influenced by other microorganisms in the mixed culture system. The culture temperature was set at 20°C, a temperature requiring longer incubation period. Concerning activated sludge and heterotrophs, the Gils (1964) at normally 25°C, the incubation period is 6 days. Tezuka (1968) reports at 30°C, the culture period is between 6 and 7 days. Chida et al. (1971) states at 20°C, the incubation requires 10 days. And the IBP Method (1969) insists at 30°C, the period is between 7 and 10 days of incubation.

The relation between incubation period and the number of bacteria in this test was as shown in Figs. 5.3 and 5.4.

Fig.-5.2 Nitrification Bacteria and Ultrasonic Treatment Time

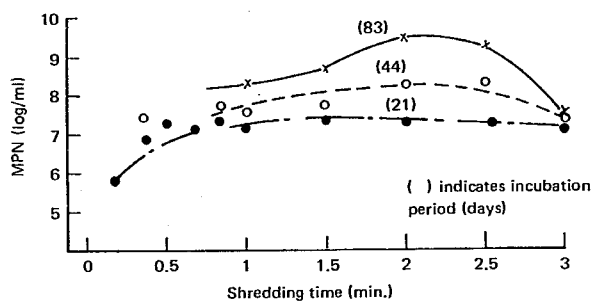


Fig.-5.3 Number of Bacteria and Incubation Period

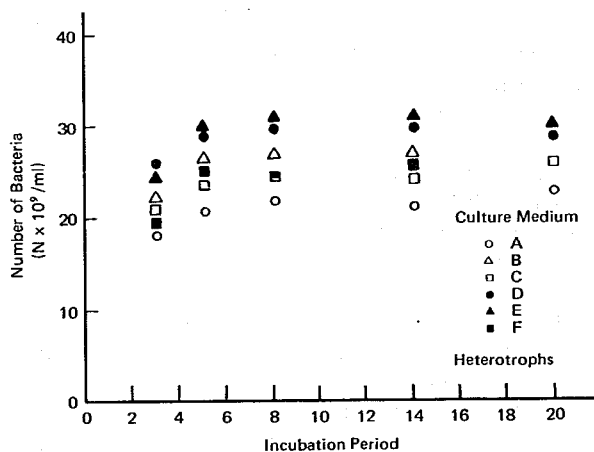
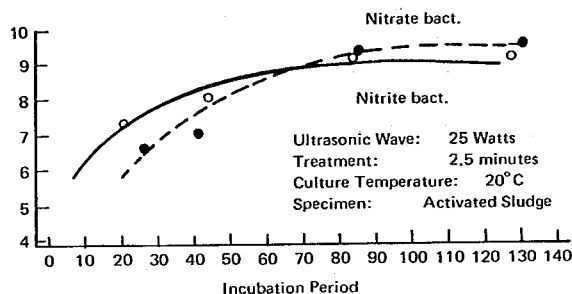


Fig.-5.4 Incubation Period and Number of Bacteria



The heterotrophs, after eight days, have shown fixed values. This tendency was also observed in other specimens. Accordingly, the culture of heterotrophs was conducted at 20°C and the incubation period being 10 days. With regards nitrification bacteria, Meikle John (1975) reports 25°C for two weeks. IBP states at between 20 and 22°C, the period is over 60 days. Matulewich et al. (1975) states that at 28°C, the incubation period for nitrate bacteria is between 20 and 55 days and nitrite bacteria between 108 and 113 days. When compared with heterotrophs, both the nitrate and nitrite bacteria require longer incubation periods. As shown in Fig. 5.4, at 20°C, the equilibrium condition was reached after more than 60 days. However, with the passing of days, after the 60th day, the nitrification bacteria showed a tendency to further increase. This inclination differed with the types of specimens, thus making the determination of incubation period difficult. Bacteria that turn positive after 100 days of incubation period, or those with extremely slow multiplying rate, were found impossible to propagate in the biological treatment system except under special conditions. In optimum condition, the generation time (tg) of nitrification bacteria is regarded to be between 10 and 12 hours. On the other hand, to estimate the incubation period by judging the number of days needed to reach the specified nitrification extent based on the growth rate of nitrifiers and the actual amount of nitrifiers when nitrites and nitrates produced by nitrification were detected, it is as follows:

From this study, it became obvious that the nitrification bacteria population more than about 10^3 and 10^4 N/ml, and thus the post-culture bacteria was estimated to be 10^4 N/ml. When incubation is conducted by the MPN Method, the nitrification bacteria amount would be 1 N/test tube of 5 ml at a certain dilution stage. From this, when the incubation period is sought by setting the generation time at 12 hours, it will be about 8 days. In case of marine nitrification bacteria, Yoshida (1967) states the generation time would be 40 hours at 20°C while Kimata and his group (1961) insist that the incubation period will be more than 2 months. When the generation time is 40 hours, the incubation period will be 22 days. By considering this value and the logarithm derived from the environmental changes in the test tube by the MPN method, it may be appropriate to define those that turned

positive at about 40 days of incubation as nitrification bacteria. The culture temperature should be between 25 and 27°C, or the optimum temperature of nitrification bacteria.

5.2.3 Studies of Culture Media for Determination of Heterotrophs

Various types of culture media are being developed for measurement of bacteria contained in activated sludge and in streams, lakes and swamps. Here, comparison of six different types of culture media was conducted. Fig. 5.5 shows the results of 14 days of incubation period. Except for specimen No.4, no drastic differences were observed. As shown in Photo. 1, the colonies in media E and F were small compared to others and made measurements difficult. Here, of the remaining four specimens, culture medium D enabled easiest measurement. Therefore, it was decided to introduce culture medium D (Trypton Glucose) for measurement of heterotrophs.

Fig.-5.5 Bacteria Number and Culture Media

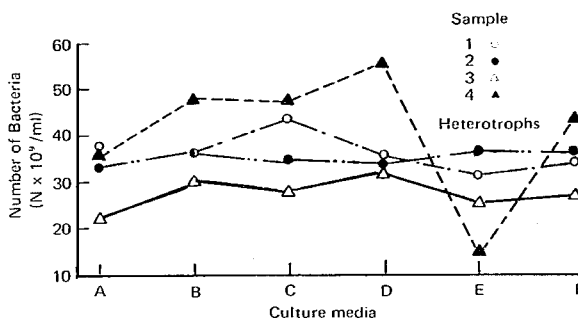
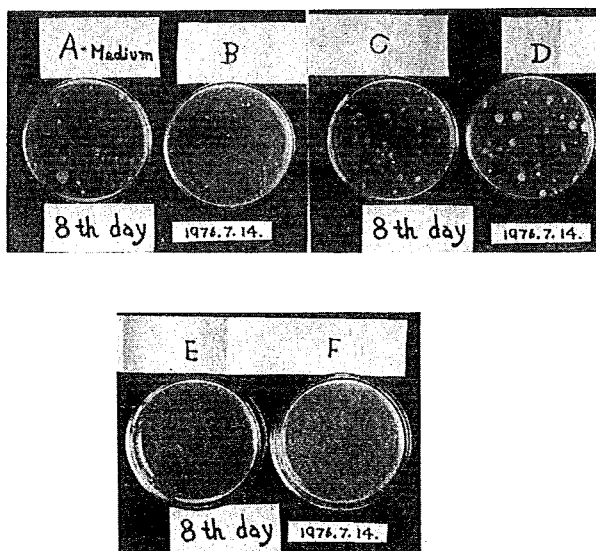


Photo-1 Comparison of Colony Size in Tested Culture Medias



5.3 SUMMARY

When conducting measurements of nitrification bacteria and heterotrophs contained in activated sludge, comparisons and studies of culture media were made only of dispersion method of sludge, incubation period and heterotrophs. The ultrasonic shredding unit was introduced to disperse sludge with an output of 25 w for 2.5 minutes. The incubation period was 10 days at 20°C for heterotrophs. However, with regards nitrification bacteria, there were difficulties in determining the incubation period. It was decided that the appropriate incubation period for nitrification bacteria was between 20 and 40 days based on tg, etc. Among introduced six different types of culture medium no drastic differences were observed. However, in view of the fact that the size of the colony was comparatively large and measurement easy, it is recommended adopting the Trypton Glucose culture medium.

II. FIELD SURVEY ON NITRIFICATION AT EXISTING SEWAGE TREATMENT PLANT

The studies were conducted to clarify the condition of nitrification at an existing activated sludge plant, in order to acquire a firm grasp of the relationships between nitrification and various contributing factors in specific reference to laboratory tests. Survey items include the nitrification rate, number of nitrifying bacteria, fauna, etc. in the aeration tank.

The hydraulic load at the plant surveyed is relatively low, and nitrate nitrogen is detected in its effluent almost throughout the year. The plant has a design capacity for treating 200,000 m³/day of inflow, and its present inflow is approximately 150,000 m³/day. This plant, Arakawa STP is located in Saitama Pref..

1. METHOD OF SURVEY

The survey was conducted using one bay of aeration tanks having a length of 85 m, with sampling conducted at four points equidistant from each other between the inlet and outlet of aeration tank. Sampling time was set at 11:00 hours when hydraulic load is considered to be relatively stabilized. Operational factors such as hydraulic load and MLSS were not controlled for this purpose, and survey was made once a month.

Water temperature, pH, DO, BOD, COD, N, nitrifying bacteria, fauna, are measured and analyzed.

The nitrification rate was obtained in terms of the yield of nitrate and nitrite nitrogen per unit time during the period taking the highest rate. The lag time was taken as the time differential between the inlet of aeration tank and the formation of nitrate and nitrite nitrogen.

2. RESULTS OF SURVEY

Table 1 shows the summary of the 1977 survey results. As seen in the table, the water temperature ranged from 12.5 to 24.8°C, and the aeration time from 5 to 7 hours. SRT (sludge retention time) influencing the standing crop of nitrifying bacteria exceeded 14 days which, however, could have been longer because withdrawal of excess sludge was conducted not continuously but intermittently at a rate of once in three days or a week. pH generally maintained at the neutral level. BOD-SS loading recorded less than 0.1 g/ss·g/day in most cases, although a maximum of 0.16 g/ss·g/day was observed once. The aeration tank is relatively run at low loadings. However, the hourly variation of BOD-SS is unknown because 24-hours survey was not conducted. DO registered 0.3 ~ 5.6 mg/l. As this value was obtained by settling the sample for liquid-solid separation and by applying Winkler's azide modification method to the supernant, it is probable that DO in the aeration tank was slightly higher.

Judging the degree of nitrification on the basis of the above data, it can be said that the water temperature worked as the rate determining factor of the activity of nitrification. Hence, the data shown in Table 1 and 2 are employed as control data for clarifying other factors of nitrification in respect to water temperature and season.

Table-1 Summary of the Results (1977)

Date	77 5/10	6/13	7/13	8/11	9/13	10/11	11/7	12/13	78 1/9	2/7	3/27
W.T. (°C)	19.9	23.5	23.2	24.8	22.5	21.5	20.5	17.0	14.5	12.5	16.5
Aeration time (h)	5.87	6.59	5.48	5.93	4.56	5.25	6.04	5.74	6.22	6.84	5.86
pH	6.2	7.0	6.8	6.5	6.9	6.8	6.6	6.7	6.8	7.0	7.1
DO (mg/l)	3.3	0.5	0.3	1.2	5.6	4.4	0.3	0.3	0.7	1.0	3.1
MLSS (mg/l)	4,205	4,700	2,237	3,400	1,434	3,000	3,849	3,800	3,300	3,714	3,000
MLVSS (mg/l)	2,405	3,000	1,407	2,210	915	1,980	1,680	2,508	2,300	2,622	1,900
MLVSS/MLSS	0.57	0.64	0.63	0.65	0.64	0.66	0.70	0.66	0.70	0.71	0.63
BOD-SS Loading	0.06		0.16	0.03	0.06	0.03	0.04	0.05		0.07	0.09
COD-SS Loading	0.02	0.02	0.03	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.03
Nitrification rate (%)	60.1	27.0			14.5		50.2	30.3	49.5	25.5	12.3
Nitrite bacteria (N/ml)	4.9×10^5	11×10^5	21×10^5	10×10^5	23×10^5	13×10^5	23×10^5	13×10^5	13×10^5	0.2×10^5	21×10^5
Nitrite bacteria (N/ml)	2.3×10^6	1.7×10^6	13×10^6	0.8×10^6	0.5×10^6	4.9×10^6	23×10^6	3.3×10^6	11×10^6	0.3×10^6	4.9×10^6
SRT (d)	69	15	18	32	24	100	60	24	20	26	14

Table-2 Summary of the Results (1976)

Date	76 5/27	6/16	7/12	7/21	8/9	9/13	9/27	10/7	11/24	11/30	12/20	77 1/17	2/21	3/16
W.T. (°C)	19.3	19.3	21.8	22.2	24.8	21.2	21.0	21.9	17.8	16.7	15.7	13.6	12.5	16.8
pH	6.6	6.7	6.8	7.0	6.9	6.9	6.7	6.8	6.95	7.01	6.99	6.95	6.97	7.02
DO (mg/l)	6.7	4.9	6.8	7.1	9.5									
MLSS (mg/l)	3,500	2,000	2,000	3,000	2,300	1,500	2,500	2,500	4,490	1,960	2,680	2,520	2,510	2,330
MLVSS (mg/l)	2,230	1,180	1,300	2,040	1,580	880	1,680	1,540	3,160	1,350	1,840	1,900	1,800	1,880
MLVSS/MLSS	0.64	0.59	0.65	0.68	0.69	0.59	0.67	0.62	0.70	0.69	0.69	0.75	0.72	0.81
BOD-SS Loading	0.047	0.094	0.034	0.023	0.027	0.020	0.053	0.064	0.032	0.091	0.14	0.17	0.12	0.22
Nitrification rate (%)	64.3	71.6	83.8	72.1	92.4	64.9	90.2	82.7	96.6	87.1	55.9	30.5	31.8	15.7
Aeration time (h)	5.10	5.10	5.10	4.08	5.10	4.08	5.10	4.76	5.10	5.10	4.37	5.31	5.31	
SRT (d)	57	35	71	53	31	62	94	31	71	49	62	134	122	68

As for the population of nitrifying bacteria in activated sludge, Kobori et al. indicated in their report (1977) that it registered approximately 10^6 N/ml and generally maintained itself at this level when SRT was more than 10 days (20°C), and that the number of heterotrophic bacteria was $10^8 \sim 10^9$ N/ml.

In the present survey, SRT ranged from 14 to 100 days and the bacterial number determined, through the year, $10^6 \sim 10^7$ N/ml for nitrate bacteria and about 10^6 N/ml for nitrite bacteria (Fig. 1). As shown in Fig. 2, about the same bacterial numbers were detected from the results of extended aeration process. These facts indicate that where SRT longer than the generation time of nitrifying bacteria is maintained, the bacterial number in activated sludge is held at about 10^6 N/ml irrespective of SRT. While the number of heterotrophic bacteria in activated sludge is known to range from $10^8 \sim 10^9$ N/ml, that of nitrifiers is much smaller, ranging from 10^2 to 10^3 N/ml.

Fig. 3 shows the relationship between nitrification rate and water temperature. Although it is required to obtain the nitrification rate per unit bacterial number, the figure indicates the rate per MLSS as the 1976 survey excluded the measurement of

Fig.-1 Seasonal Variation of Nitrifying Bacteria in Aeration Tank

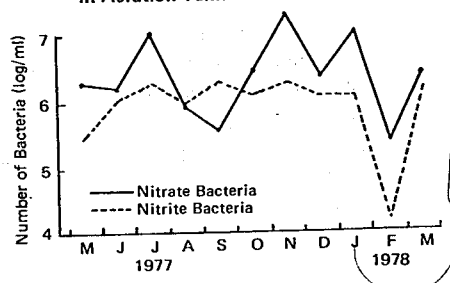


Fig.-2 Seasonal Variation of Bacteria in Aeration Tank (Extended Aeration Plant)

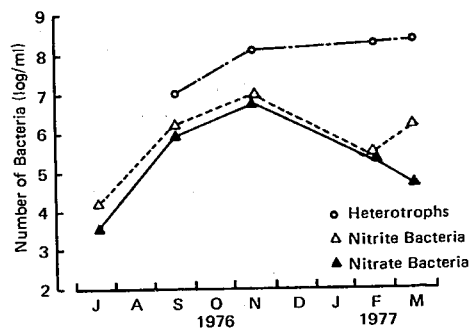
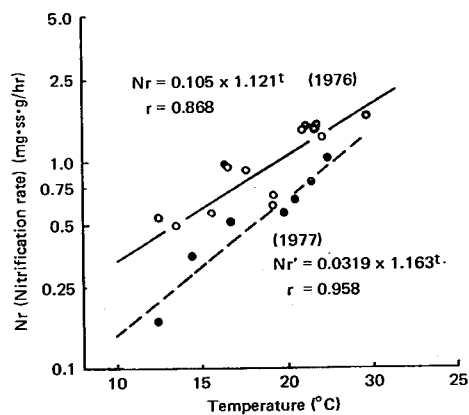


Fig.-3 Effect of Temperature on Nitrification Rate



bacterial number. As seen in this figure, the nitrification rate rose slightly when the operating factors in the aeration tank were controlled. The rate declined under normal operating condition, which is perhaps assignable to the influences of other factors than water temperature. The conceivable influences of such other factors are loading variation and DO level, and they seemed to become greater with the decline of water temperature. Temperature coefficient obtained on the basis of the observed data was a value of 1.121 under controlled operating condition (1977 survey) and 1.163 under non-controlled condition (1976 survey). These values show fair conformity with those in relevant reports.

Observation of nitrification which takes place with the downflow in the aeration tank disclosed that it involved certain time lag. Fig. 4 showing the relationship between water temperature and lag time indicates that latter tends to become longer with the decline of the former. The exact reason of this lag time increase is unknown, but it appears probable that as the activity of nitrifying bacteria becomes weaker due to the drop of water temperature, the influences of other environmental factors become stronger. Reduction of lag time which is often evidenced in laboratory tests is essential for efficient utilization of aeration tank, and this is one of the most important problems to be solved for satisfactory nitrification at an actual plant.

Fig.-4 Effect of Temperature on Lag Time

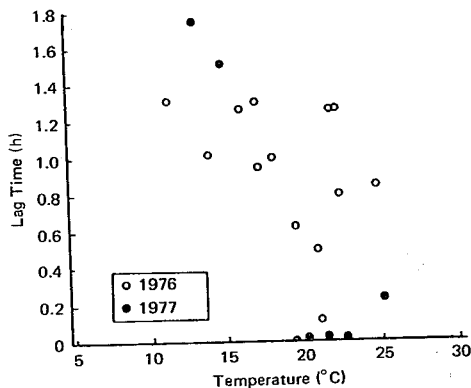


Table 3 shows the fauna in activated sludge. The fauna was predominated by activated sludge type maintaining activated sludge in a favourable condition throughout the year. Euglypha and Rotifera whose propagation is accelerated by the operational condition favourable for nitrification were observed through the year. At present, studies are being made on the possibility of using Euglypha as an indicator of nitrification condition in the aeration tank.

Table-3 Protozoa Observed Frequently during the Study

Date	N/ml										
	76 5/10	6/13	7/13	8/11	9/13	10/11	11/7	12/13	77 1/9	2/7	3/27
Litonotus	40	40	591	100	40		620	400	820	229	1,480
Arcella	1,060		617	1,160	460		340	1,560	1,460	7,233	1,460
Euglypha	480	340	711	1,400	120		640	380	40	130	100
Aspidsca	180	20	720	240	280		880	940	1,360	3,862	760
Vorticella	1,900	60	231	2,840	840		3,480	1,080	320	4,123	140
Espitylis	640	1,420	103	620	620		2,120	1,960	1,060	9,492	20
Opercularia	220		180	60	520		220	340	200	164	60
Acinata	60		51	80	20		180	80	60	65	60
Rotifera	280	140	695	2,900	340		40	340	340	229	240
W.T. (°C)	19.9	23.5	23.2	24.8	22.5	21.5	20.5	17.0	14.5	12.5	16.5

Fig. 5 shows the effect of nitrification rate and water temperature on the population of Euglypha which is one of the Protozoa detected when SRT is long. It was found that the number of Euglypha increased/decreased in proportion to the nitrification rate and water temperature, its coefficient of correlation with water temperature being 0.64. From this fact, it was discovered that the number of Euglypha is directly indicative of the degree of nitrification in the aeration tank. This relationship also applies to a plant employing extended aeration process as it was noted that Euglypha was dominant when the $\text{NH}_4\text{-N}$ concentration in the effluent was less than 1 mg/l.

Fig.-5 Effect of Nitrification Rate and Temperature on Number of Euglypha

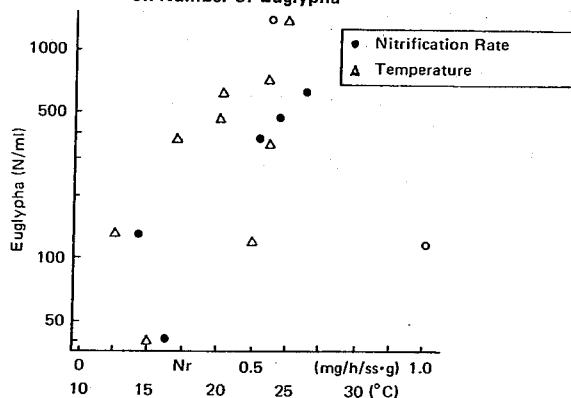
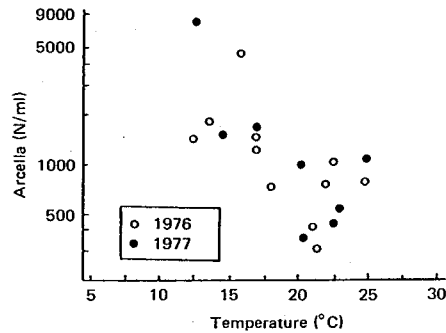


Fig. 6 shows the relationship between water temperature and population of Arcella. As seen in the figure, the number of this amoeba was inversely proportional to water temperature at a correlation coefficient of 0.72. Arcella is observed, just as Euglypha, when SRT is long, but it increases with the decline of water temperature.

It is planned that studies on index fauna will be continued as the operation and maintenance of aeration tanks can be performed with a minimum of time and labour by the use of such fauna as indicators.

Fig-6 Relation between Temperature and Number of Arcella



3. SUMMARY

The findings of the survey introduced above can be summarized as follows.

- 1) Number of nitrifiers in activated sludge is on the order of 10^6 N/ml.
- 2) While there a diversity of factors influencing the nitrification at existing sewage treatment plants, the nitrification rate can be maintained at a high level by controlling environmental factors affecting it and by operating the plant as constant load as possible.
- 3) Nitrification reaction in the aeration tank involves a lag time, which is an important matter to be considered for designing and operating nitrification plant.
- 4) For the purpose of satisfactory maintenance of aeration tank, its operating condition can be determined by the bacterial population (biomass) and aeration time on the basis the relationship between nitrification rate and water temperature. Also, as mentioned, the operating condition needs to be determined with consideration of the lag time involved in the nitrification.
- 5) There is probability that Euglypha will be used as an indicator of the degree of substantial nitrification.

III. NITRIFICATION ACCELERATION BY ALUM ADDITION TO THE PRIMARY SEDIMENTATION TANK

INTRODUCTION

To induce nitrification, it is necessary to accelerate growth of nitrifying bacteria in the treatment process. When compared with other bacteria related with water treatment, nitrifiers are comparatively slow in growth. Therefore, to accelerate the growth of nitrifying bacteria, it is indispensable to lengthen the retention time of micro fauna existing in the treatment process to help growth of nitrifiers.

In the activated sludge process, the SRT (Sludge Retention Time) of the activated sludge process is a significant factor to control. The SRT is expressed as a ratio between the amount of solids existing in the treatment process and the amount of solids discharged outside of the treatment process as effluent SS or waste activated sludge. Therefore, to extend the SRT means either to increase the amount of solids in the treatment process or to decrease the amount of solids discharged.

To maintain solids in the treatment process, there are means to elevate the return sludge rate, to prepare a sludge storage tank and others. To decrease discharged solids, considerations can be made to either lower the influent organic load or the influent SS load that will in turn decrease the amount of solid production.

This report is a summary of experiments that were aimed at accelerating nitrification by extending the SRT as a result of suppressing solid production by lowering the organic load in the aeration tank after adding alum as a coagulation agent to the primary sedimentation tank.

1. OUTLINE OF THE FACILITIES

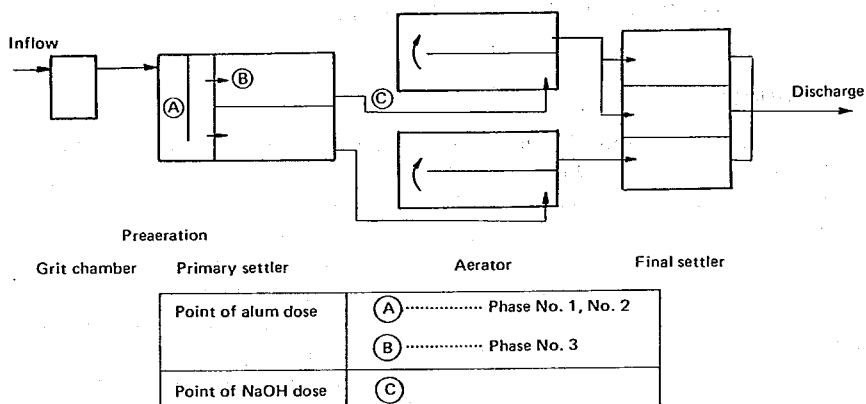
The studies were conducted at the Nishiyama Sewage Treatment Plant in Nagoya city. With treatment capacity of 20, 000 ~ 30,000 m³/day, it is a plant handling influent composed of only domestic sewage. Fig. 1 shows the facilities and the flow-diagram.

From the primary sedimentation tank to the final sedimentation tank, it can be broken up into two independent bays – Bay No. 1 (the lower part of Fig. 1) and Bay No. 2.

In experimental phases No. 1 and No. 2 alum was added to the preaeration tank while the primary effluent was supplied to the aeration tank in the Bay No. 1, and the primary effluent was added with NaOH and its pH values adjusted before being sent into the aeration tank in the Bay No. 2. In phase No. 3, the addition of alum to the primary sedimentation tank was stopped in the Bay No. 1, and continued only in the Bay No. 2.

Furthermore, in the Bay No. 1, except during phases No. 1 and No. 2, the conventional activated sludge phases No. 1 and No. 2, the conventional activated sludge process was employed in its operation. On the other hand, in the Bay No. 2 prior to the subject experiments, tests were conducted on adding alum to the aeration tank.

Fig.-1 Flow Diagram of Nishiyama STP



2. INFLUENCE ON TREATMENT DUE TO ADDITION OF ALUM TO PRIMARY SEDIMENTATION TANK

First, the experimental conditions for both bays during the subject experiments are listed in Table 1. The MLSS values that show a great difference between the two bays in Table 1 was considered to be the difference in the capacity of the final sedimentation tanks.

Table-1 Summary of Operational Conditions

Phase	No.1 1977. 9.13 ~ 10.15		No.2 10.15 ~ 11.9		No.3 11.9 ~ 1978. 1.26	
Bay	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
Flow (m ³ /d)	14,570	14,570	13,920	13,920	12,180	12,180
Aeration time (hrs)	2.55	2.06	2.65	2.13	2.96	2.32
Return sludge rate (%)	20.6	49.4	21.6	51.7	24.6	59.1
Air flow (times)	1.6	3.3	1.7	3.4	2.0	3.9
MLSS MLVSS (mg/l)	703 562	2125 1382	687 502	1999 1361	831 643	2607 1832
SVI	97	63	98	69	113	90
BOD-SS load (kg/kg/d)	0.450	0.149	0.688	0.236	0.666	0.153
SRT (d)	6.3	37.6	2.9	13.4	1.9	13.6
Alum does as Al (mg/l)	6	6	3	3	0	6
NaOH addition	No	Yes	No	Yes	No	Yes

With regards the influence of the alum addition to the primary sedimentation tank, it was divided into two groups: the influence to primary treatment and that to the secondary process.

Concerning the influence to the treatment at the primary sedimentation tank, Table 2 summarized the primary sedimentation effluent values and the removal rate which were based on the data obtained between March 1975 and March 1978. From this Table, the followings can be pointed out:

- a. BOD, COD and TOC removal rates improved. Especially, the removal rate of soluble matters markedly improved. With regards the removal rate of suspended matters, there was no significant change.
- b. SS removal rate hardly changed.
- c. Phosphorous removal rate changed markedly from 17.4% to 51.9%.
- d. Although slightly, K-N and $\text{NH}_4\text{-N}$ removal rates increased.
- e. pH values dropped around 0.3 and 0.5.
- f. Total alkalinity of influent without alum addition increased slightly. But with addition, it dropped a little.

Besides the above mentioned points, the increase in primary sludge production and the improvement of primary influent transparency can be quoted.

Table-2 Changes in Primary Effluent Quality with Alum dose

	No addition		Alum addition (6 mg Al/l)	
	Effluent Quality	Removal Rate	Effluent Quality	Removal Rate
BOD (T)	73.4	42.1 (%)	51.5	58.4
BOD (S)	43.7	14.1	29.4	47.2
COD (T)	43.2	35.5	28.6	51.9
COD (S)	22.0	5.2	—	—
TOC (T)	52.2	30.0	41.4	40.2
TOC (S)	26.6	12.2	22.2	30.7
K-N	23.1	9.7	19.2	25.1
$\text{NH}_4\text{-N}$	13.5	-5.9	11.6	4.6
T-P	3.08	17.4	1.84	51.9
SS	46.7	67.5	47.1	66.6
T-Alkalinity	89.6		52.9	
pH	6.6 ~ 7.3		6.3 ~ 6.8	

(mg/l)

Concerning the influence to secondary treatment, data obtained between mid September and mid November were collected and compared. The results of data

comparasions are shown in Table 3. However, the 1975 and 1976 data are of operations by the conventional system and 1977 of operations by adding alum to the primary sedimentation tank.

From Table 3, the followings can be pointed out:

- a. The effluent values and the removal rate of BOD and COD did not show much changes.
At BOD (T), the improvements on the removal rate and the effluent values were perhaps due to the fact that oxygen consumption by nitrification in a BOD bottle was small.
- b. With regards TOC, the removal rate deteriorated.
The reasons are yet unknown.
- c. Nitrification virtually did not occur, and K-N, $\text{NH}_4\text{-N}$ removal rate dropped.
- d. With regards phosphorous, both residual concentration and removal rate increased.
- e. Due to drop in waste activated sludge production, the SRT became longer.

Table-3 Secondary Effluent Quality when Alum is Added in Primary Settler

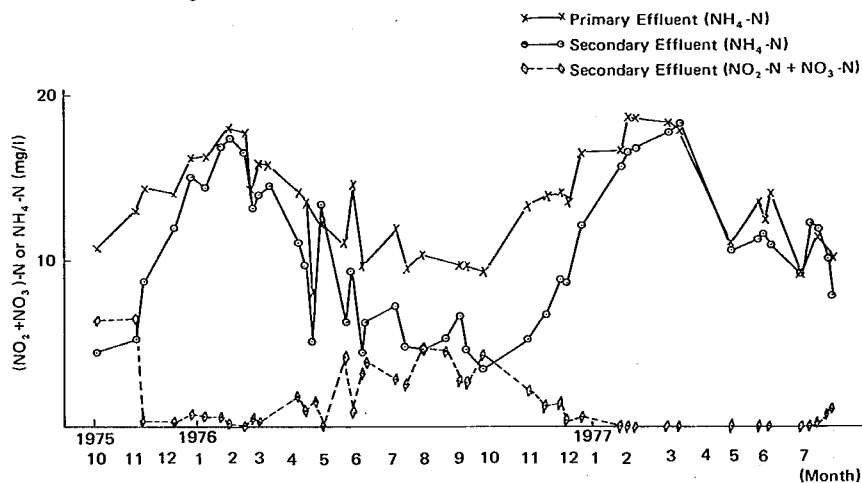
Year	1975		1976		1977	
	Effluent quality	Removal rate	Effluent quality	Removal rate	Effluent quality	Removal rate
BOD (T)	19.5	68.3(%)	27.2	55.9(%)	11.8	77.4 (%)
BOD (S)	3.7	89.8	7.6	79.5	5.7	81.5
COD (T)	11.1	71.7	13.2	73.5	10.8	62.4
COD (S)	7.5	55.3	9.3	57.7	—	—
TOC (T)	11.8	65.5	10.1	71.9	23.0	54.0
TOC (S)	8.2	59.7	—	—	19.0	33.6
K-N	8.6	61.3	7.9	60.8	14.8	24.4
$\text{NH}_4\text{-N}$	5.4	58.2	5.4	56.5	10.7	9.5
$\text{NO}_2\text{-N} + \text{NO}_3\text{-N}$	5.5	—	3.4	—	0.7	—
T-P	1.62	37.7	1.60	37.3	0.65	61.8
SS	9.8	77.6	13.2	65.9	6.8	82.2
MLSS	1227		730		646	
SRT (d)	—		3.4		4.6	
Mode of Operation	Conventional		Conventional		Alum addition in primary settler	

3. ACCELERATION OF NITRIFICATION

3.1 NITRIFICATION BY CONVENTIONAL PROCESS

Fig. 2 shows the actual results of the Bay No. 1 demonstrating to what extent can nitrification be expected in the conventional operating process.

Fig.-2 Seasonal Variation of Nitrogen at Conventional Process



The $\text{NH}_4\text{-N}$ concentrations in both the primary sedimentation tank effluent and the secondary treatment effluent were higher in winter and lower in summer, thus showing seasonal changes. The difference between the two, in other words the $\text{NH}_4\text{-N}$ removal rate (nitrification rate), was approximately 0% in winter and between 50% and 60% in summer.

3.2 THE EFFECTS OF pH ADJUSTMENT WHEN ADDING ALUM TO PRIMARY SEDIMENTATION TANK

The SRT during summer when nitrification developed was between 2.5 and 3.5 days by conventional operation. By adding alum to the primary sedimentation tank, sufficient length was obtained with regards SRT. But, despite this fact, nitrification was insufficient, perhaps, due to the drop of pH value in the aeration tank. It is known that the activity of nitrifying bacteria reaches its peak when pH are between 7 and 8. But, the pH value in the primary effluent dropped to 6.3 ~ 6.8 when alum was added, and it is assumed that the value has further dropped owing to nitrification activity. Therefore, in the Bay No. 2 tests were conducted by adjusting the pH values with NaOH for the purpose to lighten the pH and to give sufficient alkalinity for nitrification.

NaOH was added at the primary sedimentation tank, and pH adjustment was made according to the pH meter installed in the lower stream. The target pH value was between 7.8 and 8.2. Fig. 3 shows the influence of pH adjustment to the pH value in the aeration tank. This shows how the pH values changed at the end of the

aeration tank with regards non pH adjustment (Bay No. 1) and pH adjustment (Bay No. 2). The Fig. shows that when pH adjustment was not conducted, the pH value dropped markedly from night to the following morning. The minimum pH value recorded was about 5.0. In contrast, when pH adjustment was conducted, there was no pH value drop at night, and the value was maintained throughout the day at between 6.0 and 7.0.

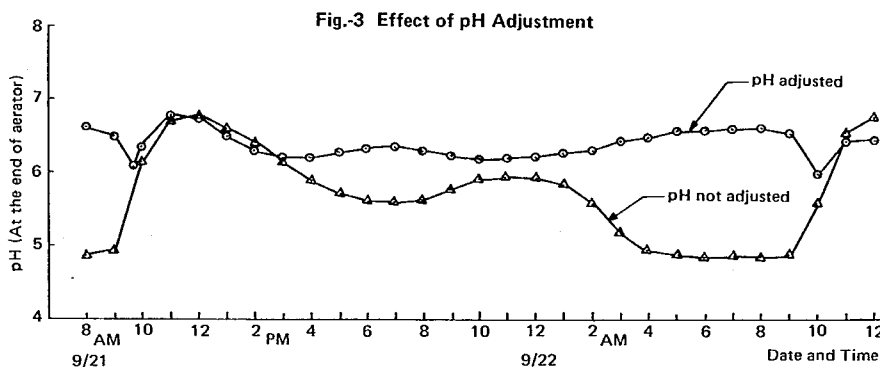


Fig. 4 shows the daily changes in $\text{NH}_4\text{-N}$ concentration in the effluent of both the Bay No. 1 and the Bay No. 2. The Fig. summarizes the measurements conducted by the automated continuous colorimetric analyzer. The average of around-the-clock measurements from 9:00 am to 8:00 am the following morning is plotted as the value of a single day.

In the Bay No. 2, the daily average of 2 ~ 5 mg/l of $\text{NH}_4\text{-N}$ in the effluent continued until mid-December, and from the latter part of December it gradually increased.

In the Bay No. 1, it can be pointed out that nitrification virtually did not develop when compared with that in the Bay No. 2 and in the conventional Bay No. 1.

From these results, even when SRT is sufficient, if the pH is too low, it can be anticipated that the nitrification will not be achieved. Therefore, an experiment was conducted. The results of this test are as shown in Fig. 5. As it was not possible to monitor the effluent in the Bay No. 2 at that time, it was substituted by expressing the changes of $\text{NH}_4\text{-N}$ in the effluent of the filters. The influence of suspending pH adjustment have shown immediate results on the following day as the daily average of 1.6 mg/l was boosted to 6.6 mg/l. Also, the recovery after resuming pH adjust was fast and returned to normal in a signal day. This testified to the fact that the effects of pH adjustment were great and showed immediate results.

Fig. 4 Change in Ammonia Nitrogen

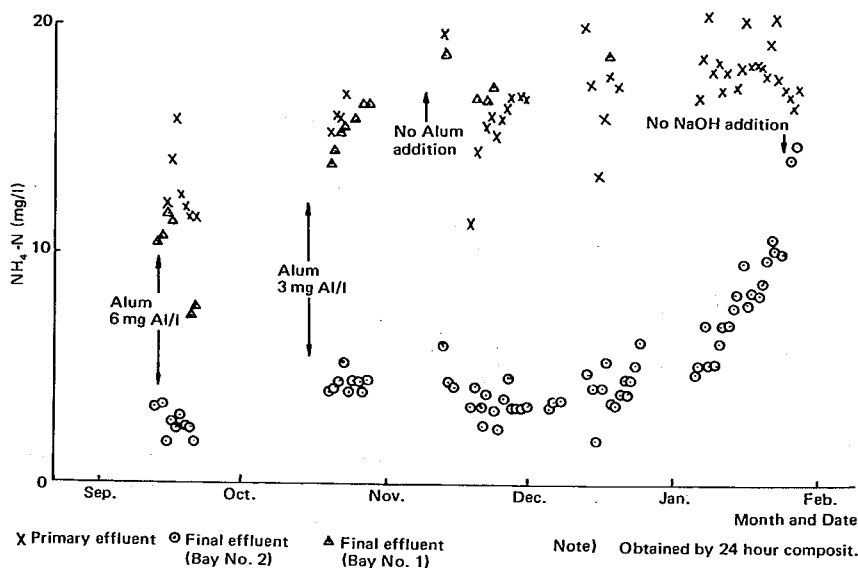
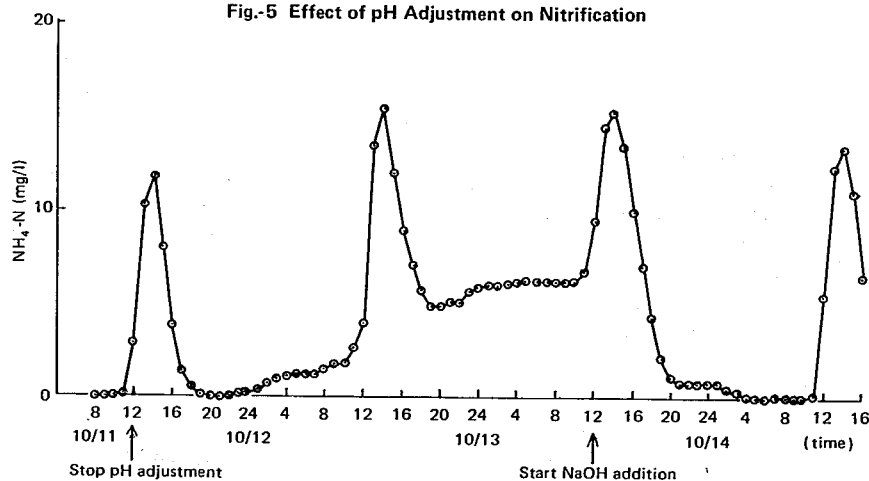


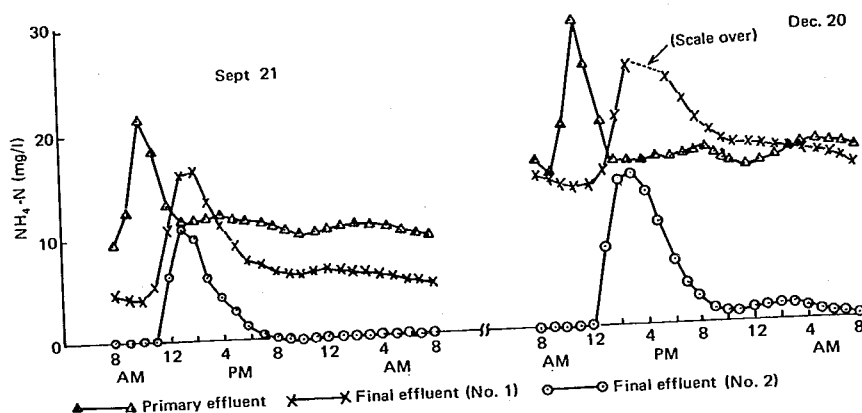
Fig. 5 Effect of pH Adjustment on Nitrification



3.3 NITRIFICATION AT HIGH LOADING

The $\text{NH}_4\text{-N}$ concentration in the effluent varied greatly in a signal day. This is illustrated in Fig. 6. As shown in the Fig., except for the 9 hours between 11 a.m. and 8 p.m., the $\text{NH}_4\text{-N}$ was totally nitrified and marked 'zero' in the Bay No. 1. The peak time during 11 a.m. and 8 p.m. came a little later than the peak time of primary effluent owing to the inflowing $\text{NH}_4\text{-N}$ being discharged without totally nitrified.

Fig.-6 Hourly Variation of Ammonia Nitrogen



During other hours than the peak time, nitrification was sufficient, thus showing that nitrification was insufficient during hours when either the influent volume or the influent concentration increased. It is regarded necessary to contrive means to heighten MLSS at least during high loading time.

This trend remains the same even in winter.

3.4 NITRIFICATION IN WINTER

When studying the Bay No. 2 data as shown in Fig. 4, nitrification continued even in December and the nitrification rate began to drop from the latter part of December. Similar to the seasonal changes observed in Fig. 2, this is considered to derive from the drop in the water temperature.

In the Bay No. 1 as shown in Fig. 2, it has lost its nitrification ability in January. In contrast, in the Bay No. 2, it maintained a nitrification rate of between 40 and 50 percent even in the latter part of January showing the strong influence of the SRT length.

It is considered difficult to prevent drop in nitrification ability due to water temperature drop despite sufficient SRT and pH adjustment.

4. SUMMARY

The results of the study are summarized as follows:

- The organic loading to the secondary process can be decreased and the SRT can be extended when alum is added to the primary sedimentation tank.
- To extend SRT is necessary to induce nitrification. When SRT is sufficiently long, nitrification activity can be kept high even in winter.
- pH adjustment was necessary to obtain completely nitrified effluent.
- Control measure to increase MLSS at high loading is necessary to maintain substantial nitrification.

IV. STUDIES ON NITRIFICATION PROCESS AT SMALL-SCALE SEWAGE TREATMENT PLANT

1. INTRODUCTION

The Nasu plant used for this study is located in a coppice of Kuroiso town, Tochigi Prefecture and is designed for treating wastewater from the service area of an expressway running through a hilly area. Its operation is subject to seasonal fluctuation. Users of the service area increase particularly in periods including many holidays such as early January, May and August. In these periods, raw sewage increases in both volume and strength.

Wastewater comes from the restaurant and water closet in the service area. At present, only the final effluent from the plant is used as flushing water on the water closet, although a mixture of effluent and tap water (1 : 1) was used at the initial stage of the plant operation.

Sewage treatment at this plant is conducted by the combined application of activated sludge process and filtration. Final filtered effluent is discharge into a nearby river through an agricultural waterway. As the effluent is used for irrigation, its target quality is set at less than 5 mg/l for BOD, SS and $\text{NH}_4\text{-N}$. Considering the functions of the plant, this target can be attained for BOD and SS. Hence, removal of $\text{NH}_4\text{-N}$ or nitrification is the main objective of sewage treatment at the plant.

This report introduces the existing state of the plant facilities, with specific reference to the nitrification process. As for nitrification denitrification process, studies are being made to obtain further detailed data.

2. OUTLINE OF THE PLANT

The plant is operated to treat raw sewage from the restaurant and water closet by the extended aeration process in order to attain the effluent standards shown below.

A portion of the effluent is reused as flushing water for the water closet, and the remainder is discharged into the agricultural waterway.

1) Effluent Standards

BOD	Less than 5 mg/l
SS	- Ditto -
$\text{NH}_4\text{-N}$	- Ditto -
E. coli group	Less than 3,000 N/ml

2) Design Flow and Water Quality of Raw Sewage

Average daily flow	860 m ³ /day
Maximum hourly flow	89.6 m ³ /h
BOD	200 mg/l
SS	250 mg/l

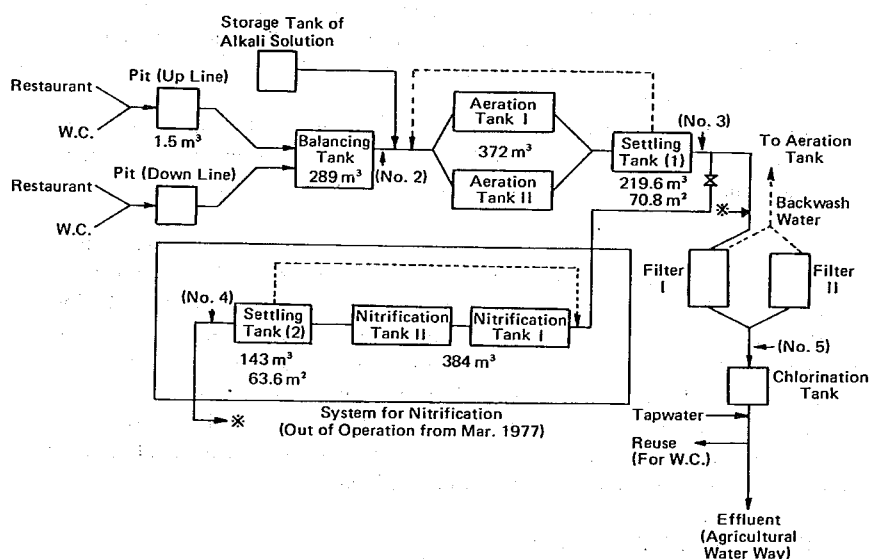
3) Treatment Process (Fig. 1)

The plant is designed for the combination of extended aeration and filtration. As shown in Fig. 1 illustrating the initially planned flow chart, the plant is com-

posed of balancing tank (flow equalization), aeration tanks and settling tank for removing organics, nitrification tanks and settling tank for oxidizing nitrogen compounds, filters for removing solids, and chlorination tank.

Retention time of both aeration tanks and nitrification tanks is about 10 hours at the design flow. Actual flow is about a half of design flow. Dual media filters of sand and anthracite are used.

Fig.-1 Outline of the Plant



1) Operation by Initially Proposed Flow Chart

At the early stage of plant operation, treatment was carried out according to the initially proposed flow chart. However, as the detention time of aeration tank turned out to be more than 20 hours, nitrification occurred in the aeration tank, resulting in the reduction of pH down to about 5. In the nitrification tank, on the other hand, activated sludge was found only to a negligible extent and its segmentation caused turbidity increase. Hence, it was found meaningless to operate the nitrification tanks at that mode.

2) Proposed Operation for Improvement of Nitrification Efficiency

In order to raise the nitrification efficiency as well as the operational efficiency of the whole plant, the plant configuration was improved from March 1977 by suspending the operation of the nitrification system (central boxed section in Fig. 1) and by starting pH control in the aeration tank. The nitrification tanks thus put out of operation were used for aerobic sludge digestion.

3) Further Improvement for Nitrification-Denitrification

In March 1978, the plant configuration was further improved by introducing nitrification-denitrification process aimed at removing total nitrogen. This im-

provement, intended basically for introduction of a single stage nitrification-denitrification process, consists of the following main alterations.

The aeration tanks were converted to anaerobic tanks, a denitrification zone was formed by dosing methanol in the middle portion of the nitrification tanks, and end portion of the tank was used for re-aeration.

Studies are in progress on this introduced process.

Method of Survey

The survey, covering a period from January 1976 to March 1977, was conducted in two ways, 24-hour composite sampling and analysis carried out once week and 24-hour grab sampling conducted once in two months.

The survey points are shown in Fig. 1, and survey items included pH, transparency, alkalinity, SS, BOD, COD, nitrogen in various forms, fauna, bacteria, etc.

3. OUTLINE OF SURVEY RESULTS

3.1 RESULTS OF TREATMENT BY INITIALLY PROPOSED FLOW CHART

As a result of surveys conducted on March 1 and 2, 1976 according to the initially planned flow chart, the following findings were obtained.

Although organic matters such as BOD and COD were sufficiently removed, the effluent registered a transparency of 20 ~ 40 cm and contained micro flocs which were not removed by filtration. These particles were of the size small enough to pass through the filter paper pore size of 12 μ .

Residual concentration of $\text{NH}_4\text{-N}$ ranged from 3.3 to 4.4 mg/l and averaged 3.7 mg/l. In the weekly sampling analysis, it recorded a value of 2 ~ 13 mg/l. At that stage of operation, tap water mixed with effluent as dilution water to meet standard, and the diluted effluent was reused as flushing water of water closet in service area.

pH was reduced from 6.8 ~ 7.6 (average : 7.4) to 3.9 ~ 4.0, and alkalinity registered zero. In the weekly 24-hour survey conducted, however, effluent pH showed considerable fluctuation, ranging from 3.8 to 6.6. Because of the low pH of effluent, alkali solution is added at the outflow side of the nitrification tank.

Nitrification rate recorded 13 ~ 78%, which is indicative of the possibility of conducting sufficient nitrification despite the water temperature of 8 ~ 10°C. Judging from the decline of pH, it appeared that the nitrification was suppressed due to the shortage of alkali required for oxidation of ammonia.

Scum was formed in large quantities in aeration tanks and nitrification tanks. Microscopic examination disclosed that the scum was air bubbles entrapped in oily film. The scum disappeared after its pH was adjusted to 8 ~ 8.5. Activated sludge presented a fauna predominated to a substantial degree by Rotifera and Euglypha, which is characteristic of the extended aeration process.

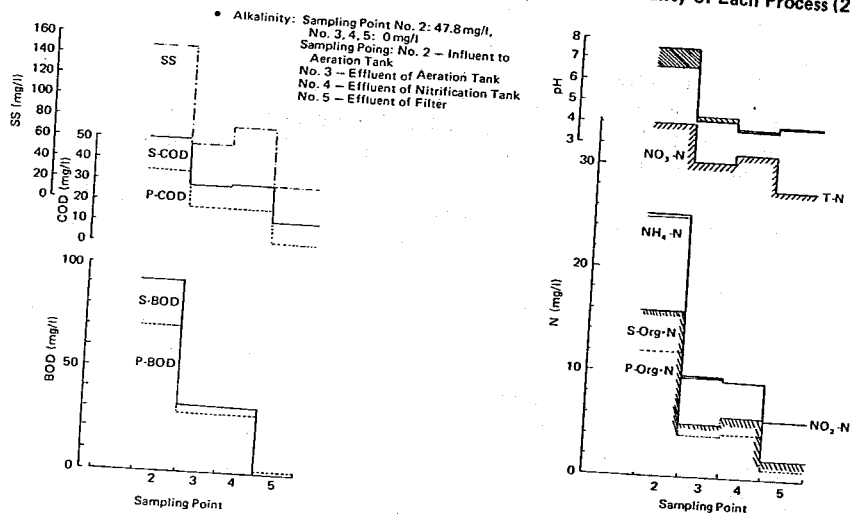
As for the functional performance of flow balancing tank, aeration tanks and filters, the following findings were obtained.

- 1) The balancing tank equipped with diffusers, is a fairly useful facility in that it can mitigate loading fluctuations by virtue of its large capacity and is also capable of turning raw sewage aerobic (raw sewage in balancing tank contains

- protozoa).
- 2) The aeration tanks suffice for removal of organic matters and oxidation of nitrogen as the aeration time is 24 hours at the present flow. However, the low pH in the tanks needs to be adjusted.
 - 3) The nitrification tanks are not necessary at present because the aeration tanks suffice for both removal of organic matters and oxidation of nitrogen (Fig. 2).
 - 4) The filters are indispensable for the extended aeration process like this plant. Specifically, the extended aeration process brings activated sludge close to the state of endogenous respiration, often causing flocs of activated sludge to be segmented or nitrified. This results in the denitrification in the settling tank, whereby nitrogen gas is produced to cause activated sludge to float up and overflow the weirs. Even in such a case, the filters are useful in improving the effluent transparency.

From the findings described above, it is concluded that 1) pH in the aeration tanks should be adjusted to about 8 in order to hold $\text{NH}_4\text{-N}$ concentration in the final effluent at less than 5 mg/l at all times, and 2) considering the present flow, the nitrification tanks can be put out of operation without any hindrance to the plant operation.

Fig.-2 Average Water Quality of Each Process (1) Average Water Quality of Each Process (2)



3.2 PROPOSED IMPROVEMENT MEASURES BASED ON INITIAL OPERATIONAL CONDITION

1) pH Control

For the purpose of controlling pH, NaOH was selected for addition as 25% solution due to its nature. The injection dosage, about 60 kg/day, was determined for oxidizing TKN totally to nitrate so that the target pH of 8 ~ 8.5 would be attained by the plant operation.

2) Modification of Treatment Process

The nitrification tank was put out of operation for use as aerobic digestion tanks, and the treatment process was consequently modified as follows.

Raw sewage → Balancing tank → Aeration tank →

Settling tank → Filters → Reuse or discharge

After effecting the above two measures, the survey was continued with the dual purpose of removing organic matters and attaining 100% nitrification efficiency.

3.3 RESULTS OF SURVEY OF PROPOSED IMPROVEMENT MEASURES

3.3.1 Effects of pH Control

Summary of the survey results is shown in Figs. 3.1 ~ 3.3. By effecting pH control, removal rate of organic matters recorded 93 ~ 98% for BOD and 71 ~ 88% for COD. Removal of SS at secondary settler was also increased, but these filtered effluent showed the similar water quality as it did before pH control.

SS concentration in secondary effluent declined after pH control, although it was unknown whether this was to be ascribed to the increased bio-coagulation of activated sludge or to the shortening of aeration time. Particularly notable among the effects of pH control was the fact that the transparency of final effluent increased to more than about 1 m as a result of augmented SS removal in the filters. On examining SS in secondary effluent, it appeared that fine segmented particles of activated sludge flowed out in a sort of colloidal state when pH ranged from 4 ~ 5. After pH control, however, such fine particles disappeared and secondary effluent contained particles large enough to be entrapped in the filter, which is perhaps assignable to the shortening of aeration time by about a half. When pH ranged from 4 to 5 in the aeration tank, micro flocs in secondary effluent could hardly be trapped even if filtered by GFC. It may as well be added here that the minimum size of particles that can be entrapped by dual media filter of sand and anthracite is reported to be larger than 7 ~ 10 μ .

Fig. 3-1 Summary of the Results

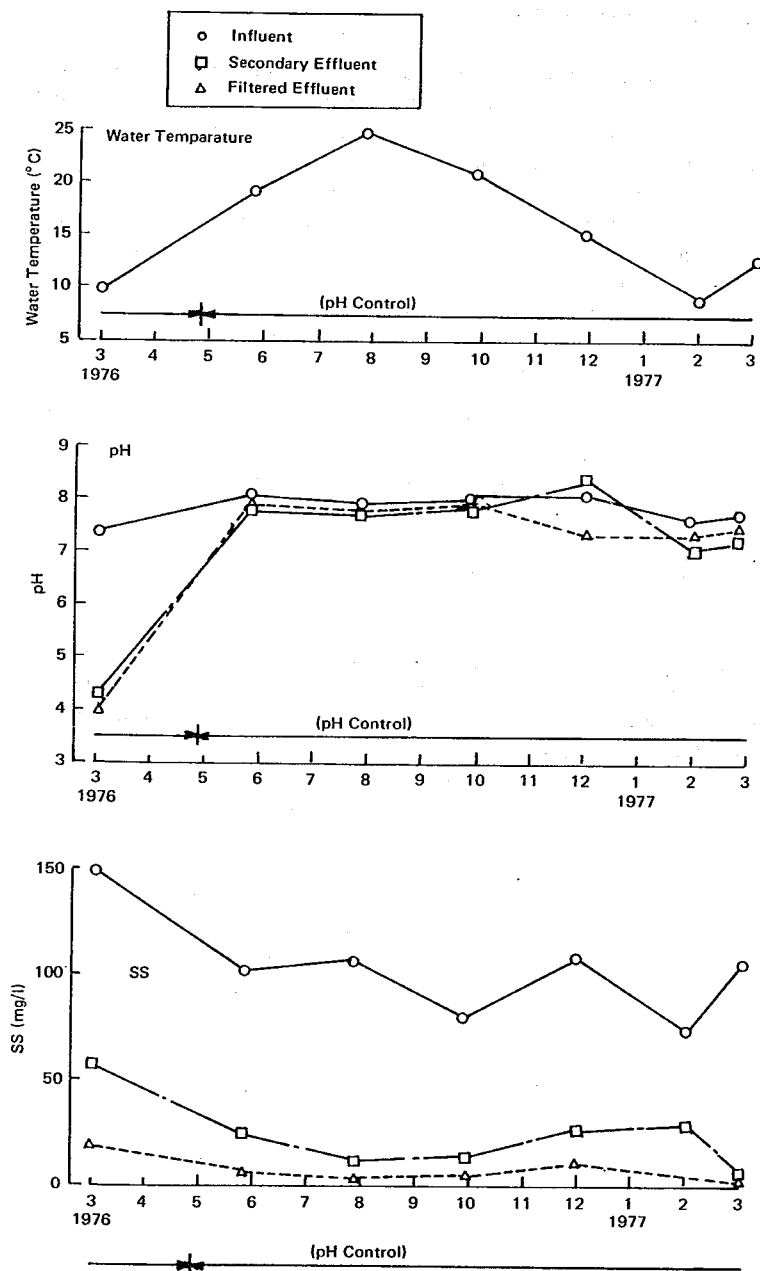


Fig.-3.1

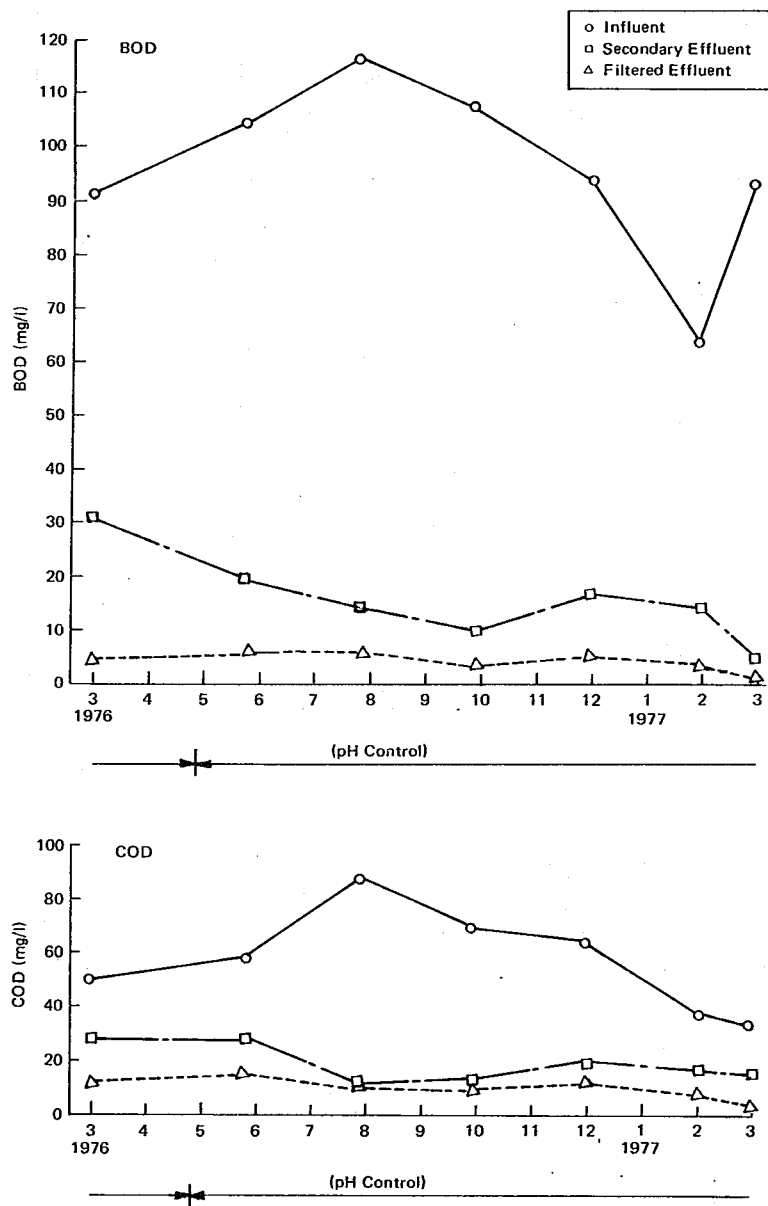


Fig.-3.3

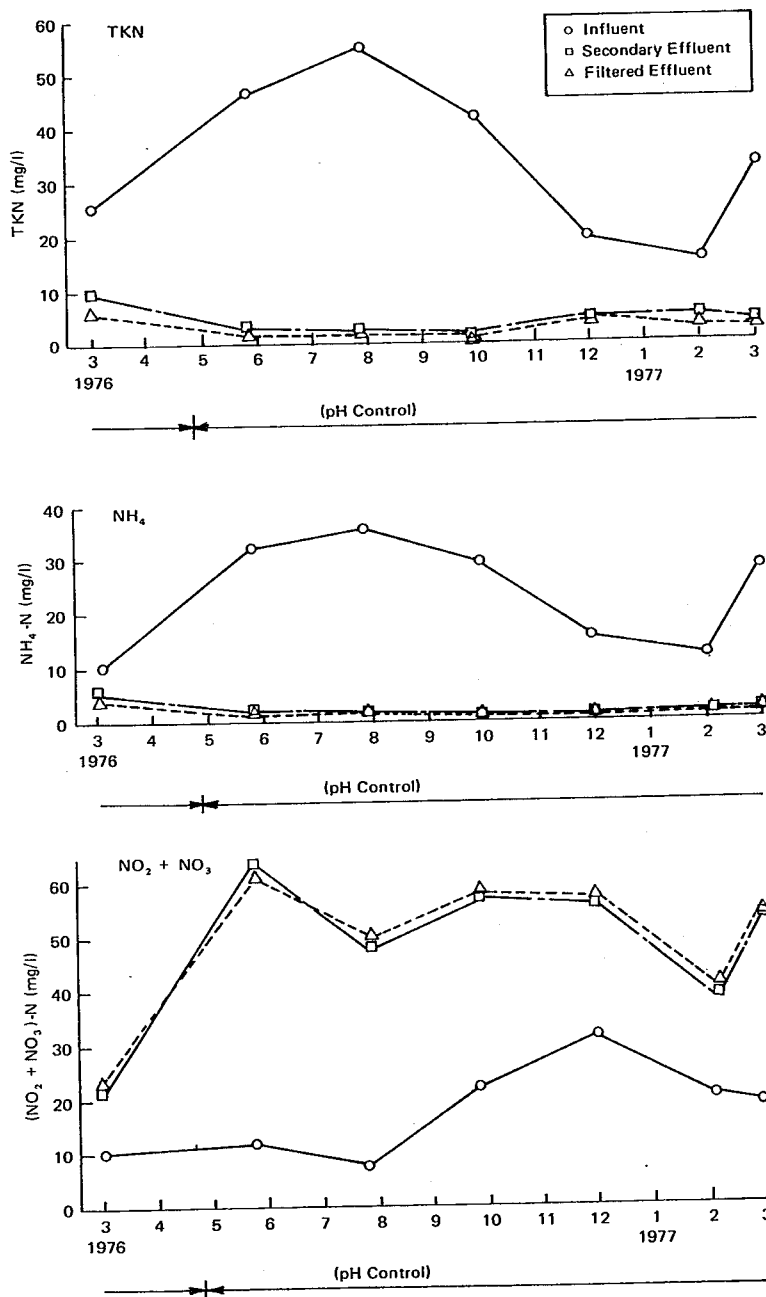
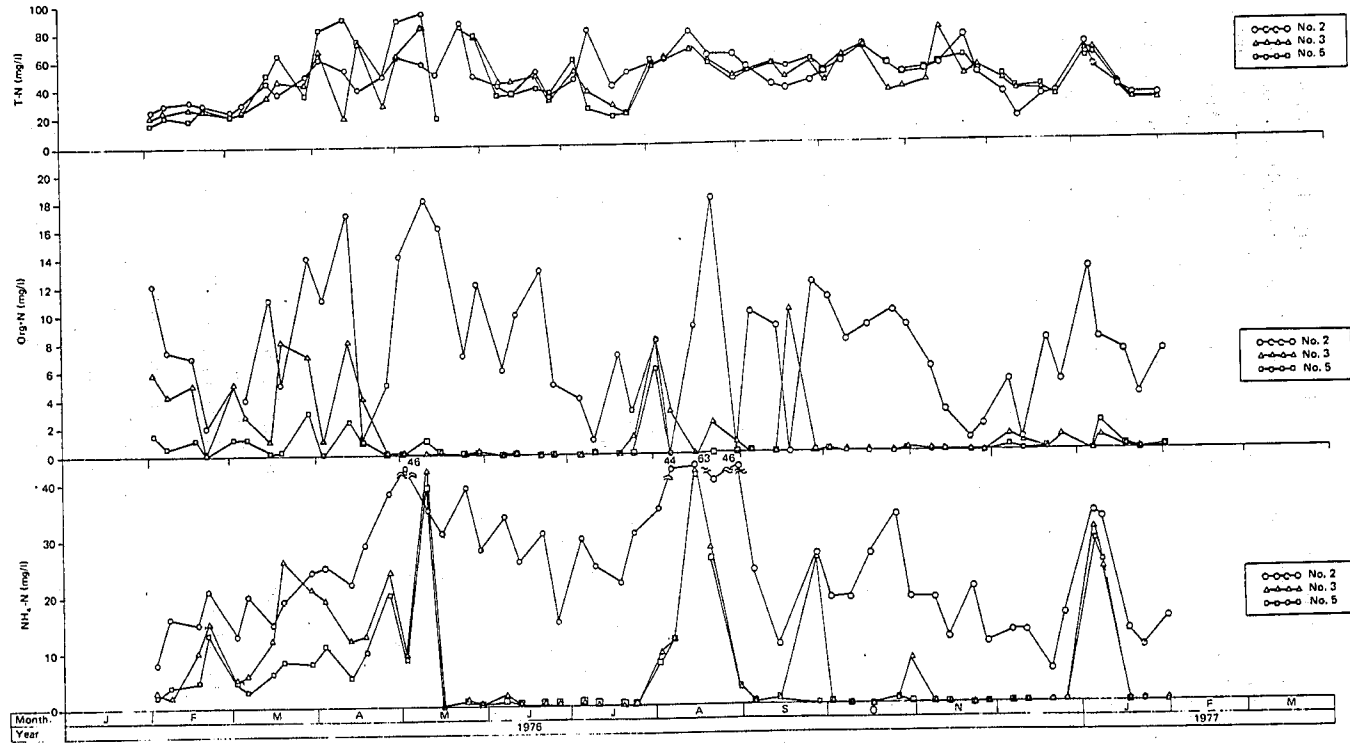


Fig. 4 Results of Survey



As for nitrogen, TKN and $\text{NH}_4\text{-N}$ in secondary effluent dropped to less than 5 mg/l and to about 1 mg/l, respectively, indicating that pH control exhibited a high nitrification efficiency. However, the weekly 24-hour composite survey (Fig. 4) disclosed that the nitrification rate declined to 30 ~ 40% in August and January when the aforementioned service area was most frequently utilized, with $\text{NH}_4\text{-N}$ in final effluent recording 41 mg/l in August and 25 mg/l in January. A diversity of reasons can be conceived of as contributing to this phenomenon, such as the shortening of aeration time due to increased inflow of wastewater, decline of activated sludge density, sharp changes in pH, inflow of toxic or harmful substances, etc. However, since none of them can be identified as the decisive reason, further studies must be conducted to cast light on this problem.

The plant operating factors are shown in Table 1. The aeration time is as long as 20 ~ 40 hours. Even if inflow increases to designed 800 m³/day, therefore, an aeration time of about 10 hours can be secured, which is long enough for removal of organic matters and nitrification under normal condition. Settling time, ranging from 12 to 24 hours, is also long enough to make the supernatant water considerably transparent, provided that activated sludge is condensed satisfactorily in the settling tank. MLSS is maintained at 1,200 ~ 3,400 mg/l, averaging 3,000 mg/l as seen in the table. BOD-SS loading is about 0.02 kg/kg/d operational factors discussed above, it may be said that the plant has considerably large surplus capacity.

Table-1 Operating Factors

	Date	Inflow (m ³ /d)	Aeration Time (hr)	Settling Time (hr)	Overflow Rate (m ³ /m ² /d)	Discharge Loading (m ³ /m ² /d)	MLSS mg/l	Inflow BOD Loading (kg/d)	Inflow SS Loading kg/d	BOD-SS Loading (kg/ss·kg/d)
1	1976 3.1~2	380.2 (15.9 m ³ /h)	23.5	13.9	5.4	12.7	1,670	14.3	56.6	0.02
2	5.24~25	223.8 (9.3)	40.0	23.5	3.2	7.5	3,140	14.0	23.5	0.01
3	7.26~27	292.1 (12.2)	30.6	18.0	4.1	9.8	2,950	18.9	31.3	0.02
4	9.27~28	297.1 (12.4)	30.1	17.7	4.2	10.0	2,620	13.3	23.8	0.01
5	11.29~28	401.8 (16.7)	22.2	13.1	5.7	13.5	2,900	26.4	43.4	0.02
6	1977 2.14~15	440.6 (18.4)	20.3	12.0	6.2	14.8	2,940	21.2	31.5	0.02
Average		339.3	27.8	16.4	4.8	11.4	2,703 *(1,910)	18.0	35.0	0.02

*pH Control

3.3.2 Relationship between pH and Nitrification Rate (Fig. 5)

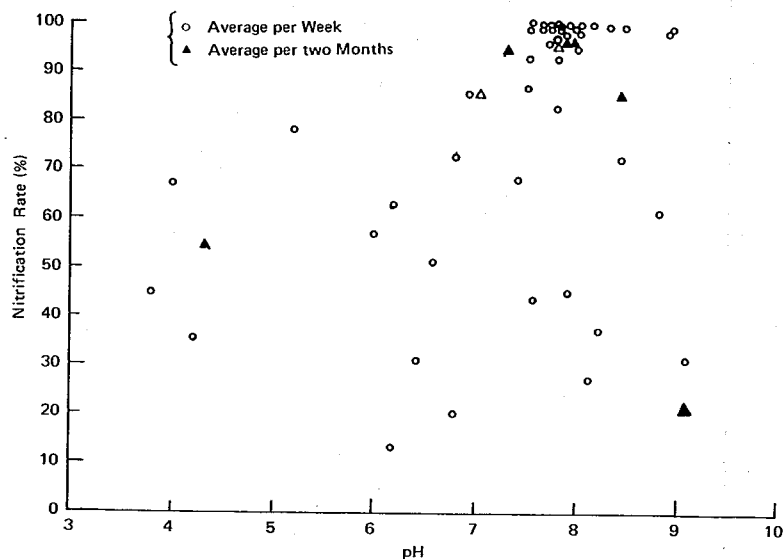
Optimal pH for nitrobacteria is known to be 8 ~ 8.5. As for the relationship between the nitrification rate and pH, opinions differ from researcher to researcher, though to a minor extent.

In one of the papers dealing with this subject, it is reported that a nitrification rate of more than 90% can be obtained within a pH range of 7 ~ 9, which was confirmed by the experiment conducted at the Public Works Research Institute.

During the present survey, a nitrification rate of more than 85% was observed within a pH range of 7 ~ 9 except in May, August and January. When pH was lower than 7, the highest nitrification rate observed was about 80%. For satisfactory op-

eration of the plant, therefore, it is advisable to maintain pH at about 7.5 ~ 8.

Fig.-5 Effect of pH on Nitrification Rate



3.3.3 Relationship between Water Temperature and Nitrification Rate (Fig. 6)

The effect of water temperature on the nitrification efficiency is not simply but influenced by the retention time of sludge in the treatment plant (SRT), so that simple comparison of the two is liable to produce a misleading conclusion.

In the case of this plant where SRT is very long, however, activated sludge maintains its activity of nitrification at a high level and pH remains constant after its control. As this makes it possible to regard that all environmental conditions excluding temperature are free from variation, the nitrification rate was compared with water temperature.

Before effecting pH control when the water temperature ranged from 8 to 13°C and pH was at a low level, the nitrification rate was subject to a large fluctuation, ranging from 13 to 86%.

After pH control, the nitrification rate recorded more than 90% except in May, August and January while the water temperature ranged from 8 to 25°C, indicating that the water temperature had practically nothing to do with the nitrification rate. Hence, the fluctuation of nitrification rate before pH control can be assigned not to the influences of water temperature but to the shortage of alkalinity. The survey also disclosed that the residual concentration of $\text{NH}_4\text{-N}$ held itself at less than 1 mg/l for the greater part of the year (Fig. 7).

Fig.6 Effect of Temperature on Nitrification Rate
('76. II ~ '77. III)

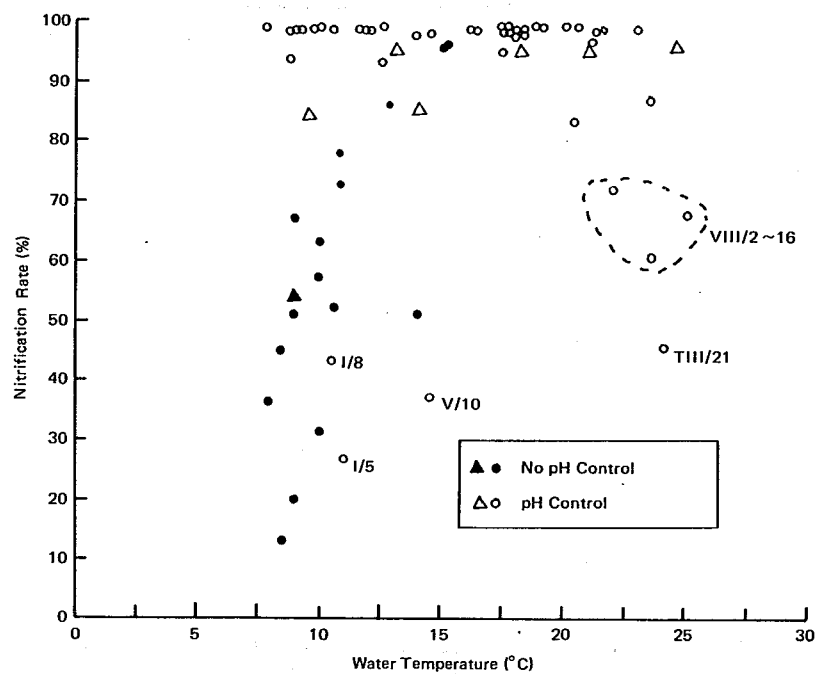
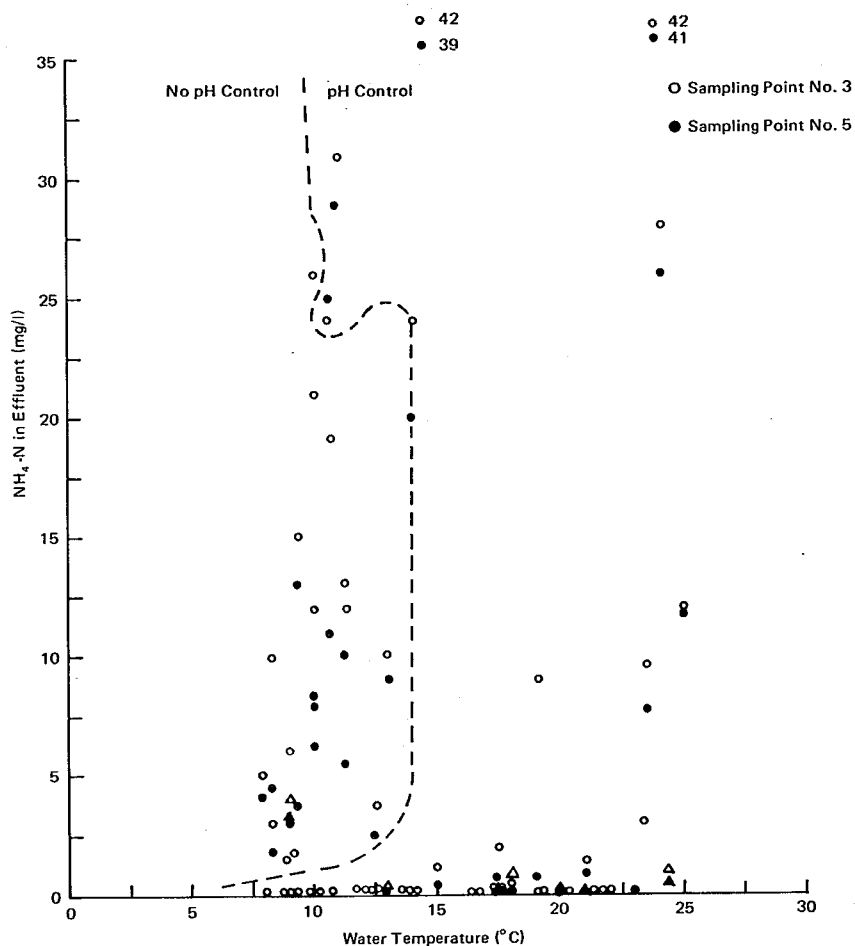


Fig.-7 Effect of Water Temperature on $\text{NH}_4\text{-N}$ in Effluent

3.3.4 Relationship between pH and Total Alkalinity, and Effect of Alkalinity on Nitrification Rate (Figs. 8 and 9)

The relationship between pH and alkalinity as disclosed by the survey indicates that, unlike the values obtained from the neutralization titration curve, pH changed only to a limited degree even when alkalinity presented heavy fluctuations. Specifically, pH maintained a level of about 7.5 ~ 9 when alkalinity ranged from 160 to 400, which indicates that overdose of NaOH will not exert any adverse influence on biological treatment process. As pH can be held at 7.5 ~ 8 if alkalinity of about 180 ~ 200 is present, it will be possible to save the chemical cost considerably by adding NaOH so as to maintain this alkalinity.

As for the effect of alkalinity on the nitrification rate, a high rate of nitrification can be ensured at an alkalinity of more than 160 as shown in Fig. 9.

It is to be noted, however, that if alkalinity declines below 100, pH could decrease and the nitrification rate also becomes instable.

Fig.-8 Relation between Alkalinity and pH

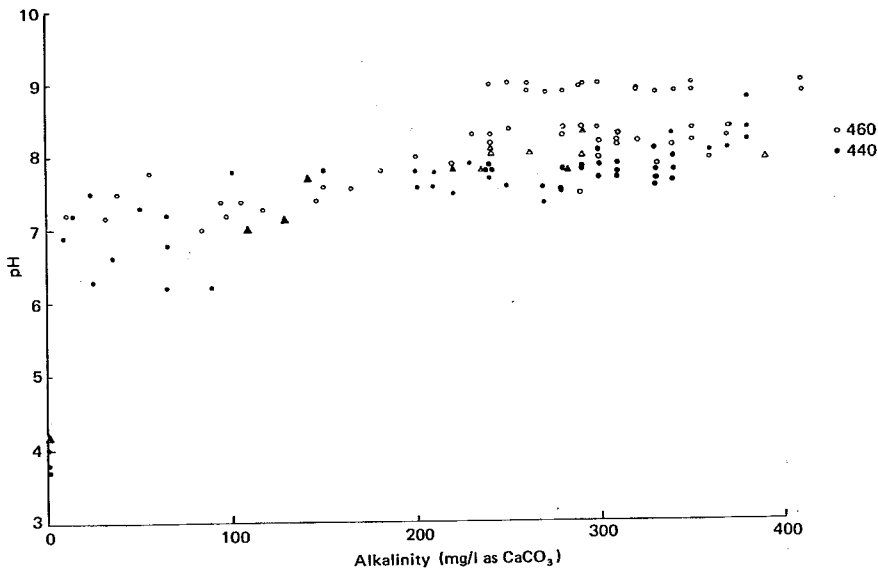
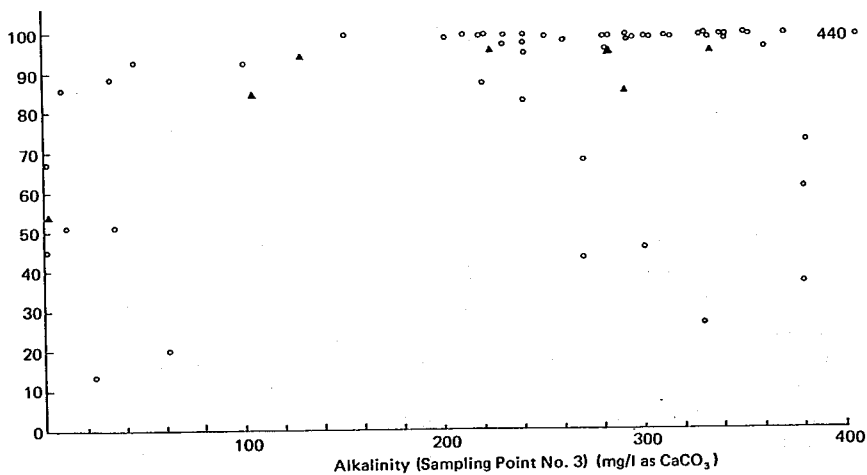


Fig.-9 Effect of Alkalinity on Nitrification Rate



3.3.5 Total Sludge Production

As sludge production data before pH control were limited and sludge formation was subject to a large fluctuation, the total sludge production in the plant was obtained by summing up the sludge volumes recorded from April 1976 to March 1977.

As can be seen in Fig. 10, sludge production through the year depicts two patterns. Specifically, the volume of sludge varies by temperature as shown below.

High temperature season — May ~ October:

(Water temperature — $15 \sim 20^{\circ}\text{C}$) SS — 4.3 kg/day

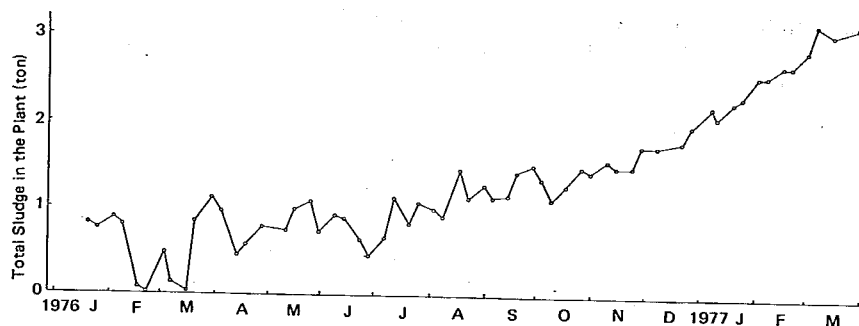
Low temperature season — November ~ April:

(Water temperature — $8 \sim 15^{\circ}\text{C}$) SS — 13.6 kg/day

The coefficient of correlation between sludge production and season was 0.6 for the high temperature season and 0.9 for the low temperature season. Sludge production in the low temperature season was about three times as large as that in the high temperature season.

The increase of MLSS in the aeration tank cannot be estimated with accuracy only on the basis of sludge production because the respiration and fauna of activated sludge works as a contributing factor. However, calculation was conducted on the basis of SS increase and tank capacity, which disclosed that the daily increment of MLSS is 12 mg/l in the high temperature season and 37 mg/l in the low temperature season. Hence, it can be concluded that the monthly increment of MLSS is about 400 mg/l in the high temperature season and about 1,000 mg/l in the low temperature season.

Fig-10 Seasonal Variation of Total Sludge



3.3.6 SRT

SRT is one of the important incentive factors to maintaining substantial nitrification of activated sludge process. It is generally accepted that the longer SRT, the higher the activity can be maintained.

Data of weekly survey indicates that SRT increased from about 45 days in March (before pH control) to 230 ~ 270 days in the May ~ September period, recording about 80 days in the subsequent low temperature season, which is long enough for the growth of nitrifying bacteria.

Month	Mar.	May	Jul.	Sept.	Nov.	Feb.
SRT (days)	45.7	272	255	227	79.3	80.4

$$\text{SRT} = \frac{\text{Total volume of activated sludge in the plant}}{\text{Discharged SS} + \text{Waste activated sludge}}$$

In order to maintain nitrification when the water temperature is about 10°C, more than 12 days of SRT is reported to be required. From the data given above, therefore, it can be concluded that year-round nitrification can be expected of the plant.

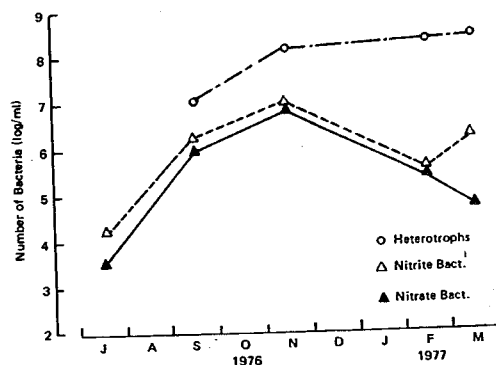
3.3.7 Micro Fauna

The fauna of activated sludge is composed of bacteria, Protozoa and Metazoa. Protozoa is classified into swim t., worm t. and fixed 6., the latter two dominating when activated sludge is in a condition favourable for their propagation. When extended aeration is carried out and sludge has high activity of nitrification, on the other hand, Metazoa and Euglypha of Protozoa prevail. Swim t. dominates when the organic matter loading is high or the water temperature is low.

The survey revealed that Euglypha, Vorticella, Litanotus and Rotifera were found relatively frequently through the year. It is known that Vorticella and Litanotus emerge in the normal activated sludge, and Euglypha and Rotifera when SRT is long (in extended aeration). In the aerobic digestion tank, it was found that Euglypha was dominant. The frequent occurrence of large numbers of Euglypha and Rotifera is indicative of the probability that SRT is longer than 20 days.

As for bacteria, those working for removal of organic matters (about 10^8 N/ml) and nitrobacteria (about $10^6 \sim 7$ N/ml) were identified, which suggests that the bacterial activity is maintained at a high level both for removal of organic matters and for nitrification (See Fig. 11).

Fig. 11 Seasonal Variation of Bacteria in Aeration Tank



Installation of filters is very important especially at a plant expecting nitrification. The flocs of activated sludge entrapped in the filter contained lots of microorganisms. Biological examination in November disclosed that these microorganisms included 73,000 N/ml of *Euglypha* and 18,000 N/ml of mastigopha, the concentration of the former being about twice as large as in the aeration tank and that of the latter about 18 times as large. About 10,000 N/ml of Rotifera was also entrapped, but the great majority was found dead. Other general bacteria and nitrobacteria were found alive in the flocs in a quantity of about $10^7 \sim 8$ N/ml.

Backwash waste contains a far less quantity of microorganisms than in the aeration tank as it is returned only about once in 48 hours, so that it may be contributing to the bacterial activity in the aeration tank only to a small degree. However, it is much more meaningful to return the backwash waste to the aeration tank than to discharge it outside the nitrification system because of its rich bacterial activity mentioned above.

3.3.8 Consumption of NaOH

NaOH consumption was estimated from the raw sewage flow, and from alkalinity, TKN and pH of influent.

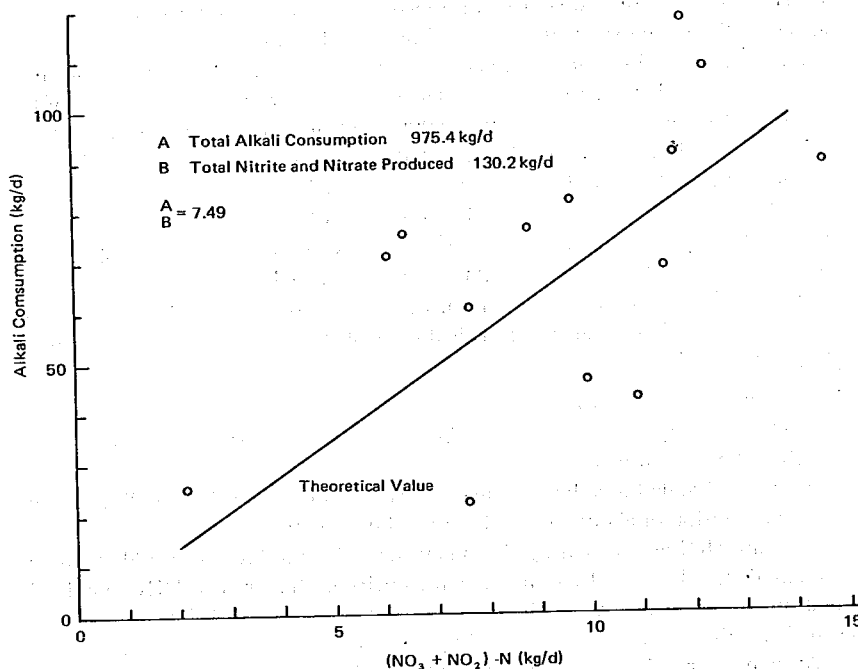
NaOH was added at a dosage rate of 170 ml/min of 25% solution. With a daily NaOH consumption of about 61 kg, pH was maintained at 8 ~ 8.5.

Influent TKN as revealed by the survey ranged from 7 to 16 kg-N/day, averaging 9.8 kg/day. The NaOH requirement for nitrifying this inflow TKN completely turned out to be 56 kg/day. As it was confirmed that nearly 100% of influent TKN was nitrified, the estimated dosage of 61 kg/day can be considered to be adequate.

After pH control was effected, secondary effluent presented a residual alkalinity of 100 ~ 390 as CaCO_3 mg/l. This points to the need for controlling NaOH dosage by checking the residual alkalinity in order to reduce overall NaOH consumption.

Although the optimal pH for the activity of nitrobacteria is 8 ~ 8.5, it is known that nitrifier in activated sludge exhibits the same high activity at pH 7 ~ 9. Hence, it is considered possible to maintain a high nitrification rate even if the plant is run with pH value held at 7.5 ~ 8.

Fig. 12 shows the relationship between $(\text{NO}_3 + \text{NO}_2)\text{-N}$ and alkali consumption. Oxidation of 1 mg of $\text{NH}_4\text{-N}$ calls for the input of 7.1 mg of alkali theoretically, but the actual alkali consumption is usually smaller than this theoretical value. In this case of the plant, however, alkali consumption of 7.5 mg.

Fig.-12 Relation between $(\text{NO}_3 + \text{NO}_2)\text{-N}$ and Alkali Consumption

3.3.9 Water Balance

In order to clarify the water balance at the plant, the monthly values of total tap water consumption, restaurant water consumption, dilution water volume, total reuse water volume and inflow volume were obtained to determine the average daily value for each, and the total reuse volume was divided into dilution water volume and final effluent volume by applying the mixing ratio of dilution water and inflow.

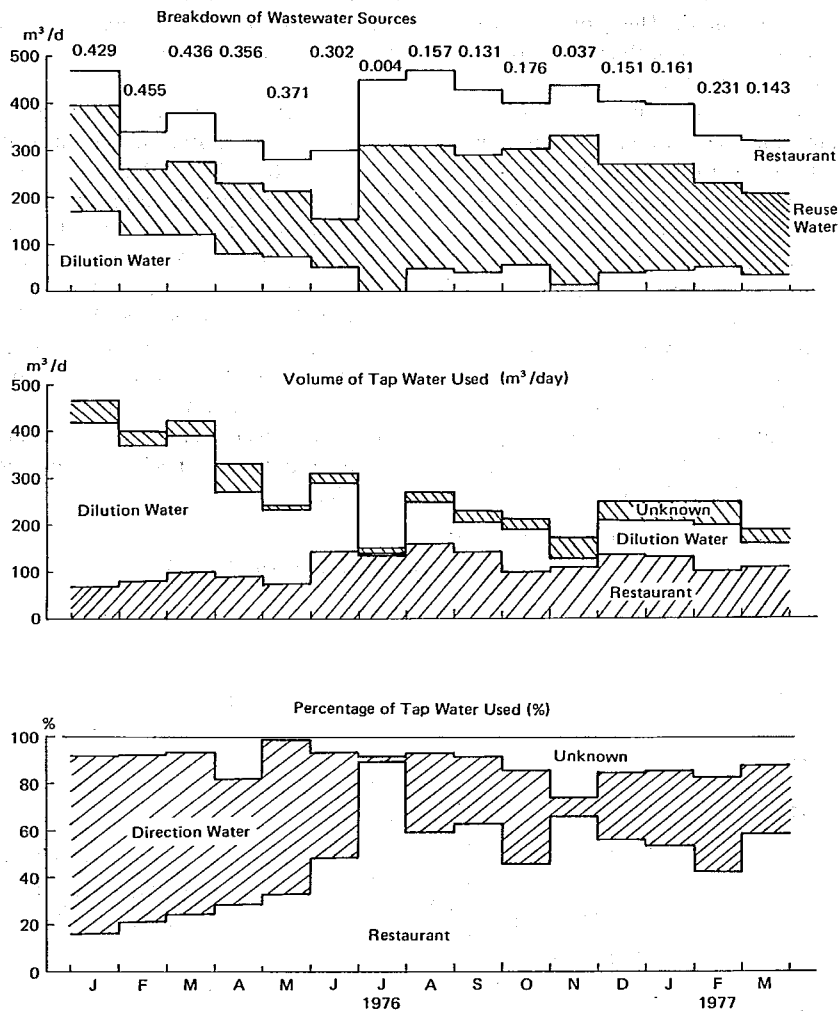
During the period from May to August, inflow ranged from $280 \text{ m}^3/\text{day}$ to $470 \text{ m}^3/\text{day}$. The maximum daily inflow, which is not confirmed yet, will have to be clarified by future studies as it is possible that inflow into the plant is influenced by daily inflow volume especially in August and January when the residual concentration of $\text{NH}_4\text{-N}$ records a high value.

Tap water consumption decreased after pH control was put in practice. This was due to the dwindled use of tap water for diluting final effluent to meet standard. Tap water consumption at the restaurant showed a slight upward trend during the survey period.

Fig. 13 shows the breakdown of influent. As seen in this figure, the inflow volume showed a tendency to decrease from January to June, increase in July, and drop again from August to March. From summer to autumn, the inflow was relatively large, registering about $400 \sim 450 \text{ m}^3/\text{day}$, which is likely to be ascribable to the increased inflow of reuse water.

The share of reuse water in the total inflow started rising from about July when the water quality was stabilized by pH control, and recorded about 60% from July to March, accompanied by the increased inflow of dilution water. This will give rise to augmented volume and concentration of various salts and nitrate in circulating effluent.

Fig.-13 Wastewater Mass Balance



3.3.10 Nitrate in Reuse Water and Influent

After effecting pH control, tap water consumption for diluting effluent declined because the effluent transparency increased to more than 100 and its $\text{NH}_4\text{-N}$ concentration became as low as less than 1 mg/l. As a consequence, effluent reuse rate became higher, with the result that $\text{NO}_3\text{-N}$ concentration showed a tendency to increase both in influent and effluent. Specifically, $\text{NO}_3\text{-N}$ concentration in final effluent which was in the neighbourhood of 22 mg/l before pH control increased to 40 ~ 100 mg/l. This growing tendency of nitrate nitrogen concentration will pose itself as a serious problem if restriction is placed on total nitrogen concentration at some future date.

Fig. 14 shows the relationship between $\text{NO}_3\text{-N}$ flowing into the plant in reuse water and that carried in the inflow sewage. $\text{NO}_3\text{-N}$ concentration in the influent kept on rising from June to November, and it is likely that this tendency will continue in future. The concentration dropped in December but the reason for this is not known. The concentration in reuse water is far higher than that in influent. The shaded section in Fig. 14 indicates the unknown portion. Assuming that this section represents the portion denitrified between the reuse water inlet and the balancing tank outlet, calculation of the denitrification rate produces the results shown in Fig. 15 which indicates about 50% denitrification rate for the period from April to September and 30 ~ 40% rate from October to December. The figure shows that denitrification did not take place only for a few months in winter.

While the location of the exact denitrifying point calls for another survey, it is possible that denitrification has taken place in the inflow pit. This in turn calls for further studies to be made to clarify the $\text{NH}_3\text{-N}$ balance.

Fig.-14 Change in Nitrate and Nitrite
(Influent Nitrogen vs. Renovated Water Nitrogen)

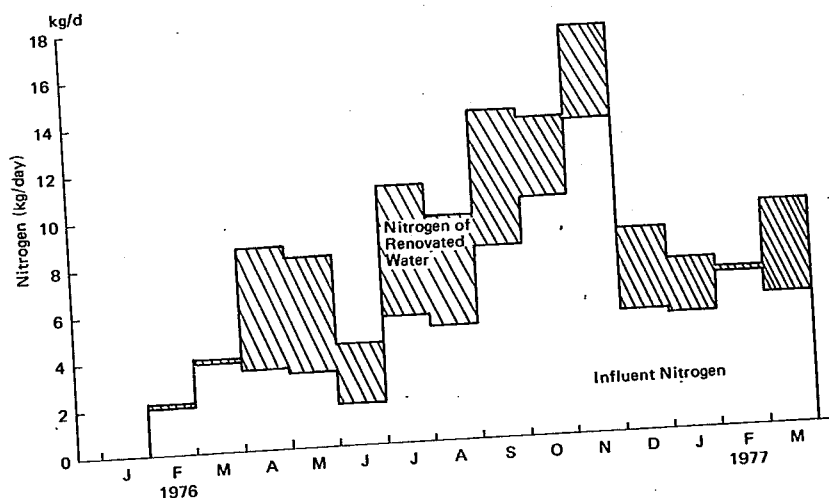
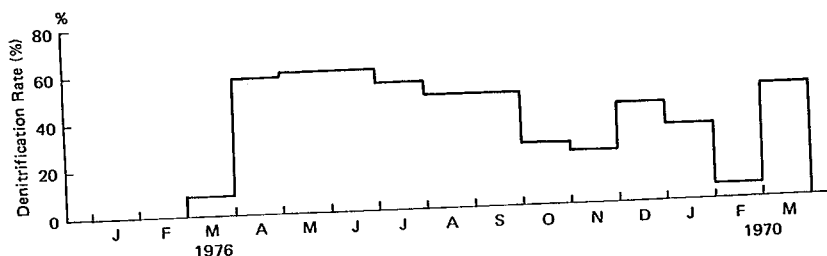


Fig.-15 Denitrification Rate



4. SUMMARY

By conducting pH control at the plant, the following facts were made clear.

- 1) Flushing water for water closet can be supplied without diluting effluent with tap water.
- 2) Nearly 100% nitrification rate can be maintained through the year. According to the weekly survey, however, a high ammonia concentration was detected due to retarded nitrification in May, August and January when the service area is utilized by many people. It may become necessary to resume the operation of nitrification tanks depending on the cause of this high residual ammonia concentration which needs to be cleared up by another survey.
- 3) Daily sludge production is estimated to be 10 ~ 40 mg/l. Since the plant is provided with a filters, frequent sludge with drawal is not considered essential. Further, the long SRT will make it possible to hold the nitrification activity at a high level through the year.
- 4) NaOH Consumption
NaOH was dosed at a rate of 61 kg/day with pH held at 8 ~ 8.5. This dosage proved to be generally acceptable because the calculation worked out on the basis of the weekly 24-hour survey produced a dosage of 56 kg/day. Considering the activity of nitrobacteria in activated sludge, it will be possible to run the plant with pH value held at 7.5 ~ 8.
- 5) Nitrogen concentration in the effluent increased as a result of the augmented share of reuse water in the total inflow (more than 50%) and attainment of 100% nitrification rate. It will therefore be found necessary to incorporate denitrification at a future date.

CHAPTER 2
THE PREVENTION OF FORMATION AND REMOVAL OF
CHLORINATED ORGANICS IN WASTEWATER

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CHAPTER 2

THE PREVENTION OF FORMATION AND REMOVAL OF CHLORINATED ORGANICS IN WASTEWATER

1. INTRODUCTION

Since chlorinated organics such as chloroform had been detected in tap water and was suspected to be relevant to be carcinogenic, extraordinary attention has been paid to chlorinated organics centering on trihalomethane. Chloroform is known to be a product of reaction between chlorine and precursors, and the uncovering of the identity of precursors seems to be magnetizing the attention of those concerned. Chlorinated organics are giving rise to many concerns related to water treatment. And these problems are considered relevant to wastewater treatment as follows:

- 1) Chlorination disinfection is also introduced in wastewater treatment.
- 2) As some water treatment plants are located in the lower reaches of a wastewater treatment plant, there are possibilities of wastewater effluents being reused. In this case, there should be a possibility of precursors being contained in the wastewater effluent.
- 3) The breakpoint chlorination of sewage has something to do with the production of chlorinated organics.

This report deals with the above mentioned problems with special emphasis placed on 3). The breakpoint chlorination process is one of the processes of removing ammonia nitrogen, and the process is presently being experimented by the Public Works Research Institute, Ministry of Construction at a pilot plant in the Toba Sewage Treatment Plant in Kyoto. The pilot plant is equipped with an automatic control unit to control the ratio between ammonium and chlorine, and carbon column to remove residual chlorine. With the use of the automatic control unit, over 90 percent of ammonia nitrogen removal has been achieved. However, as there remained a certain amount of organics in the wastewater effluent, it was suspected that the dosed chlorine reacted with such organics to produce chlorinated organics.

2. REACTION OF CHLORINE AND ORGANICS

2.1 IDENTIFICATION OF CHLORINATED ORGANICS

As the breakpoint chlorination process requires dosing of a large amount of chlorine, the production of chlorinated organics was anticipated. The identification of chlorinated organics was conducted by employing a Gas-Chromatograph Mass-Spectrometer (GC-MS). The identified compounds in the breakpoint chlorination effluents are listed as follows:

carbon tetrachloride, trichloromethane (chloroform), trichloroethylene, tetrachloroethylene, dibromomethane, dibromochloromethane; tribromomethane (bromoform), m-p-dichlorobenzene, o-dichlorobenzene, 1,2,4-trichlorobenzene and 1,2,3-trichlorobenzene.

2.2 REACTION OF CHLORINE AND NITROGEN-CONTAINING COMPOUNDS

Besides ammonia nitrogen, there are other nitrogen-containing organic compounds that consume chlorine in wastewater.

Although nitrogen-containing organic compounds or organic nitrogens are found in low concentration in the secondary effluent, they are discovered in the primary effluent at a ratio of about 1 : 1 with ammonia nitrogen. When primary effluent is to be discharged after chlorination, there is a possibility that nitrogen-containing organic compounds react with chlorine to produce organic chloramine.

In Fig. 1, sodium hypochlorite (NaOCl) was added to eight different nitrogen-containing compounds to draw chlorine dissipation curves. The compounds selected were:

aniline and cadaverine dihydrochloride as amine, N-1 naphthylacetamide and thymidine as amide, 4-aminoazobenzene as azo, histidine and tyrosine as amino-acid, and humic acid.

Fig-1 Chlorine Dissipation Curve of Nitrogenous Compounds

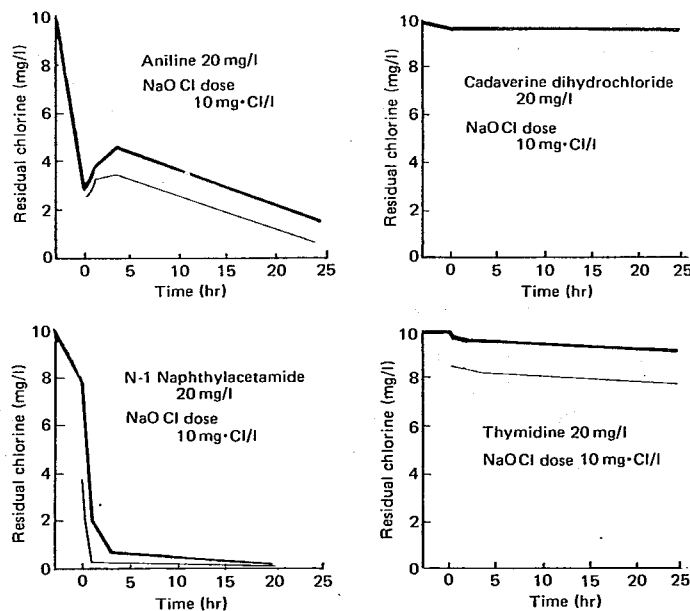
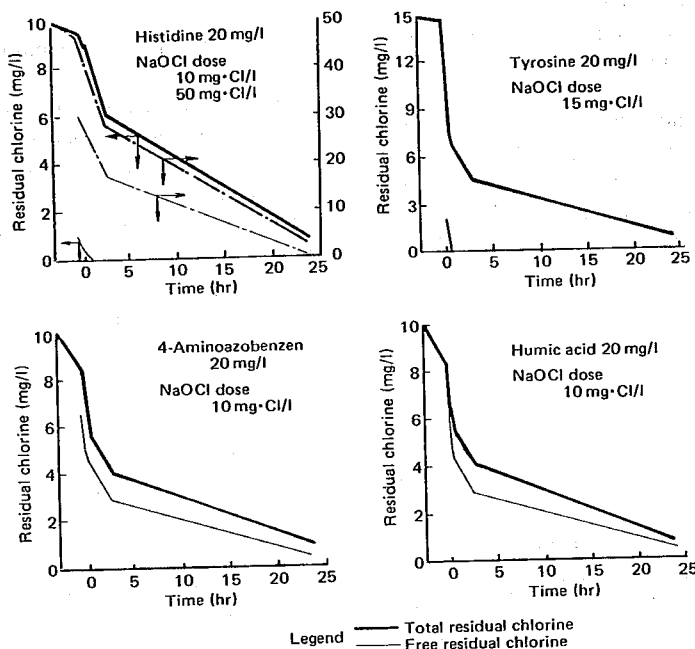


Fig-1 (Continued)



The measurement of chlorine was based on the DPD method. The difference between the thick line and the thin line in Fig. 1 is the amount of organic chloramine formed. Organic chloramine is composed of cadaverine dihydrochloride, histidine and tyrosine. With the reaction time, the residual chlorine in histidine and tyrosine decreased and was considered to partly have changed into aldehyde. Thymidine consumed little chlorine. Aniline, N-1 naphthylacetamide, 4-aminoazobenzene and humic acid produce little organic chloramine. As these compounds have the property of aromaticity, there may be substitution reaction occurred with these compounds and chlorine. The products of reaction between aniline and chlorine have partly become clear by using the GC-MS. When 10 mg·Cl/l of sodium hypochlorite was added to 20 mg/l of aniline solution, three substitution products of O-chloroaniline, m·p-chloroaniline and 2,4-dichloroaniline and non-reacted aniline were identified. The ratio of each compound was: O-chloroaniline 2.8%, m·p-chloroaniline 1.9%, 2,4-dichloroaniline 0.5% and non-reacted aniline 47.4%. All these total 52.6%. However, it was not possible to identify the remaining 47.4%.

Also, chloroform was measured in the solutions of the above mentioned compounds 24 hours after addition of chlorine. Namely, 15 μ g/l of chloroform was detected in 4-aminoazobenzene solution and 60 μ g/l in humic acid solution. Humic

acid is known as a precursor in producing chloroform. Chloroform was not detected from other compounds.

Although the reactivity of chlorine and nitrogen-containing compounds was high, the reaction velocity was comparatively slow.

Primary effluent contained ammonia nitrogen or nitrogen-containing organic compounds. It is known that the reaction velocity between ammonia nitrogen and chlorine is fast. Accordingly, when chlorine is dosed to the primary effluent, it is considered that the chlorine first reacts with ammonia nitrogen and produces inorganic chloramine. When compared with chlorine, chloramine is reported to be inferior in reactivity. Also as chlorine dose on a disinfection level is only a few mg Cl/l, free chlorine of high reactivity was hardly detected. From the above reasons, it was concluded that chlorine dosing on a disinfection level rarely produce chlorinated organics and organic chloramine.

3. FORMATION OF CHLORINATED ORGANICS

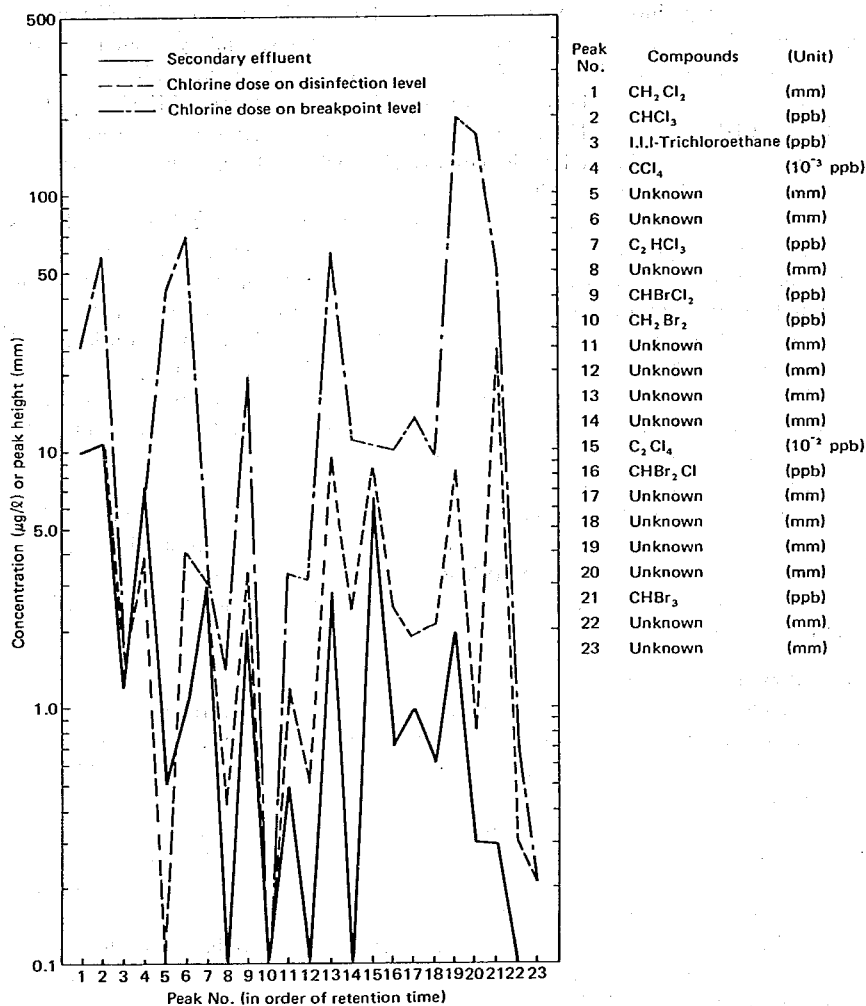
The formation of chlorinated organics is reported to be subjected to chlorine dose rate, reaction time, pH and temperature. In this study, effects of chlorine dose rate and reaction time was determined.

3-1 CHLORINE DOSE RATE

Tests were conducted to determine to what extent chlorinated organics were formed by the dosing rate of chlorine on a disinfection level and on a breakpoint level. The rate of chlorine dose on a disinfection level was 5 mg·Cl/l and on a breakpoint level between 100 and 200 mg·Cl/l. The reaction time was about 1 hour. The wastewater were collected from five wastewater treatment plants in Tokyo and her neighborhood. Analysis were conducted by employing GC equipped with ECD on compounds with a low boiling point such as chloroform, etc.

Fig. 2 shows the results of tests for the secondary effluent. Totally there were 23 different peaks detected, although not all the secondary effluent samples were responsible for the 23 peaks. The average number of peaks in the secondary effluent itself was 9.9. When chlorination was conducted on the secondary effluent on both the disinfection and breakpoint levels, respectively, each recorded an average of 12.5 peaks.

Fig.-2 The Effect of Chlorine Dose on Secondary Effluents



When comparing the secondary effluent and the disinfected effluent, except for peaks No. 13, 19 and 21, no marked differences were confirmed. The reason why No. 21 marked a great difference was perhaps due to the large value of 65 $\mu\text{g/l}$ detected in the effluent of one sewage treatment plant. This sewage treatment plant is located on a coastal line where its influent contained more than 2,000 mg/l of chloride ion concentration due to the intrusion of sea water. Therefore, as the bromide ion concentration was higher than in ordinary wastewater, it was considered to have resulted in the more formation of bromide compounds. This, on the other hand, indicates if bromide ion exists, the reactivity between chlorine and

organics becomes higher.

When dosing chlorine on a breakpoint level, it has shown a drastic difference in the height of the peaks when compared with those of the secondary effluent. Those distinct differences were in peaks No. 1, No. 2, No. 5, No. 6, No. 9, Nos. 12 ~ 14, and Nos. 16 ~ 21. Of these, the compounds identified were CH_2Cl_2 , CHCl_3 , CHBrCl_2 , CHBr_2Cl , and CHBr_3 . Although confirmed existing in the wastewater, the compounds that inevitably do not associate with chlorination are CH_3CCl_3 , CCl_4 , C_2HCl_3 , CH_2Br_2 and C_2Cl_4 .

ECD is a detector which has a peculiar sensitivity to halogenide. Also ECD's sensitivity differs greatly according to the types of compounds. By ignoring the differing sensitivity of ECD, chlorinated organics formed on both the disinfection level and the breakpoint level based on the secondary effluent were estimated from the heights of peaks. As a result, it was 1.69 times on the disinfection level and 14.8 times on the breakpoint level of the secondary effluent respectively.

In case of the primary effluent, when similar assumptions were made, it resulted in the same tendency. The results were 1.18 times on the disinfection level and 16.6 times on the breakpoint level of the primary effluent respectively.

From these results, when chlorine is dosed on a breakpoint level to the wastewater, although each chemical compounds is not identified, it has become obvious that a variety of chlorinated organics are formed in short time. Of all the identified compounds, the concentration of trihalomethane was the highest. And, if the reaction time is further lengthened, it is assumed that the concentration of trihalomethane will increase.

3.2 REACTION TIME

A large amount of chlorine is dosed to remove ammonia nitrogen by the breakpoint chlorination process. But as the breakpoint being the border, the forms of the residual chlorine differ. Inorganic chloramine exists before the breakpoint while free chloramine and free chlorine little exist. To obtain the above three conditions, chlorine was dosed to the secondary effluent. After chlorine dosing, analysis of chloroform formed were conducted at the first hour and at the 24th hour. The chloroform concentration at pre-breakpoint, breakpoint and post-breakpoint changed from 12 to 14, 39 to 43, and 88 to 260 $\mu\text{g/l}$, respectively. However, before the breakpoint and at the breakpoint, there were no marked changes in the chloroform concentration even after 24 hours. In the post-breakpoint condition, or in a condition when free chlorine exists, the chloroform concentration increased by three times with the reaction time. This indicates the fact that the secondary effluent contains a good amount of precursors that have potential to form chloroform.

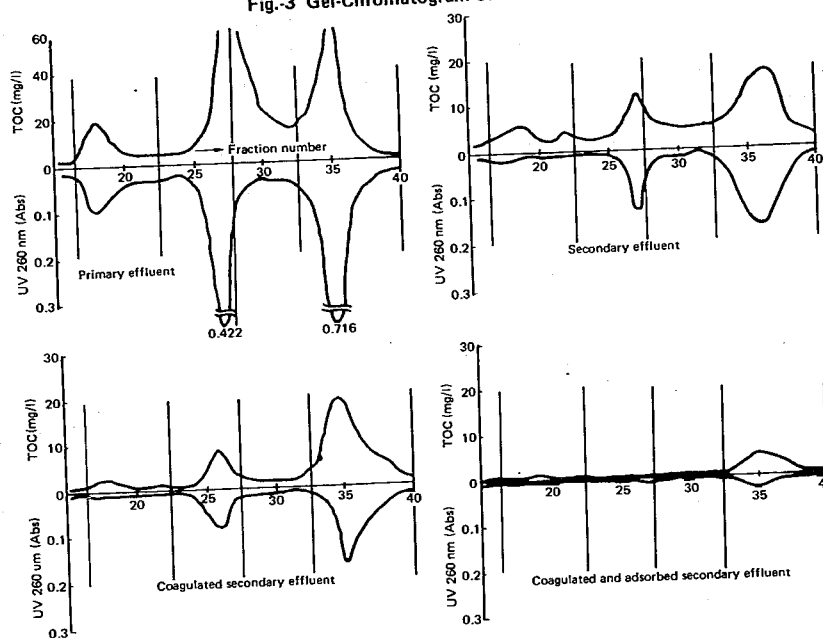
4. REMOVAL AND PREVENTION OF CHLORINATED ORGANICS FORMATION

4.1 REMOVAL OF PRECURSORS

4.1.1 Laboratory Tests

Gel filtration chromatography (GFC) is one type of liquid chromatography and is used as a means to evaluate the removal effects of soluble organics. Fig. 3 shows the gel chromatograms of the primary effluent, the secondary effluent, the coagulated secondary effluent and the coagulated and carbon adsorbed secondary effluent.

Fig. 3 Gel-Chromatogram of Wastewater



The gel conditions are as listed below:

gel bed	Sephadex G-15
developer	H ₂ O
fraction volume	10 ml

The sample used for gel filtration chromatography was filtered by the milipore filter of 0.45μ and then condensed to 20 times by a rotary evaporator. Concentrated organics were separated by gel filtration chromatography after the condensed solution was filtered by 0.45μ filter. The loss of soluble organics by gel filtration chromatography was about 50 percent, and the recovery rate of soluble organics by gel filtration chromatography was over 90 percent.

From the gel filtration chromatography, the soluble organics are divided into four groups: Group I is composed of organics of over 1,500 molecular weight, Group II is consisted of organics with 260 nm adsorbance, Group III was organized

by organics with no 260 nm adsorbance, and Group IV was made up of organics colored brown with 260 nm adsorbance.

When studying the gel filtration chromatography, the secondary effluent of the activated sludge treatment is generally low in TOC when compared with the primary effluent, and shows that activated sludge process is effective in removing the organics in Group III. When secondary effluent underwent a chemical precipitation process, organics in Group I were removed and those in Group II and Group III remained. However, when carbon adsorption is conducted, only a negligible amount of organics of Group IV was detected.

Table 1 shows the studies made on the chloroform formation in each group dosing chlorine to the samples divided into four at the gel filtration chromatography. The amount of chlorine dosed was about 10 mg Cl/l. The reaction time was about one hour, and sodium sulfite was dosed to stop reaction. From Table 1, the following facts become clear:

Table-1 Chloroform Formation by Chlorination

	Not Chlorinated ($\mu\text{g/l}$)	Chlorinated ($\mu\text{g/l}$)	GFC Fraction (%)				
			Group I	Group II	Group III	Group IV	Total
Primary effluent	7.8 (40.6)	61.4	10.2	15.7	8.2	27.3	61.4
Secondary effluent	3.7 (14.8)	48.6	6.4	8.7	6.8	26.7	48.6
Coagulated* secondary effluent	1.8 (13.4)	39.5	3.0	9.9	6.3	20.3	39.5
Coagulated and adsorbed secondary effluent**	0.8 (7.7)	4.4	1.3	1.3	0	1.8	4.4

() Soluble TOC, mg/l

* Coagulant Alum, mole ratio Al/p = 3

** Coagulant Alum, mole ratio Al/p = 3
activated carbon Colgon Firtasorb 300, SV = 5

- 1) When comparing the primary effluent and the secondary effluent, despite the TOC removal being 67 percent, the chloroform concentration only dropped by about 20 percent. Therefore, the removal of precursors can not be expected in the activated sludge treatment.
- 2) When comparing the secondary effluent and the coagulated secondary effluent, the chloroform concentration has dropped by 18.7 percent. Then, the coagulation process can not be considered that effective in removing precursors.
- 3) Carbon adsorption was most effective in the removal of precursors.
- 4) Group IV was brown in color and was considered to be formed by compounds resembling humic acid or fulvic acid. Of the chloroform formed in the primary effluent, the secondary effluent and the coagulated secondary effluent,

chloroform belonging to Group IV occupied nearly half.

- 5) Group II and Group IV organics with UV 260 nm adsorption produced a significant amount of chloroform. In the primary effluent, the chloroform produced by organics in Group II and Group IV accounted for nearly 70 percent of the total. Similarly, in the secondary effluent, they accounted for about 73% and in the coagulated secondary effluent about 76%.

4.1.2 Pilot Plant Tests

As shown in Table-1, activated carbon is quite effective in removing precursors.

As the pilot plant in Kyoto, studies on carbon capacity were made by feeding the effluent of the breakpoint chlorination process on the filtered secondary effluent and the filtered-adsorbed secondary effluent. As the test periods and the operation conditions of the carbon columns for both effluents differed, accurate comparison was not possible. The following shows the results of the tests:

Chloroform Concentration after Breakpoint Chlorination ($\mu\text{g}/\ell$)

Influents of BPC process	average	range
filtered	36.2	11.9 ~ 80.5
filtered-carbon adsorbed	29.7	9.3 ~ 63.8

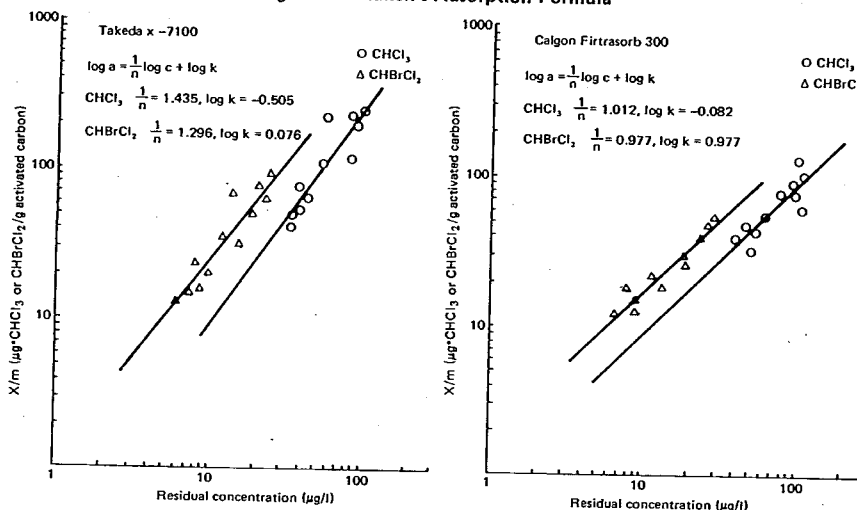
Studies of the results reveal that the residual chloroform concentration only dropped by 18 percent in the filtered-adsorbed secondary effluent compared with the filtered secondary effluent. At the pilot plant, the contact time of the carbon column was 36 minutes in a six-month continuous operation, and reactivation was conducted on once per six month basis. Accordingly, in this condition, the precursors in the wastewater within six month period seem to have broken through.

4.2 REMOVAL OF CHLORINATED ORGANICS

Fig. 4 shows the Freundlich's adsorption formula employing activated carbon of granulated Takeda X-7100 and Calgon Firtrasorb 300. The initial concentrations of chloroform and bromodichloromethane were set at 119 and 32 $\mu\text{g}/\ell$, respectively. The temperature was between 24 and 25° centigrade.

From the Fig. 4, the following became clear:

Fig.4 Freundlich's Adsorption Formula



- 1) Bromodichloromethane is adsorbed more easily than chloroform.
- 2) The adsorption capacity differed a little according to the types of activated carbon. But the chloroform per 1 gram of activated carbon or the adsorption capacity of bromodichloromethane (x/m) at the most was $100\mu\text{g}$ order.

At the Kyoto pilot plant, to remove the chloroform formed by the breakpoint chlorination process, tests were conducted by employing Takeda X-7000. The apparent contact time was 20.7 minutes. From the first week to the fourth week, the average removal rate of chloroform for each week was 80.0, 55.9, 53.9 and 40.4%, respectively. The chloroform adsorbed in the activated carbon during the operation in the 4th week was $54.8\mu\text{g}\cdot\text{CHCl}_3/\text{g}$. Accordingly, the chloroform adsorbed by the activated carbon was very small, thus removal of chloroform by activated carbon can not be highly expected.

The detected dichlorobenzene and trichlorobenzene in the effluents at the Kyoto plant were as follows:

Concentration ($\mu\text{g}/\ell$)				
	m·p-DCB	O-DCB	1,2,4-TCB	1,2,3-TCB
Chlorination	2.2	3.2	0.48	0.45
Chlorinated-adsorbed	0.11	0.51	0.70	0.02

The concentrations of dichlorobenzene and trichlorobenzene were both $\mu\text{g}/\ell$ order. And except for 1,2,4-TCB, it was considered that these compounds were comparatively easily adsorbed into the activated carbon.

5. SUMMARY

The chlorinated organics formed by the wastewater breakpoint chlorination process was low in concentration and various. Although the identified compounds were limited in number, of those identified trihalomethane (chloroform, bromodichloromethane, dibromochloromethane and bromoform) had comparatively high concentration.

To prevent the formation of trihalomethane in high concentration in the process of breakpoint chlorination, the following can be recommended:

- 1) Conduct carbon adsorption prior to chlorine dosing to remove precursors.
- 2) The rate of chlorine dosing should not exceed the breakpoint.
- 3) To shorten as possible the reaction time of chlorine and organics. The residual chlorine should readily be removed.

It is most effective to adsorb by granular activated carbon to remove precursors of trihalomethane. However, a long lasting effect of granular activated carbon can not be expected. According to the gel filtration chromatography method, it was anticipated that the organics with UV 260 nm adsorbance made up the precursors.

Chlorination on a disinfection level presented no special problems with regards chlorinated organics although there was possibility of bromine compound formation when the bromide ion concentration was high in the wastewater.

CHAPTER 3
PILOT PLANT STUDY OF TANNARY WASTE TREATMENT
BY OXYGEN ACTIVATED SLUDGE PROCESS

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3. Application of Oxygen Activated Sludge Process for Tannary Waste Treatment	102
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CHAPTER 3

PILOT PLANT STUDY OF TANNARY WASTE TREATMENT BY OXYGEN ACTIVATED SLUDGE PROCESS

1. INTRODUCTION

From old days in Hyogo Prefecture, centering Himeji city, a large number of tanneries have clustered around specific areas. A total of 9 such tannery communities are found in the prefecture in Himeji City, Kawanishi city, Tatsuno city and Taishi town. In Himeji city, there are the Takagi area, Shigo and Gochaku areas, Kawanishi area, Fukui area and Jippo area with 234, 99, 37, 20 and 9 tanneries respectively.

From early days, Himeji was noted for its production of 'Himeji Leather', a white leather finished by its unique tanning process. However, with the passing of time, vegetable tanning was introduced and also chromic tanning. And today, the majority of tanneries employ the vegetable-chromic tanning.

The majority of the tanneries are either small-sized enterprises or privately-run plants. The average number of workers at an enterprise level is 32.6 and 5.6 at a privately run level. Owing to the fact that it is privately-run plant galore in the city, the average number of workers of all plants in Himeji is as low as 7.5.

The manufacturing process of tanneries in Hyogo prefecture including Himeji city can be divided as follows: (a) preparing, (b) tanning, and (c) finishing. Fig. 1.1 shows the process in detail. Tanneries use a great amount of industrial water and about 70 percent of the water consumed is used up at the preparing stage. Table 1.1 shows the amount of water used at a chromic tannery plant processing about 30 kilograms of raw leather (said capacity), and also the wastewater quality and organic and other pollutant loads. Waste from chromic tanneries contains a large amount of suspended solids, organic matters and tri-valent chromium.

Fig.-1.1 Manufacturing Flow-chart of Chromic Tannery

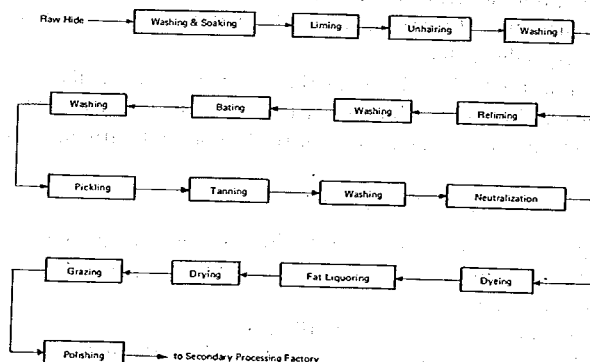


**Table-1.1 Composition of Waste Water from Chromic Tannery held
300 kg Raw Hide Treatment Capacity**

Items	Processing	Washing & Soaking		Liming & Un- hairing	Washing		Retliming	Washing	Bating	Washing	Pickling	Chromic Tanning
		Pre- para- tion	Main Waste		1st & 2nd Washing	3rd Washing						
Weight of Hide	(kg)	330	—	—	—	270	—	—	—	—	—	—
Water Consumption	(t)	1,650	1,650	1,650	3,300	1,350	1,350	4,450	810	4,450	270	270
Wastewater Discharged	(t)	1,530	1,620	1,610	3,260	1,320	1,330	4,500	800	4,410	320	260
pH		6.3	7.1	12.6	12.4	12.3	12.7	12.5	9.3	8.9	3.0	3.3
Total Solids	(mg/l)	49,710	12,420	25,708	3,873	2,364	5,687	817	3,882	572	54,193	68,503
Dissolved Solids	(mg/l)	47,550	12,070	22,960	3,549	2,057	4,980	638	3,172	520	53,953	68,443
Suspended Solids	(mg/l)	2,515	350	2,748	324	307	707	179	710	52	240	60
Ash	(mg/l)	46,960	11,928	15,300	1,343	1,451	2,714	419	2,447	287	50,280	52,003
Ignition Loss	(mg/l)	2,750	493	10,408	1,530	913	2,973	398	1,435	285	3,913	16,500
Total Nitrogen	(mg/l)	552	111	1,670	179	132	204	38	760	73	191	75
Dissolved Total Nitrogen	(mg/l)	403	83	1,554	164	116	182	19	712	69	183	67
Chloride	(mg/l)	26,709	4,628	2,422	843	592	628	135	771	188	20,824	9,903
Iodine Consumption	(mg/l)	43	14	3,184	232	54	405	34	16	—	2	—
Calcium	(mg/l)	70	38	2,470	396	221	1,445	160	243	52	731	157
CODMn	(mg/l)	8,881	890	13,007	1,309	1,148	2,162	201	419	27	1,866	3,899
Cr ₂ O ₃	(mg/l)	—	—	—	—	—	—	—	—	—	—	7,071

Each city having such groups of tanneries within its administrative area in Hyogo Prefecture has already constructed pre-treatment facility and is exerting efforts to treat waste by sedimentation. This pretreatment facility, in most cases, is composed of grit chamber, screens (coarse and fine screens), pumps (screw pump), sedimentation tanks provided with track-mounted sludge scraper (some with flocculation basins), sludge thickeners, sludge heat treatment units (heating the sludge between 90 and 100 degrees centigrade to denature the protein contents and to facilitate dehydration), vacuum filters and deodorization installation to remove odor.

The industrial waste from tanneries is conveyed to the pre-treatment facility via covered concrete rectangular sewers or concrete pipes by gravity. Therefore, it is necessary to prevent organic solids from depositing as possible in the sewers. And to do this, a rotary fine screen is installed in each factory to receive screened effluent into the sewer.

The existing pre-treatment facilities were designed to remove about 70 percent of suspended solids, but in future further studies will be made to increase the design removal rate of suspended solids.

The sedimentation tank effluent of the pre-treatment facility contains 600 — 800 mg/l of BOD, therefore a biological treatment is envisaged. This study was conducted to determine its design criteria of the biological treatment facilities.

2. STUDIES CONDUCTED IN THE PAST

Several experiments were conducted in the past concerning biological treatment of tannery wastes in Himeji city on laboratory scale and pilot plant scale. Results are summarized as follows;

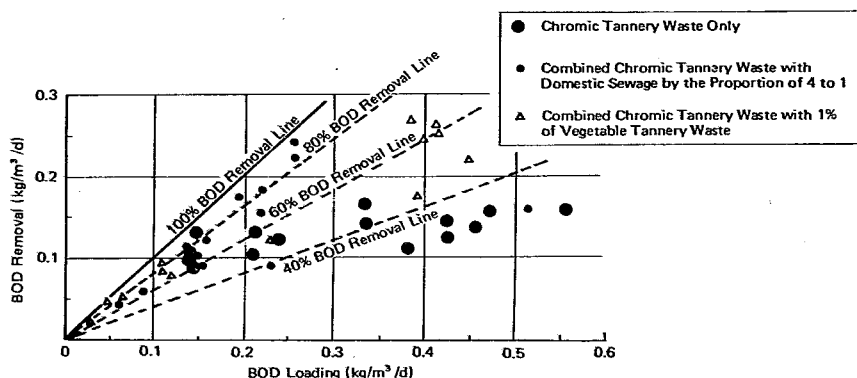
(1) The experiment of low-rate trickling filter process

This experiment was conducted in 1968 — 69 at the Public Works Research Institute of the Ministry of Construction. The experiment was conducted in a

constant temperature room of 20°C by using a specially prepared laboratory scale trickling filter apparatus. The influent used in the experiment was (i) chromic tannery waste only, (ii) mixture of chromic tannery waste and domestic sewage at a ratio of 4:1, and (iii) mixture of chromic tannery waste and 1 percent vegetable tannery wastewater.

With regards experiment results, although the pH of the influent changed on the alkali side between 9 and 12, the pH of the effluent was stable between 8 and 8.5 indicating the existence of a strong buffer action. In other words, it became obvious that the treatment was possible without any pH control. The BOD removal against BOD Load and the removed BOD are as shown in Fig. 2.1. The BOD removal when the BOD Load was below 0.05 kg/m³.d and when below 0.1 kg/m³.d was over 80 percent and between 70 and 80 percent, respectively. However, in the experiment using chromic tannery waste only as influent, the BOD removal did not exceed 0.15kg/m³.d. The experiment for mixing chromic tannery waste and domestic sewage, have shown the most stable treatment results.

Fig.-2.1 BOD Loading vs. BOD Removal at the Laboratory Test of Low-rate Trickling Filter



(2) Aerated Lagoon Experiment

This experiment was conducted at the same time with the above mentioned low-rate trickling filter process at the Public Works Research Institute. The influent used in the experiment was the same as those used in the low-rate trickling filter process except for increasing the mixing rate from 1 percent to 5 percent of vegetable tannery waste.

The aerated lagoon test on a laboratory scale was conducted in the constant temperature room at 10°, 20° and 30° centigrades, respectively. The experiment results as shown in Fig. 2.2 have shown that the BOD removal was greatly affected by changes in temperature, and, that the BOD removal dropped markedly in low water temperatures. Also in the experiment using influent mixed with chromic tannery waste and domestic sewage, as shown in Fig. 2.3, the best treatment results were obtained.

Fig.-2.2 Detention Time vs. Remaining BOD at the Laboratory Test of Aerated Lagoon (Chromic Tannery Waste Only)

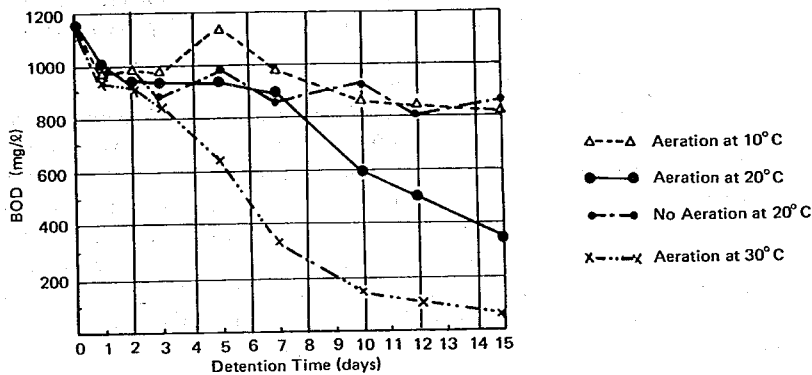
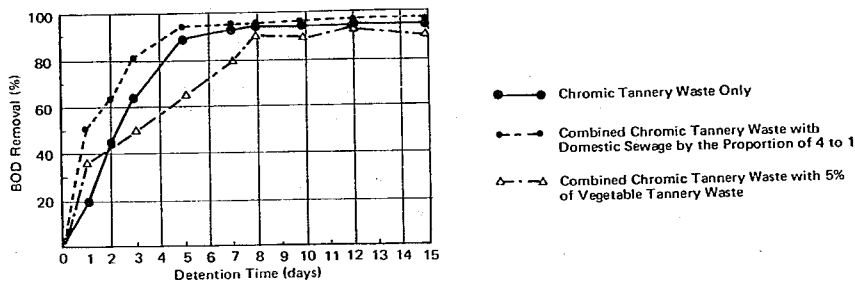


Fig.-2.3 Detention Time vs. BOD Removal at the Laboratory Test of Aerated Lagoon (20°C)



(3) Experiment of Activated Sludge Process in Extended Aeration

In this experiment, influent containing chromic tannery waste only was used. And the test was held outdoors employing a small scale pilot plant. At that time, the pretreatment facility in Takagi area was in operation. Therefore, the effluent from this pretreatment facility (plain sedimentation) was used for the activated sludge treatment experiment.

The average quality of pretreated wastewater was BOD 782 mg/l, COD_{Mn} 311 mg/l, SS 120 mg/l, total chromium 7.1 mg/l and pH 8.0 – 11.8. pH was controlled in advance by dosing sulfuric acid. The aeration tank was operated by the completely mixing mode at MLSS 3,000 – 4,000 mg/l. And the experiment was conducted from fall to spring. Fig. 2.4 shows the relations between the BOD Load and treatment efficiency.

Comparatively favorable treatment efficiency was obtained when the BOD Load was under 0.1 kg/MISS.kg/d. But the fluctuation in effluent quality was inevitable and sludge bulking phenomenon was observed.

(seek operation condition during this period to secure target effluent quality) and the evaluating operation term of which the treatment results of the designated operation condition are evaluated.

The aforementioned experiments i) and ii) were held twice in summer and winter, and the evaluating operation term for each season was instituted.

In experiment i), the pretreatment effluent was supplied by a constant feed pump. In experiments ii) and iii), the typical influent flow pattern was given from the measured influent flow results. Furthermore, in experiment iii), without changing the flow pattern in experiment ii), domestic sewage equivalent to $1/2$ of the total volume was to be fed constantly. Fig. 4.1 and Fig. 4.2 respectively show the flow patterns used in experiments ii) and iii).

Fig.-4.1 Fluctuation Flow Pattern of Chromic Tanneries Waste Only

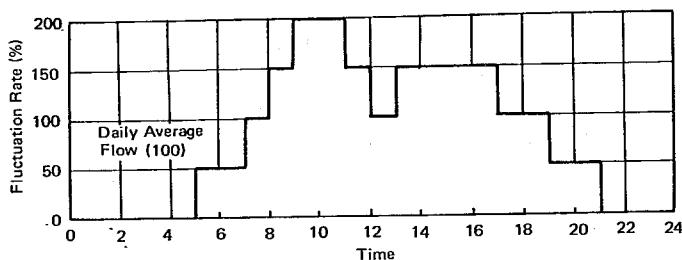


Fig.-4.2 Fluctuation Flow Pattern of Mixed Chromic Tanneries Waste with Domestic Sewage

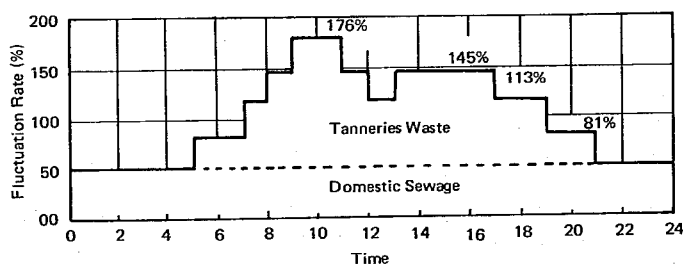
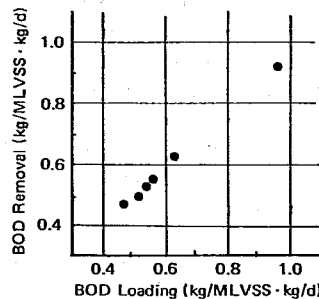


**Fig.-2.5 BOD Loading vs BOD Removal
at the Pilot Plant of
Pure Oxygen Activated
Sludge Process**



3. APPLICATION OF OXYGEN ACTIVATED SLUDGE PROCESS FOR TANNARY WASTE TREATMENT

From the experiments held in the past, it has become clear that the most favorable treatment efficiency can be expected from the pure oxygen activated sludge process. When introducing the pure oxygen activated sludge process, the following advantages can be expected:

- i) pH control is not necessary for the tannery waste treatment.
- ii) As it is possible to maintain MLSS in the aeration tank at a high concentration, it is possible to decrease in aerator capacity or shortening of aeration time.
- iii) There is a possibility of preventing the sludge bulking phenomenon.
- iv) The oxygen supply deficit that is likely to occur in high organic waste treatment can be prevented.

Of the reasons cited, it was decided most appropriate to introduce the pure oxygen activated sludge process in treating tannery waste. Also, as Himeji city is planning to construct a coastal station for LNG (Liquid Natural Gas) transported from abroad in the near future, there is a great possibility of obtaining cheap oxygen produced at this station and conveyed through a pipe line. That was another reason why oxygen activated sludge process was adopted.

However, in the past oxygen activated sludge process experiments, the test periods were as short as four months and were held at summer time. Therefore, at this study, the following problems must be served:

- a) Even during day time, the fluctuation of tannery waste quantity and quality is great. However, at night time and on Sundays, there is virtually no wastewater coming in.

Therefore, it was requested to determine whether the waste from tanneries should be treated with diurnal variation or equalized condition.

- b) Experiment results of through the four seasons by oxygen activated sludge process were not available.

Therefore, it was required to conduct experiments in winter to obtain necessary data to design facilities.

c) The effluent from the pretreatment facilities at Takagi area and Shigo & Gochaku areas are expected to be transported to the Himeji Tobu Wastewater Treatment Plant located near the coast by an exclusive pipe line extending about 6 kilometers.

The effluent from these pretreatment facilities totals about 28,000 m³/d. It was required to determine whether it is better to separate this effluent from other domestic sewage for exclusive treatment or should be combined with domestic sewage and others at a ratio of 1:1.

d) The effluent standard of BOD 20 mg/l (maximum: 25 mg/l) is to be applied to the effluent from the Himeji Tobu Wastewater Treatment Plant. Also in the Seto Inland Sea water areas, the total emission of wastewater load by COD_{Mn} is to be regulated after 5 years. Presently, the total dischargeable load by COD_{Mn} from this wastewater treatment plant is undecided. Therefore, it is necessary to consider the removal of COD_{Mn} when conducting this experiment.

e) In Japan, three types of oxygen activated sludge processes are put on the market. They are the UNOX system, the MAROX system and the EBARA-Infilco system. It is important to study thoroughly the merits and demerits of each system and select the most economical and effective system for operation when designing the actual facilities of the Himeji Tobu Wastewater Treatment Plant.

To solve the problems mentioned above, pilot plants of the three companies were installed in the compound of the Takagi Pretreatment Facility to conduct 15 month experiments. The pilot plants of the three companies were each operated by engineers from their own. Also, city officials and members of private consulting firms cross checked the water quality data and the operating data to assure fairness in giving engineering evaluations of the three systems.

Himeji city, in order to instruct, supervise and evaluate the experiments at the three pilot plants, has organized the Engineering Evaluation Committee of Tanneries Waste Treatment Experiment in Himeji. The members of this committee included officials from the Public Works Research Institute of the Ministry of Construction, Hyogo Prefectural Industrial Research Laboratory, Public Works Department of Hyogo Prefectural Government and Environmental Department of Hyogo Prefectural Government.

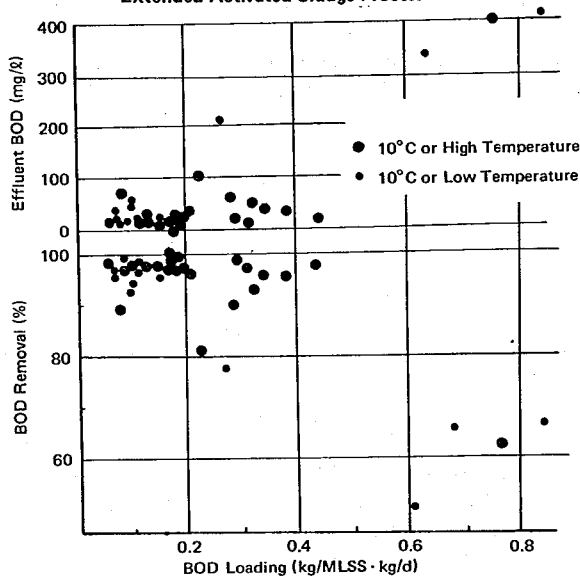
4. EXPERIMENT PROGRAM AND PROCEDURE

As the experiments of the pilot plants of three companies were conducted to obtain fundamental data and to confirm the problems with regards operation and maintenance to design the Tobu wastewater treatment plant, the following condition was given:

- i) Experiment of constant feed of tannery waste only
- ii) Experiment of varied feed of tannery waste only
- iii) Experiment of mixed feed of varied tannery waste and constant domestic sewage.

With regards each experiment listed above, the self-active operation term of which the operation condition is designated by free judgement of each company

Fig.-2.4 BOD Loading vs. Effluent BOD and BOD Removal
at the Small Scale Pilot Plant Test of
Extended Activated Sludge Process



(4) Preliminary Experiment of Pure Oxygen Activated Sludge Process

This experiment, similar to the experiment in (3), used effluent from the pretreatment facility of Takagi area and was conducted at a pilot plant mounted on a trailer. The water quality of the influent was the same as (3) but the experiment was conducted only limited period of between summer and fall. The experiment was held as follow: Aeration time: 3.5 – 6 hours; and MLSS 6,500 – 7,600 mg/l . There was no pH control in this experiment.

Part of the experiment results is shown in Fig. 2.5. As the figure shows, when the BOD Load was 0.37 – 1.07 $\text{kg/MLVSS} \cdot \text{kg/d}$, the BOD removal rate was over 97 percent, thus a linear relationship between BOD Load and BOD removal was obtained. Furthermore, oxygen consumption in the aeration tank was roughly the same as BOD removal. The total chromium in the activated sludge changed greatly from 510 to 31,000 mg/kg , but when SRT was kept long, chrome accumulated in the activated sludge and have shown a tendency to affect biological activity.

Prior to the commencement of the experiments, experiment plan for the next 15 months was compiled. But as the start of the experiments was in winter and too much time was consumed on the acclimation of activated sludge, the initial plan was postponed. As a result, the experiment was held under experimental conditions as shown in Fig. 4.3.

Fig.-4.3 Pilot Plant Experimental Plan for Chromic Tanneries Waste Treatment

Jan'77	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan'78	Feb.	Mar.	Item
															Domestication of Activated Sludge
															Committee Decided Constant Feed Operation of Tanneries Waste Only
															Self-decided Constant Feed Operation of Tanneries Waste Only
															Evaluation of Each Operation
															Self-decided Varied Feed Operation of Tanneries Waste Only
															Self-decided Mixed Feed Operation of Varied Tanneries Waste and Constant Domestic Sewage

Remarks:

- 1) Experimental condition for the Committee decided constant feed operation of tanneries waste only was detention time of six hours and mixed liquor suspended solids of 6,000 mg per litre in the aeration tanks.
- 2) Experimental condition for evaluation of each operation was decided with understanding of the Committee on the basis of the proposal of each manufacture. It was the major premise that the effluent was maintained both BOD of 20 mg per litre or less and CODMn of 50 mg per litre or less.

Of the operating conditions for pilot plants shown in Fig. 4.3, the standard operating conditions centering in February of 1977 were: detention time 6 hours, and MLSS over 6,000 mg/l to operate the pilot plants. Also during the evaluating operating period, each company, based on the results of the self-active operating period, was asked to submit its operating conditions to the Committee for approval. In this instance, the BOD of the effluent was set within 20 mg/l and CODMn within 50 mg/l as a target.

Of the three companies, Ataka Kogyo Co. which owns the MAROX system submitted a proposal in July 1977 to conduct the oxygen activated sludge process experiment in two stage process to the Committee. And thus, the MAROX system has employed the two stage process ever since August of 1977.

In Fig. 4.4 (a) and (b), the pilot plant of MAROX system, in Fig. 4.5 the pilot plant of EBARA-Infilco system and in Fig. 4.6 the pilot plant of UNOX system and their flow sheets are shown.

Also in the tannery waste only supply experiment, as the phosphorous content in the raw water was insufficient, phosphorous was added to conduct the experiments.

Fig.-4.4(a) Flow-Chart of Pilot Plant
(Single Stage Marox System)

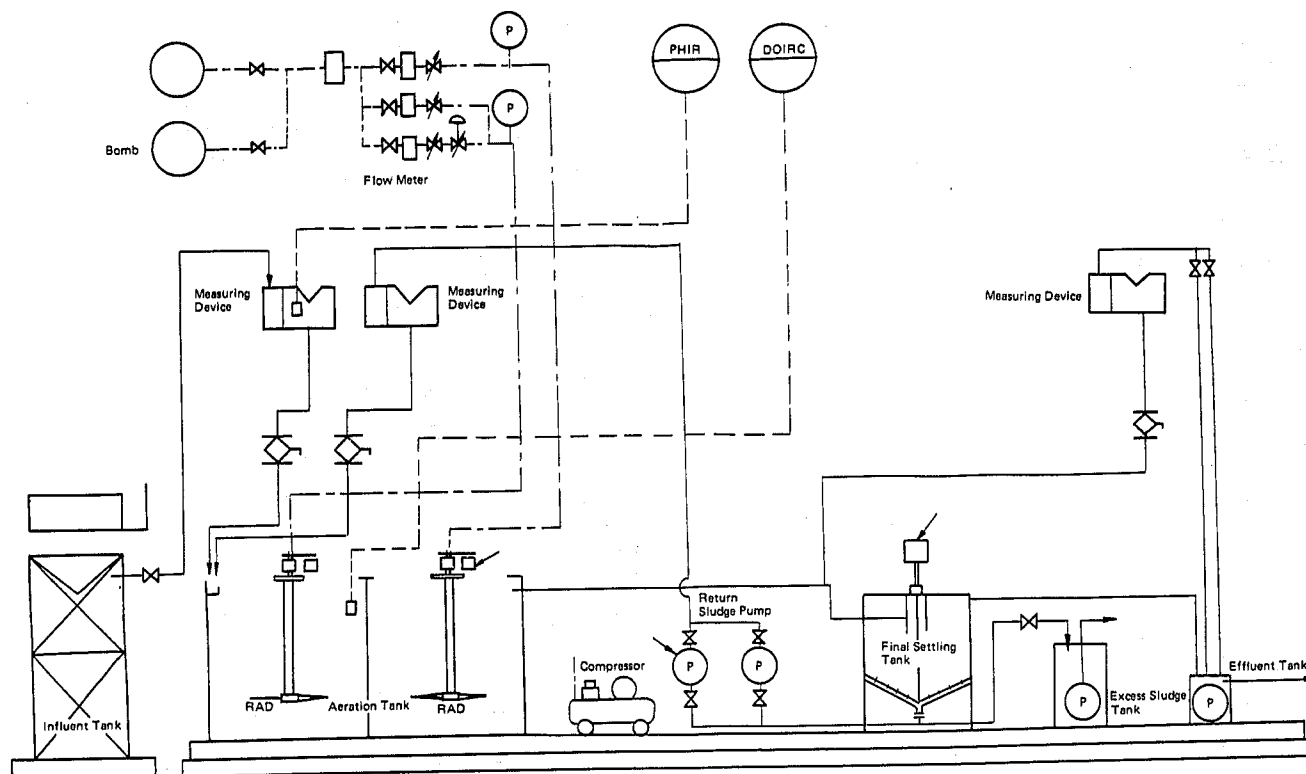


Fig-4.4(b) Flow-Chart of Pilot Plant
(Two Stage Marox System)

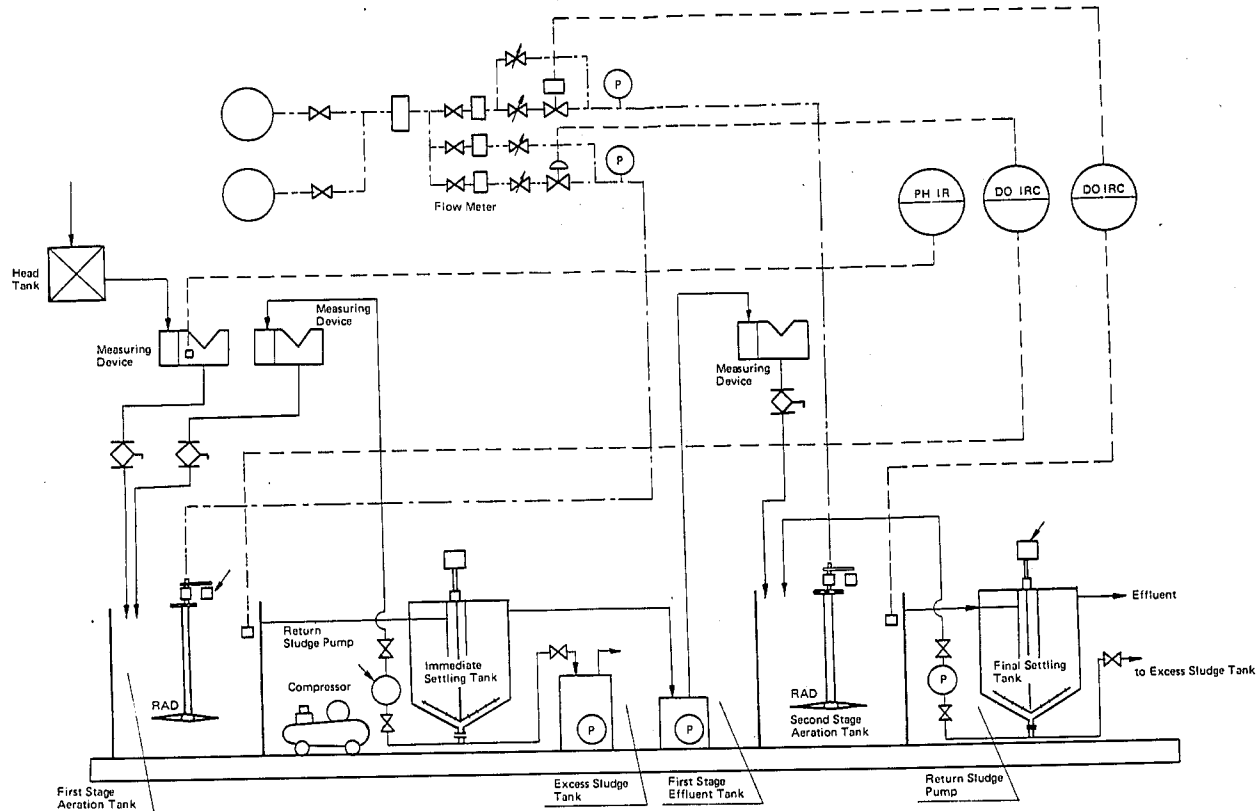


Fig-4.5 Flow-Chart of Pilot Plant
(Ebara Infilco System)

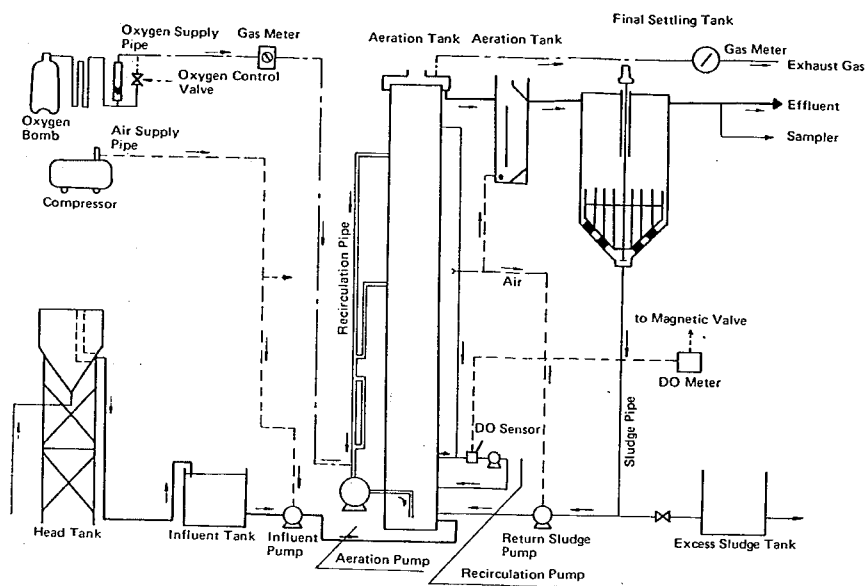


Fig.-4.6 Flow-Chart of Pilot Plant
(Unox System)

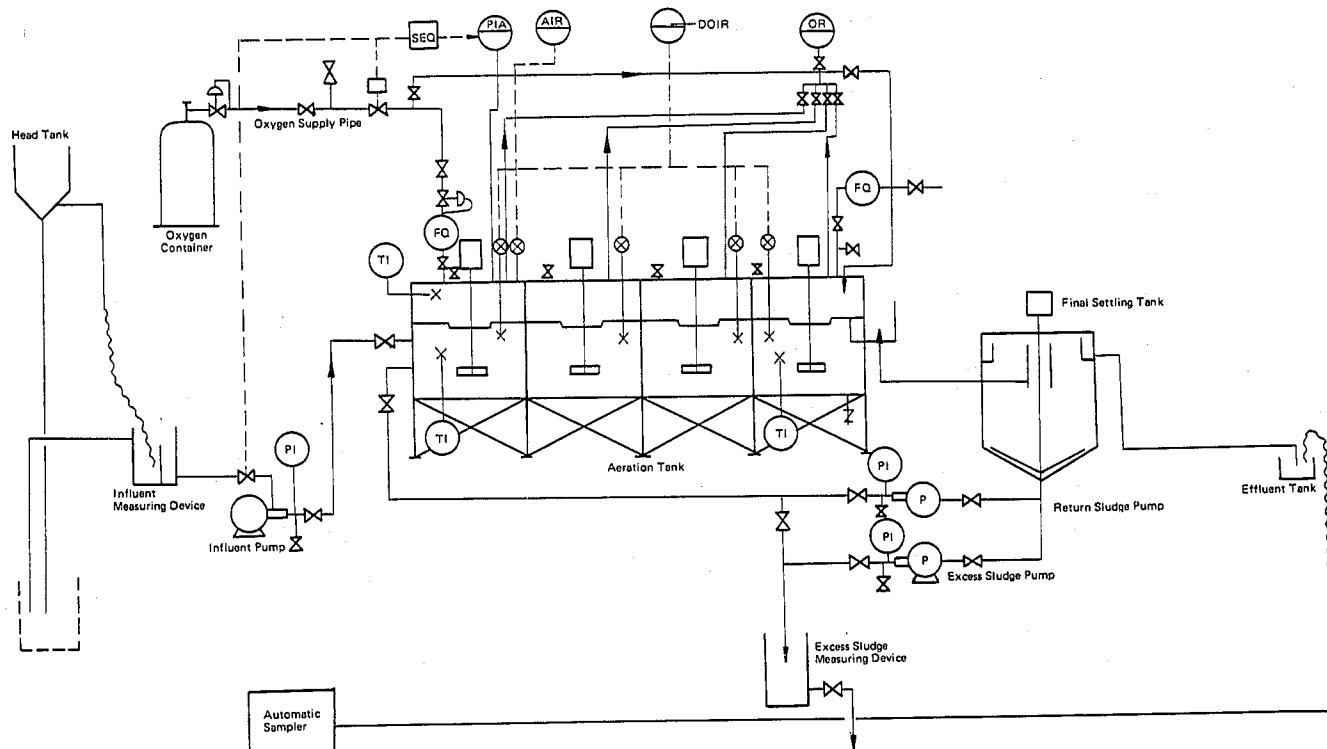


Table 5.1 Summary of Experimental Result

Name of System	Month of Experiment	Feb. '77	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan. '78	Feb.	Mar.										
	Committee Decided Experimental Condition	Constant Feed of Tannery Waste Only										Varied Feed of Tannery Waste Only				Mixed Feed of Varied Tannery Waste and Constant Domestic Sewage		Varied Feed of Tannery Waste Only		Constant Feed of Tannery Waste Only					
Maxox System	Experiment Nos.	1	2	3	4	5	6	Evaluation				Evaluation				Evaluation		Evaluation		Evaluation					
	Detention Time (hrs.)	6.0	6.0	6.0	8.0	8.0	12.0	6.0	12.0	18.0	12.0	7.6	7.6	7.6	5.7	3.8	2.8	3.9	7.6	7.6	9.0	9.0			
	MLSS (g/l)	13.5	10.7	8.1	8.8	7.5	10.2	7.6	6.5	8.7	8.9	5.7	5.2	4.9	3.6	3.0	3.9	7.3	5.3	7.2	6.0				
	MLVSS/MLSSx100(%)	66	79	84	85	84	83	87	86	84	84	86	85	87	86	86	82	75	4.9	8.3	7.2	8.6			
	Return Sludge (%)	143	155	149	257	140	222	124	86	95	73	163	148	204	394	228	171	199	248	215	195	91			
	Sa-t (MLSS-T)x10 ³	81.0	62.4	48.6	70.4	60.0	122	45.6	78	157	107	86.6	39.5	37.2	20.5	14.1	8.4	15.2	37.2	40.3	64.8	54.0			
	F/M (BOD-kg/MLVSS-kg/d)	0.35	0.35	0.42	0.31	0.34	0.16	0.40	0.22	0.12	0.19	0.29	0.38	0.43	0.72	0.66	1.10	0.72	0.42	0.42	0.22	0.28			
	SRT (days)	14.1	5.1	5.0	17.1	8.4	16.4	5.8	14.5	25.9	23.8	3.1	5.4	5.2	2.6	2.5	1.4	1.9	9.8	4.7	13.1	6.0			
	BOD (mg/l)	Influent	790	739	710	761	707	660	656	598	635	697	598	530	576	530	330	320	331	476	590	508	536		
		Effluent	130	89.7	107	89.3	154	90.2	89.3	44.1	21.8	15.4	35.2	23.2	15.9	17.8	9.91	32.3	25.2	48.7	29.4	26.7	23.4		
COD (mg/l)	Influent	434	456	405	402	416	392	373	335	350	388	354	304	336	329	215	190	194	299	377	342	408			
	Effluent	136	108	115	101	114	107	96.7	80.3	57.4	45.9	66.9	55.2	50.8	42.7	31.0	42.8	39.4	63.7	59.3	60.1	53.9			
Ebara Intifox System	Stage	Single Stage Process										Two Stage Process													
	Experiment Nos.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19					
	Detention Time (hrs.)	6.2	6.2	5.9	8.8	10.1	8.5	8.5	11.7	22.9	16.5	12.0	8.1	6.2	4.7	4.1	15.8	23.2	17.5	13.6					
	MLSS (g/l)	13.3	11.9	9.4	9.7	9.3	9.6	11.7	9.6	10.9	10.1	9.2	9.1	7.2	6.1	5.9	8.7	9.7	10.4	11.0					
	MLVSS/MLSSx100(%)	58	57	84	85	85	86	85	84	83	83	84	86	85	85	85	84	84	85	85					
	Return Sludge (%)	32	42	70	41	48	51	85	44	86	67	100	114	93	82	64	66	66	71	95					
	Sa-t (MLSS-T)x10 ³	82.5	73.8	55.5	85.4	93.9	81.6	99.5	112	250	167	110	73.7	44.6	28.7	24.2	137	225	182	150					
	F/M (BOD-kg/MLVSS-kg/d)	0.39	0.44	0.37	0.22	0.19	0.22	0.21	0.16	0.07	0.08	0.15	0.20	0.21	0.32	0.39	0.099	0.075	0.076	0.097					
	SRT (days)	14.3	4.2	9.1	5.5	13.1	17.2	18.3	13.9	25.1	26.0	17.9	17.5	22.8	6.3	6.6	45.5	31.0	34.7	18.6					
	BOD (mg/l)	Influent	763	753	724	670	632	656	604	641	626	476	586	530	340	320	331	476	590	506	536				
	Effluent	229	144	112	185	145	28.2	26.8	17.7	18.6	19.0	19.2	19.9	12.8	16.9	26.7	35.2	42.2	24.5	23.7					
COD (mg/l)	Influent	458	424	400	391	413	375	345	344	370	276	338	329	224	201	194	299	377	342	408					
	Effluent	183	120	99.1	116	133	74.6	61.1	54.0	49.2	50.1	48.6	42.6	40.0	32.5	36.8	51.2	63.6	59.5	63.7					
Uniox System	Experiment Nos.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22		
	Detention Time (hrs.)	6.0	5.0	8.6	6.0	8.6	12.0	10.0	12.0	18.9	15.1	12.6	10.1	9.0	8.2	5.1	4.5	3.8	12.0	18.0	16.0	15.0	12.0		
	MLSS (g/l)	10.7	8.5	9.8	9.8	10.2	8.5	8.2	9.3	8.1	8.4	8.6	8.8	9.0	9.6	6.8	7.0	6.2	7.2	5.8	9.4	10.7	11.5		
	MLVSS/MLSSx100(%)	73	84	86	87	86	83	82	82	82	82	83	85	85	85	85	86	87	85	84	85	87	87		
	Return Sludge (%)	41	71	100	57	80	80	67	100	158	126	105	84	85	78	48	53	64	100	150	133	100	108		
	Sa-t (MLSS-T)x10 ³	64.2	42.5	84.3	58.8	87.7	102	82.0	112	153	127	108	88.9	81.0	78.7	34.7	31.5	23.6	86.4	104	150	161	138		
	F/M (BOD-kg/MLVSS-kg/d)	0.40	0.50	0.24	0.28	0.22	0.18	0.22	0.18	0.12	0.15	0.13	0.19	0.16	0.19	0.28	0.28	0.39	0.18	0.14	0.11	0.06	0.11		
	SRT (days)	5.1	4.5	13.6	6.3	11.7	12.8	16.3	17.5	28.4	33.8	31.2	12.6	12.5	13.2	7.5	5.8	5.4	9.7	33.3	29.5	27.1	24.7		
	BOD (mg/l)	Influent	772	737	710	591	687	652	628	670	639	638	500	581	582	540	340	320	331	544	408	590	497	536	
		Effluent	115	98.7	83.1	96.0	71.9	25.2	22.0	17.0	13.5	15.4	9.85	13.6	12.8	17.6	12.4	8.95	24.6	30.5	23.2	24.6	13.7	24.4	
COD (mg/l)	Influent	436	405	513	363	412	412	347	350	376	354	356	338	344	315	224	186	193	322	266	377	327	366		
	Effluent	120	105	108	99.9	93.9	68.4	50.9	47.0	45.9	52.8	38.5	43.8	38.7	39.5	34.9	30.0	36.2	51.5	45.0	49.6	58.2	66.5		
Month of Experiment	Feb. '77	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan. '78	Feb.	Mar.											

Fig. 5.1 Experimental Results of BOD₅ and COD_{Mn} (Marox System)

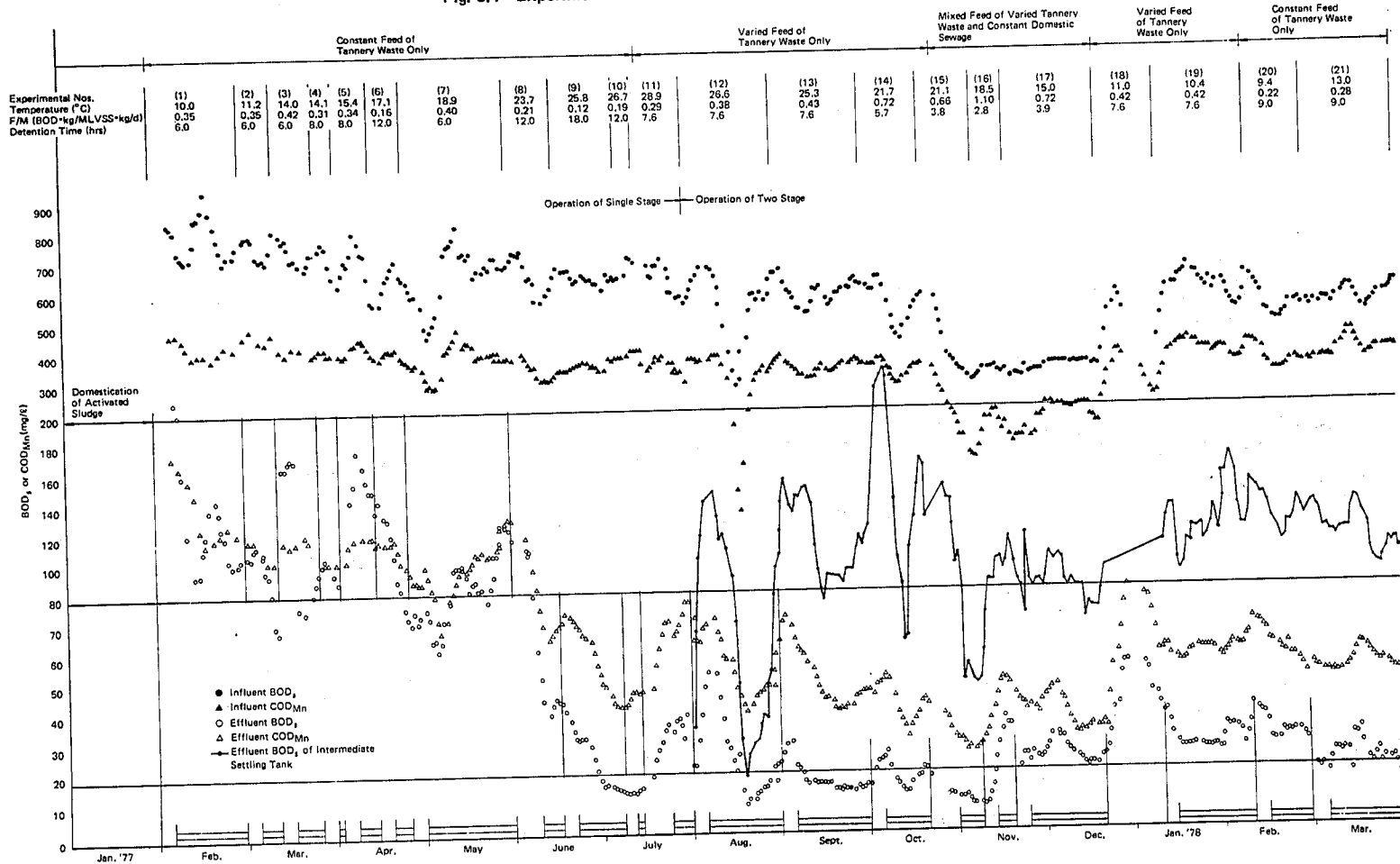


Fig. 5.3 Experimental Results of BOD₅ and COD_{Mn} (Unox System)

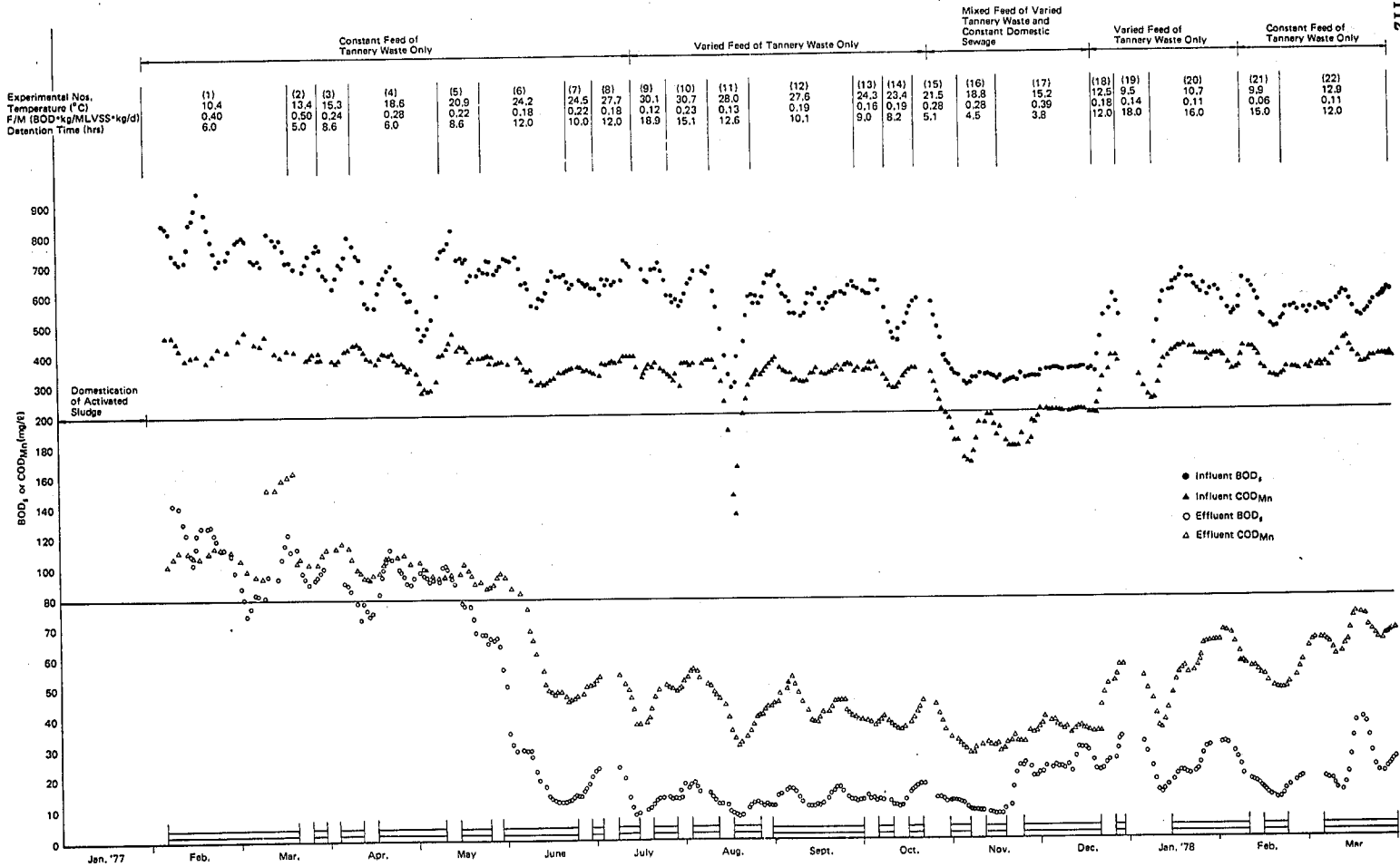
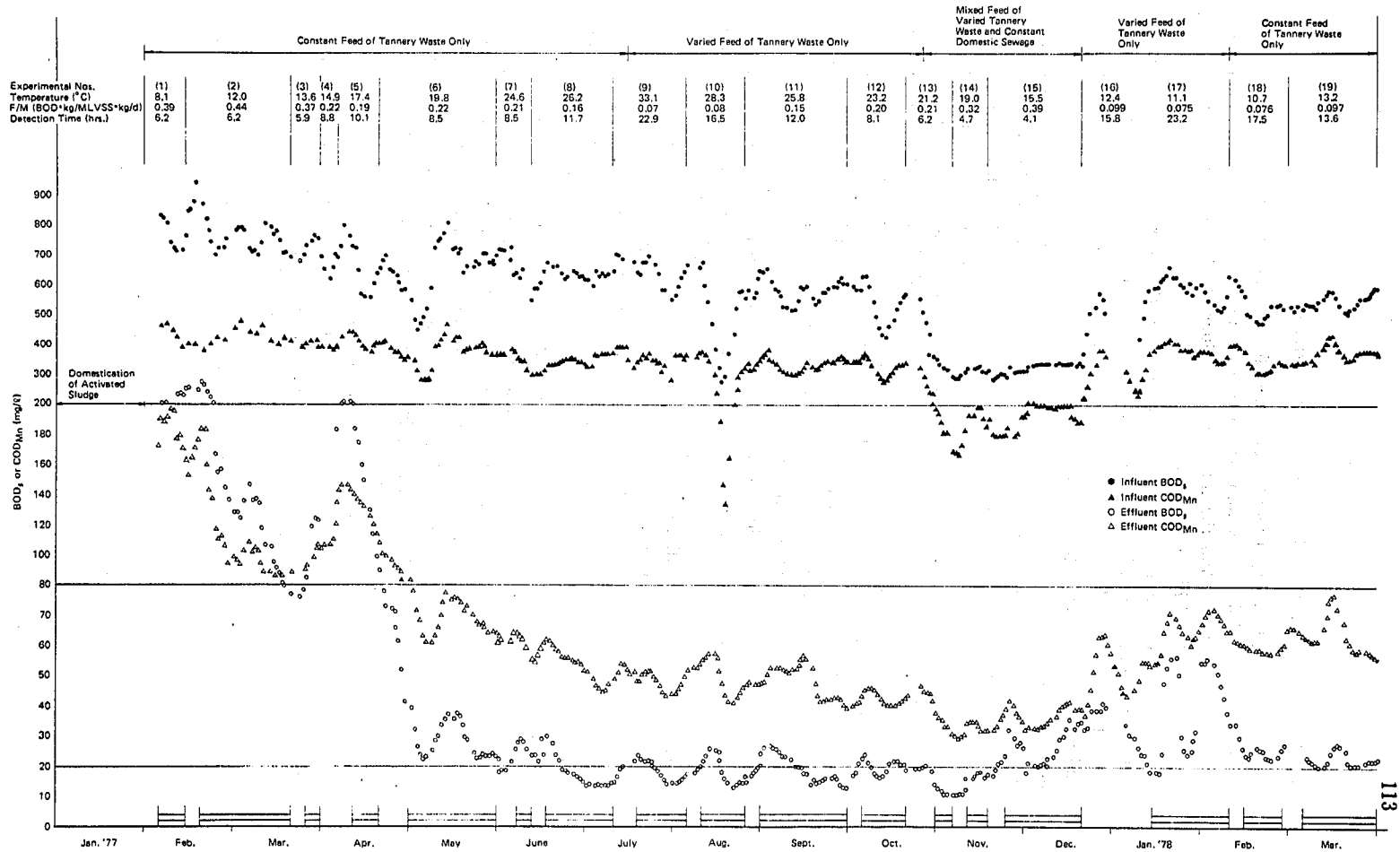


Fig. 5.2 Experimental Results of BOD₅ and COD_{Mn} (Ebara Infilco System)



5. EXPERIMENT RESULTS AND DISCUSSION

The pilot plant experiments continued for 15 months from January 1977 to March 1978. Table 5.1 summarizes the operating results of the pilot plants of the three companies. And the influent and effluent BOD and COD_{Mn} are shown Fig. 5.1, Fig. 5.2 and Fig. 5.3, respectively.

The first few months after commencement of the operations have seen both BOD and COD_{Mn} in effluent frequently exceeding the 100 mg/l level due to low water temperature. However, after six months, stable operations were obtained. And by the end of December in all operating conditions, effluent quality of 15–35 mg/l of BOD and 40–70 mg/l of COD_{Mn} was obtained. Especially, when the operating conditions were stable, it was possible to maintain the objective effluent quality of BOD being below 20 mg/l and COD_{Mn} below 50 mg/l. However, after January, being influenced by the drop in water temperature, both BOD and COD_{Mn} in effluent began to raise again despite keeping the F/M ratio at a low level.

From the results of the experiment on constant feed of tannery waste water only and the experiment on varied feed of tannery waste water only, if the latter is to be operated with a slightly lower F/M ratio than the former, it was found that similar effluent can be obtained. However, to ensure stable operation for a long period of time, it was found appropriate to introduce the influent as constant as possible by providing an equalization tank.

As the experiment on joint tannery waste and domestic sewage was operated at a higher F/M ratio than that on tannery waste only, BOD and COD_{Mn} concentrations in the effluent climbed higher than those in the experiment on tannery waste water only. Especially, in the latter half of this experiment, the water quality of the effluent was influenced by the drop in water temperature of the influent. However, if the F/M ratio can be kept at a lower level in this experiment, it will obviously bring about stable performance. During this period, although the experiment on mixed feed of constant feed of tannery waste and domestic sewage was not possible due to time restrictions, it is considered that it would have brought about good results with regards stable operation and treated water quality when conducted. To maintain BOD below 20 mg/l in the effluent in the tannery wastewater only experiment, it is necessary to constantly maintain BOD removal rate at more than 97 percent, which is very difficult to sustain in many cases in biological treatment. On the other hand, in the joint treatment with tannery wastewater and domestic sewage, BOD removal rate needs to be sustained at about 95%, thus from this point it is regarded better to select the joint treatment.

The operation of MAROX system pilot plant commenced from August in two stages. But since the F/M ratio was kept at an extremely high level, its effluent BOD concentration was higher than the single-stage pilot plant effluent of the other systems. However, if the F/M ratio can be kept lower in the operation than the experiment conducted, it is considered possible to sustain the objective BOD value. When employing the two stage process, although it has the merit of conducting operations at a higher F/M ratio than the single-stage process, it has the disadvantage of requiring an intermediate settling tank. Further studies should be made before

selecting either the single stage process or the two stage process.

The influent pH was between the range of 9 and 11.5, but pH of pilot plant effluent even without pH control was maintained between the range of 6.5 and 7.5. From these facts, when introducing the oxygen activated sludge process, there is no need of performing pH control. The drop in pH level in the effluent was observed more markedly in the covered type aeration tank than the open type aeration tank.

SVI of the mixed liquor was in the range of 50 – 160 and was normally kept at a level between 80 and 110. In either experimental conditions, there was no bulking of activated sludge observed. Similar values of SVI were obtained in both the experiment on tannery wastewater only and on the experiment on tannery wastewater mixed with domestic sewage.

In general, at the pilot plant experiment, both the surface area rate of the final settling tank and the settling time have shown a tendency of becoming larger than the full scale actual facility. The return sludge concentration obtained in this experiment was 15 – 30 g/l by the single stage tannery wastewater only feed process and between 11 and 16 g/l by the two-stage process. The return sludge by the experiment on mixed feed of tannery wastewater and domestic sludge was between 14 and 21 g/l by the single-stage process and 8 and 11 g/l by the two-stage process. Also MLSS concentration in the aeration tank was between 8 and 10 g/l by the experiment on tannery wastewater only feed, and between 6 and 7 g/l by the experiment on combined feed of tannery waste and domestic sewage. In the two-stage process, there was a tendency that the MLSS concentration in the aeration tank was lower than the single-stage process in both experiments. This is reasoned to the fact that in the two-stage process the return sludge ratio had to be kept at a high value of between 257 and 73%.

SRT of the pilot plant showed a marked fluctuation of between 1.4 and 34 days. But, on the average, favorable effluent quality was obtained when SRT was maintained between 10 and 15 days. Even in these instances the nitrification has only slightly occurred. The total alkalinity and ammonia nitrogen in the effluent have shown a tendency of becoming higher than in the influent.

The oxygen consumption in the aeration tank was 0.62 – 1.73 kg O₂ per removed BOD 1 kg. When performing operations to hold excess sludge in the system, this value had further increased to reach a maximum 1.91 kg. The oxygen utilization ratio in the aeration tank was between 87 and 99% although actual measurements were only made of the covered type aeration tank. In general, the value exceeded 90% showing extremely good efficiency. The use of an oxygen cylinder was quoted as the reason.

The waste activated sludge volume have shown a great fluctuation of between 0.22 and 1.34 kg per BOD 1 kg. In general, when the oxygen consumption per removed BOD increased, the sludge production have shown a tendency of decreasing. In the two-stage process, oxygen consumption per BOD removal was smaller than in the single-stage process but a tendency of the increase of sludge production have been recognized.

The accumulation of chromium in sludge is estimated to reach between 40 and 50 g per 1 kg of dry solids when viewing the results of the experiment on tannery

waste only feed. Even in the case of the experiment on the combined feed of tannery and domestic sewage, the accumulation of chromium compound is estimated to reach a maximum 40 g per 1 kg of dry solids of sludge. Viewing from the fact that chromium compound of high concentration do accumulate in the sludge, extra care must be exerted to the disposal of such sludge.

Resulting from the accumulation of chromium in sludge, the total chromium concentration of between 6 and 20 mg/l contained in the influent have decreased to below 0.6 mg/l in the effluent, proving the fact that the oxygen activated sludge process is also effective in total chromium removal.

6. SUMMARY

The study was performed to compile the results of the oxygen activated sludge process treating tannery waste flowing into the Tobu Sewage Treatment Plant in Himeji city. However, detailed analysis of the results of the experiment are not contained in this report due to lack of ample time after completing the tests.

But it was truly fortunate that Mr. W. J. Lacy and Mr. R. S. Burd who both represented the American team at the 5th U.S.-Japan Conference on Sewage Treatment Technology have taken the trouble to extend their field trip to Himeji to inspect the experimental facilities.

The first stage of construction work of the Sewage Treatment Plant is expected to start in 1979, and the actual operation to commence during the 1982 fiscal year.

The results obtained from the experiment can be summarized as follows:

- (1) It is appropriate to employ the oxygen activated sludge process for tannery waste. However, extra care must be exerted to the operation and maintenance of the process. When the F/M ratio is kept at below 0.1 kg.BOD/MLVSS. kg/d, it is possible to obtain effluent with BOD 20 mg/l and BOD removal rate 97 percent.
- (2) Fluctuation of tannery waste quantity and quality is great. But if the F/M ratio can be slightly lowered at the time of constant feed, it is possible to obtain effluent with BOD of below 20 mg/l even when there is a fluctuation of influent flow. However, when considering the long period use of the biological treatment facility for stable operation and maintenance, it is desirable to provide a equalization tank for constant supply of influent.
- (3) It is advisable to introduce the method of supplying tannery waste combined with domestic sewage for stable treatment. When the mixing ratio of tannery waste and domestic sewage is 1:1, even when F/M ratio is more than 0.2 kg.BOD/MLVSS.kg/d, it is possible to maintain effluent BOD below 20mg/l.
- (4) When the two-stage oxygen activated sludge process is employed, although it is possible to operate with a high F/M ratio, it requires an intermediate tank. From the economical standpoint and so forth, further studies should be made before selecting either the single-stage process or the two-stage process.
- (5) In the treatment of tannery waste by the oxygen activated sludge process, pH control is not necessary. Judging from the experiment results, SVI is maintained at around 100 and activated sludge is free from bulking. The removal of total chromium is effectively done, but more than 50 g of total chrome per 1 kg of dry solids accumulate in sludge, thus extra care must be exerted in the disposal of

the sludge.

(6) The oxygen consumption in the aeration tank was between 0.62 and 1.73 kilogram O₂ per 1 kg of BOD removed. Also the sludge production was between 0.22 and 1.34 kg per 1 kg of BOD removed. In general, when the oxygen consumption per BOD removed increased, the sludge production have shown a tendency of decreasing.

CHAPTER 4
REMOVAL OF COLOR FROM MUNICIPAL SEWAGE
CONTAINING TEXTILE WASTEWATER

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CHAPTER 4

REMOVAL OF COLOR FROM MUNICIPAL SEWAGE CONTAINING TEXTILE WASTEWATER

1. INTRODUCTION

The cleanness or dirtiness of water should be, as a rule, determined by the amount of specific pollutants contained in the water. However, when a man judges the cleanness of a river, he is often influenced sensibly by elements which can not be specified, such as color, smell and foam of the water. Especially with regards color, there is essentially no direct or indirect regulations in the form of stream, effluent or pretreatment standards. However, even in the field of sewage treatment, there are several cases where receiving bodies of water are being offended in appearance due to the colored effluent from treatment plants which treat municipal sewage containing textile wastewater and other colored industrial wastes. This situation makes the study of color removing processes one of the major research projects. At the present stage, the method to measure the degree of color itself is insufficient. There remain many economical and technical problems to be solved including the comparison of the system of treating colored wastewater after receiving into public sewerage system with that of treating it by pretreatment facilities.

In this study, methods of color measurement are discussed and color removal from municipal sewage containing textile wastewater by activated sludge process and physical-chemical processes as tertiary application are investigated.

2. COLOR MEASUREMENT

The methods of measuring color of water can be divided into two categories: the spectrophotometric method and the visual comparison method. The former includes the mono-chromatic specification method, and the method to express the degree of color by the color difference from pure water by improving the mono-chromatic specification. The latter, however, is varied: a method of expressing degree of color by making comparison with the color of platinum - cobalt solution; a method to obtain chroma and luminance based on JIS standard color plates and to express the extent of color based on these parameters, which is stipulated in the Anti-Pollution Ordinance of Kawasaki City; and a method of expressing the degree of color by making comparisons with other suitable color scales. Furthermore, there are the sensual methods of expressing the degree of color based on the impression gained by viewing the color of water.

Generally, from the standpoint of pertinently expressing the various colors resulting from industrial wastewater, the conditions that the method of color measurement should satisfy can be listed as follows:

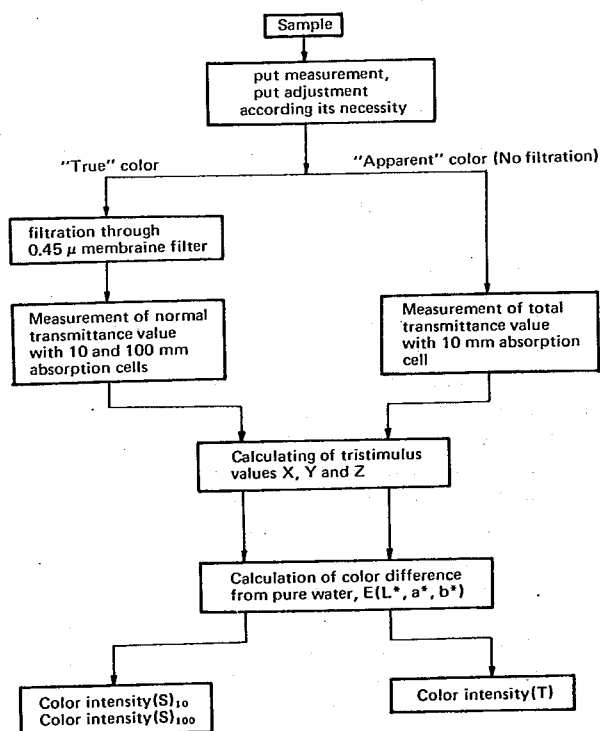
- (a) Results coincide at least roughly with the visual impression of man.
- (b) Reasonable comparisons are possible with regards colors of different hues.
- (c) Colors by dissolved substances and by suspended matters are equally evaluated.
- (d) Results are qualitative and have a good correlation, preferably linear relationship, with the concentrations of substances causing color, and

- (e) The measuring method is simple and has a good reproducibility, and personal error is small.

The above-mentioned conditions are not always perfect, even containing conditions that would partially contradict with each other. However, tentatively setting these conditions as the criteria for judgement and by comparing the various measuring methods aforementioned, the color difference expression by the spectrophotometric analysis and the method described in the ordinance of Kawasaki City are considered to be effective. Accordingly, by employing the two methods, measurements of color of various dye solutions and river waters were conducted to make preliminary studies for evaluating them. The results have shown that the two methods were not fully satisfactory but applicable for practical use. However, the spectrophotometric method was superior in quantitiveness and measurements at higher concentration, thus, the method based on the color difference was to be employed in this study.

By slightly modifying the original method, the procedure for color measurement was determined as in Fig. 1. The color difference from pure water calculated by this method is referred to as 'color intensity' in this paper. The modified points are: the stricter filtration condition and the employment of the newer $L^*a^*b^*$ system (1975 - UCS1) for calculation of color difference.

Fig.-1 Procedure for Color Intensity Measurement



Since the color of water may differ greatly depending on pH of the sample, it is adjusted to be within the range of stream standard (6.5 – 8.5) by adding 10 N sodium hydroxide solutions, when pH of the sample is outside of the range. For the measurement of color by soluble substances, the normal transmittance value of the sample within the wavelengths of 400 – 700 nm is measured after 0.45 μ membrane filtration. With regards color by suspended matters, the total transmittance value of the non-filtered sample is measured within same wavelengths. The total transmittance value mentioned here is the transmittance value combining both the transmitted light and the scattered light measured by the spectrophotometer having a photo cell with integrating sphere. The measurement of the transmittance value is based on JIS Z8722 (Methods of Measurement for Color of Materials Based on the CIE 1931 Standard Colorimetric System) and is conducted at 10mm intervals by setting the transmittance value of distilled water as 100 percent, or is performed by 10 or 30 ordinate systems in spectrophotometric color measurement to calculate the tristimulus values X, Y and Z. From these values, the color difference from pure water E ($L^*a^*b^*$) can be obtained from the following equation:

$$\Delta E(L^*a^*b^*) = (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \quad (1)$$

Here, ΔL^* , Δa^* , and Δb^* are the difference between the sample and the pure water with regards luminance parameter L^* and chromaticness parameter a^* and b^* which are defined as follows:

$$\begin{aligned} L^* &= 25(100Y/Y_0)^{1/3} - 16 \\ a^* &= 500 (X/X_0)^{1/3} - (Y/Y_0)^{1/3} \\ b^* &= 200 (Y/Y_0)^{1/3} - (Z/Z_0)^{1/3} \end{aligned}$$

In which, X_0 , Y_0 and Z_0 are the tristimulus of the light source. By using any spectrophotometer with Type C Light Source, which is designated by JIS Z8720 (Standard Illuminants and Sources for Colorimetry), can be set at 100 (percent).

The influence of dissolved substances and suspended matters to the total transmittance value is reported to be as follows: Let the total transmittance value be T , absorption coefficient of solution be K and scattering coefficient be S , respectively,

$$\log \left(\frac{1}{T} \right) = \log p e^{qd} - (p - 1) e^{-pd} \quad (2)$$

where,

$$q = \sqrt{K(K + 2S)}$$

$$p = \frac{(1 + a)^2}{4a}$$

$$a = \frac{\sqrt{K}}{\sqrt{K + 2S}}$$

d : thickness of solution.

When there is no influence of turbidity or K , S , the above equation is reduced to:

$$\log (1/T) \propto Kd \quad (3)$$

$\log (1/T)$ is in proportion to the concentration. On the other hand, when

considering the case when $K=0$, equation (2) becomes,

$$1/T \propto Sd \quad \dots\dots\dots (4)$$

$(1/T)$ is in proportion to the concentration. Accordingly, color by dissolved and suspended substances do not exhibit the same weight. However, while $(1/T)$ is small, $\log (1/T)$ is nearly equal to $(1/T)$, and the combined influence of the two can be expressed in a single parameter by incorporating the total transmittance values.

The light paths for measurement of the total transmittance values are 10 mm and 100 mm when measuring normal transmittance value of filtered samples, and the path is 10 mm when measuring total transmittance value of non-filtered samples. The color differences obtained from the measurements are referred to as color intensity $(S)_{10}$, color intensity $(S)_{100}$ and color intensity (T) respectively. The reason why the light path is limited to 10 mm when measuring the total transmittance values is the technical difficulty to capture the scattered light when the light path is long.

Fig. 2 shows examples of results of measuring the relationship between color intensity and concentration for the Pt-Co color standards and the various dye solutions. The dyes in Fig. 3 and 4 are hydrophilic ones, and thus color intensity (T) and color intensity $(S)_{10}$ are the same. The relationship between dye concentration and color intensity assumes a form resembling the exponential function as expected by equation (3). However, colors of bright hues such as yellow and green, and colors of comparatively dark hues including purple, blue and red show a slight difference in trend. With colors of dark hues color intensity reaches maximum value at comparatively low concentration. When the concentrations are same, color intensity of dye solution with darker hue is larger than that with brighter hue. Although this seems to be reasonable, there still is some room for further studies on to what extent it coincides with the impression received by visual sense.

Fig.-2 Color Intensity(S) of Pt-Co Color Standards

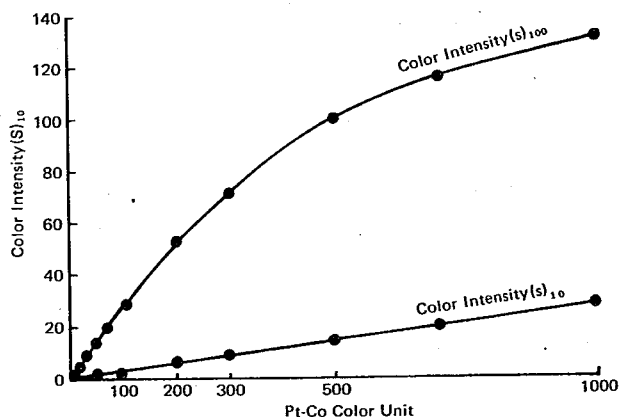


Fig.-3 Relationship between Dye Concentration (Yellowish Dye) and Color Intensity

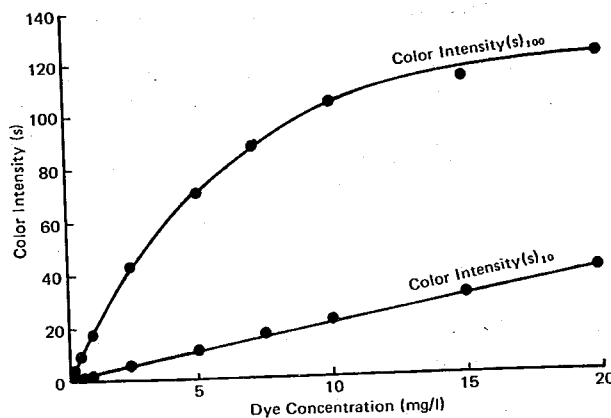
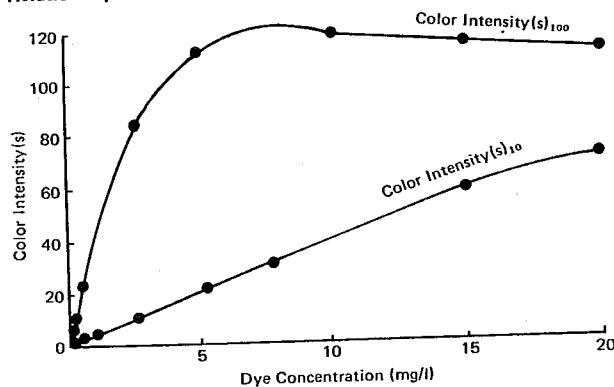


Fig.-4 Relationship between Dye Concentration (Violet Dye) and Color Intensity



At about 10 different stations in rivers flowing through the city of Hamamatsu, repeated measurements of color intensity and visual impression surveys were conducted. The visual impression tests were of simple nature, categorizing the impressions into three ranks, that is, 'clean', 'normal' and 'dirty'. The average color intensity of river water was calculated for the stations evaluated visually as 'normal'. The average color intensity (S)₁₀₀ was 2.5 and the color intensity (T) was 0.7. Although the impression of color of river water on site differs depending on water depth and the surrounding conditions, the abovementioned values give a rough idea on the limit of color of not making people feel uncomfortable and repugnance.

3. COLOR CHANGE OF WASTEWATER BY ACTIVATED SLUDGE PROCESS

With regards color removal of sewage containing textile wastewater by activated sludge process, there are reports confirming decolorization to some extent while others report no removal of color. Types of dyes and measurement methods are considered to have significant effects. Laboratory experiments were carried out in

Hamamatsu City to investigate color change of wastewater by activated sludge process using overall textile wastewater and process effluent containing specific type of dye.

Hamamatsu is famous for its production of textile goods with dye works of all types in the city. At the Chubu Sewage Treatment Plant that covers the major portion of the city, an average 109,400 m³/day of sewage was handled in 1975. Nearly 20 percent or roughly 20,000 m³/day (including textile process effluent of 14,720 m³/day) of wastewater was from textile plants. There are 29 textile plants within its service area of which 28 are located in the drainage area of one of the pumping stations, the Minami Pumping Station. The Minami Pumping Station handles about 60,000 m³/day of sewage of which nearly one-third are wastewater from textile plants. Excluding the non-colored wastewater generated at scouring and bleaching processes, colored wastewater accounts for roughly 24 percent at the Minami Plant. The quantity of dyes (including pigments) used by the previously mentioned 28 plants was about 27.3 tons per month, and as Table 1 indicates, pigments and reactive dye shared more than half of the total. When pigments are excluded, reactive dye accounted for over 50 percent of the total. Table 2 shows the percentage of dyes used in Japan in 1975. Dispersive dye is predominantly used as a whole.

Table-1 Percentage of Dyes Used in the Drainage Area of the Minami Pumping Station, Hamamatsu City

Sulphide	Leuco	Naphtolic	Dispersive	Reactive	Acid	Direct	Mordant	Basic	Pigment
6.7	9.0	4.0	0.4	35.1	2.8	2.9	0.8	0	38.3

Table-2 Percentage of Dyes Used in Japan

Sulphide	Leuco	Naphtolic	Dispersive	Reactive	Acid	Direct	Mordant	Basic	Pigment
6.2	7.1	4.3	39.6	9.1	6.6	5.5	2.6	3.1	15.9

Table-3 Color Intensity of Textile Wastewaters and Others

	Color Intensity(S) ₁₀₀	Color Intensity(S) ₁₀	Color Intensity(T)	Color Intensity(S) ₁₀ Color Intensity(T)
Reactive Dye Waste	85.0 (35.9~110)	64.3 (4.3~89.1)	66.1 (4.8~90.8)	95.5% (89.6~98.2)
Sulphite Dye Waste	59.8 (9.7~78.9)	9.6 (0.8~14.8)	37.7 (27.3~53.5)	26.4% (29.~49.3)
Dispersive Dye Waste	73.3 (20.0~100)	16.1 (3.3~34.1)	38.5 (13.0~59.0)	39.4% (8.2~57.8)
Basic Dye Waste	122 (77.8~140)	65.3 (11.6~113)	75.4 (18.5~116)	82.5% (60.5~99.5)
Night Soil	102 (101~103)	64.6 (45.1~79.9)	86.6 (85.2~88.7)	73.2% (52.1~87.0)

The upper figures are the average values and the lower figures show the range.

3.1 EXPERIMENTAL METHOD

3.1.1 Samples Used in the Experiments

The activated sludge treatment experiments conducted here were to examine removal of color from municipal sewage containing comparatively small amount of textile wastewater.

Samples of domestic sewage for the experiment were taken at the Enshuhama Sewage Treatment Plant in Hamamatsu. This treatment plant is a small one, handling only domestic sewage with an average flow of 2,500 m³/day. The population served was 10,600 as of the end of 1975. According to the result of water quality tests during a whole day, the color intensity and other water quality parameters such as BOD and SS have shown almost identical time variations by reaching the maximum at between 8 and 9 am. The range of color intensity (S_{100}) variation during a day was from 5 to 25. As the samples collected at around 11 am were considered to show an average color intensity, the influent taken at 11 am was used as domestic sewage to be mixed with textile wastewater for the experiment.

As for the samples of textile wastewater, effluent containing various types of dyes altogether and that containing specific types of dyes were used. The former was collected at the aforementioned Minami Pumping Station while the latter was collected from actual dyeing plants.

The range of color intensity variation of sewage at the Minami Station during a daytime was 20 – 25, marking its peak at between 4 and 6 pm. Thus, sewage collected at 4.30 pm was used as the samples for the experiment.

Concerning the samples containing single type of dye in each sample, on the other hand, reactive, sulphide, dispersive and basic dyes were selected as types of dyes, and wastewaters from actual textile plants were collected as the samples except for basic dye. Since there are no plants in Hamamatsu using this type of dye, synthetic wastewater by dissolving basic dye was prepared. Table 3 shows the color intensity of each wastewater used in the experiment. In the Table, the upper figures show the average values while the lower figures indicate the range.

The ratio of color intensity (S_{10}) to color intensity (T) serves as an index indicating the proportion of the color intensity caused by dissolved substances. It is quite natural that the reactive and basic dyes that are hydrophilic show larger values while hydrophobic sulphide and dispersive dyes show smaller values.

In some sewage treatment plants, night soil addition at the sewage treatment plant can be considered to cause coloring of treated water. Therefore, decoloring experiments were also conducted by using samples which were prepared by adding night soil to the domestic sewage. Color intensity of night soil is also shown in Table 3. It shows that night soil, too, has tremendously high color intensity.

3.1.2 Experimental Run, Experimental Apparatus and Experimental Conditions

Twelve experimental runs were carried out. In which, five runs are for textile wastewater containing various kinds of dyes altogether (hereinafter, these runs are called 'Mixed Dyes Waste'). For these runs, feed waters were prepared by adding the sewage taken at the Minami Pumping Station to domestic sewage so that ratios

of the textile wastewater were 1, 2, 4, 8 and 16%, respectively. Four runs are for textile wastewaters, each containing reactive, sulphite, dispersive and basic dyes separately. In these runs, percentage of textile wastewater in the feed water was 10%. In the experimental run for night soil, one percent of night soil was added to the domestic sewage to prepare the feed water. And, as controls, domestic sewages collected at 9 am and 11 am were prepared for two different runs. Table 4 summarizes the water quality of each feed water influent for each experimental run. Due to technical difficulties in the measuring devices, some figures are missing in Color Intensity (T).

Table-4 Influent Water Quality of Each Experimental Run of Activated Sludge Treatment

Name of Run	Turbidity	SS (mg/)	COD (mg/)	Color Intensity(S) ₁₀₀	Color Intensity(T)
Mixed Dyes Waste 1%	82 (50~175)	81.6 (57.0~108)	44.1 (31.7~53.5)	15.9 (13.4~20.6)	
Mixed Dyes Waste 2%	92 (50~250)	78.5 (48.8~146)	43.6 (30.4~62.1)	14.0 (9.9~19.5)	
Mixed Dyes Waste 4%	89 (33~190)	80.7 (45.0~190)	42.0 (27.1~52.5)	15.1 (10.6~23.6)	
Mixed Dyes Waste 8%	104 (53~220)	94.9 (60.8~218)	47.8 (37.6~70.6)	18.7 (13.2~37.1)	
Mixed Dyes Waste 16%	81 (22~160)	93.0 (39.1~214)	46.3 (35.3~62.7)	24.8 (12.9~42.3)	
Reactive Dye Waste 10%	114 (51~185)	89.1 (46.0~139)	50.8 (39.6~60.7)	74.1 (12.9~92.6)	15.4 (3.2~22.0)
Sulphite Dye Waste 10%	66 (37~168)	73.8 (52.7~108)	40.4 (32.4~47.9)	15.4 (10.2~22.2)	5.6 (3.6~7.9)
Dispersive Dye Waste 10%	162 (47~368)	173 (73.0~269)	82.0 (38.7~117)	23.5 (15.5~54.7)	8.9 (4.0~27.5)
Basic Dye Waste 10%	108 (45~178)	106 (69.0~150)	48.1 (36.4~56.2)	24.5 (9.3~102)	13.3 (5.3~48.3)
Night Soil 1%	156 (60~382)	124 (67.0~335)	64.3 (47.5~113)	25.1 (20.7~32.6)	5.4 (3.1~11.5)
Domestic Sewage Taken at 9 AM	99 (70~230)	122 (7.0~168)	52.1 (41.8~61.2)	17.3 (14.1~24.2)	
Domestic Sewage Taken at 11 AM	102 (42~245)	94.7 (25.0~171)	39.7 (19.4~65.1)	13.9 (11.1~18.8)	

The upper figures are the average values and the lower figures show the range.

Table 3 and Table 4 show some interesting points when compared. In the case of basic dye, after being mixed with domestic sewage, coloring caused by dissolved substances dropped markedly. Comparing with the case of reactive dye which is also hydrophilic, color intensity (S) of basic dye wastewater before mixing with domestic sewage is a little larger than that of reactive dye wastewater. But after the wastewaters are mixed with domestic sewage, the color intensity (S) of basic dyes become much smaller. This is reasoned to the fact that as the basic dye wastewater is not a real wastewater from plants and a reasonable amount of basic dyes are absorbed by the SS in the domestic sewage. Therefore, in such decoloring

treatment experiments, there is a danger of acquiring misleading results when, not employing actual wastewater from textile plants. The apparatus used for the experiment was a laboratory scale one with primary sedimentation tank of 4 liters, aeration tank of 18 liters, and final settling tank of 7.5 liters. Experimental conditions are shown in Table 5. The feed water was prepared every day from the samples taken on the same day or one day before. The feed water was mixed slowly and continuously in the storage tank to prevent sedimentation of suspended matters in the raw water.

Table-5 Experimental Conditions

Flow Rate	55 ml/min.
Settling Time of Primary Settler	1.2 hrs.
Aeration Time	5.5 hrs.
Settling Time of Secondary Settler	2.3 hrs.
Water Temperature in Aeration Tank	20°C
Experimental Period in Each Run	2 weeks

As for seed sludge of activated sludge, the activated sludge at the Chubu Sewage Treatment Plant was used for the experimental runs with textile wastewater. With regards runs with night soil and domestic sewage, the activated sludge of the Yayoi Sewage Treatment Plant in Hamamatsu that exclusively handles domestic sewage was used. The experimental period for each run was 2 weeks. With regards experimental runs with specific dyes, two weeks of acclimation period were given for each run. No acclimation period was given for other runs since water quality of feed water was similar to that of the treatment plant where seed sludge was collected. The raw sludge at the preliminary settling tank was withdrawn arbitrarily depending upon the generation of sludge. The adjustment of return sludge and the withdrawal of the excess sludge were conducted at the secondary settling tank by determining the amount based on the results of measuring the SV, MLSS, etc. of the aeration tank.

The water temperature in the aeration tank was maintained at 20°C throughout the experimental period.

The water quality of feed water and treated water was measured daily. pH, SV, and DO in the aeration tank was also measured daily. MLSS was measured 2 to 4 times during the experimental period.

3.2 EXPERIMENTAL RESULTS

Table 6 shows DO, MLSS, SVI and BOD loading in the aeration tank for each experimental run. The BOD loading indicated in the table is a rough estimate which is calculated from COD of feed water since measurement of BOD in feed water was not performed. Fig. 5 shows the removals of COD, SS and turbidity. According to Fig. 5, the removals of SS with regards sulphide and basic dyes were slightly bad. However, SVI in these runs was smaller when compared with runs of the mixed dyes waste and bulking was not observed. Rather, in runs of mixed dyes waste

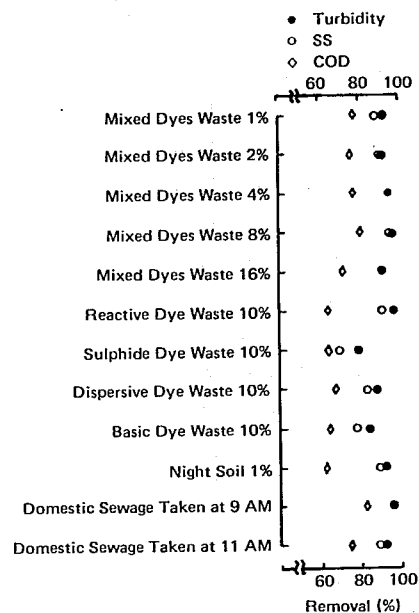
there was a tendency of causing bulking. The COD removal was about 65 percent in runs of specific dye waste and about 75 to 80 percent in runs of domestic sewage and mixed dyes waste with low ratios. In general, the COD removal because low when the textile wastewater was mixed. However, in the experimental runs with low removal rate, the BOD loading was high, therefore it was not clear whether the difference in treatment conditions or textile wastewater had caused the drop in the removal rate. Since the aim of the experiment was to investigate the decolorization effect of activated sludge process, further examinations were not conducted because the treatment condition of each experimental run was judged fairly satisfactory.

Table-6 Operating Parameters of Activated Sludge Process of Each Run

Name of Run	pH	DO (mg/)	SV (%)	MLSS (mg/)	SVI	BOD Loading (kg/SS·kg/d)
Mixed Dyes Waste 1%	7.0 (6.7~7.3)	0.9 (0.3~1.9)	19.3 (9.0~31.5)	1330 (1230~1420)	145	0.19
Mixed Dyes Waste 2%	7.2 (7.0~7.4)	0.9 (0.3~4.5)	20.6 (4.5~31.0)	1200 (1070~1330)	170	0.21
Mixed Dyes Waste 4%	7.2 (7.1~7.4)	0.4 (0.3~0.6)	27.6 (14.5~47.0)	1220 (850~1860)	225	0.20
Mixed Dyes Waste 8%	7.1 (6.2~7.3)	0.8 (0.5~1.6)	24.2 (10.5~48.0)	1490 (1170~2300)	160	0.19
Mixed Dyes Waste 16%	7.2 (6.8~7.6)	1.1 (0.3~4.1)	25.2 (3.0~73.5)	1740 (1400~2400)	145	0.15
Reactive Dye Waste 10%	7.4 (7.1~7.6)	1.2 (0.3~3.1)	13.0 (5.0~24.0)	560 (380~780)	174 (119~212)	0.52
Sulphide Dye Waste 10%	6.6 (5.7~7.2)	1.5 (0.4~2.9)	8.0 (5.0~14.0)	1320 (880~1790)	64 (48~78)	0.18
Dispersive Dye Waste 10%	6.8 (6.2~7.2)	1.8 (0.8~5.0)	12.0 (7.0~15.5)	1110 (980~1270)	99 (78~134)	0.42
Basic Dye Waste 10%	7.3 (6.9~7.8)	3.2 (0.9~6.9)	13.0 (7.0~24.0)	1060 (600~1590)	117 (98~145)	0.26
Night Soil 1%	7.6 (7.4~7.9)	1.5 (0.2~3.1)	11.5 (2.0~28.0)	1030 (970~1150)	141 (82~183)	0.36
Domestic Sewage Taken at 9 AM	7.0 (6.5~7.0)	0.7 (0.3~1.6)	18.2 (9.0~30.5)	1540 (1430~1660)	120	0.20
Domestic Sewage Taken at 11 AM	7.4 (6.1~7.0)	1.5 (0.4~4.7)	12.6 (0~24.0)	1560 (1380~1740)	80	0.15

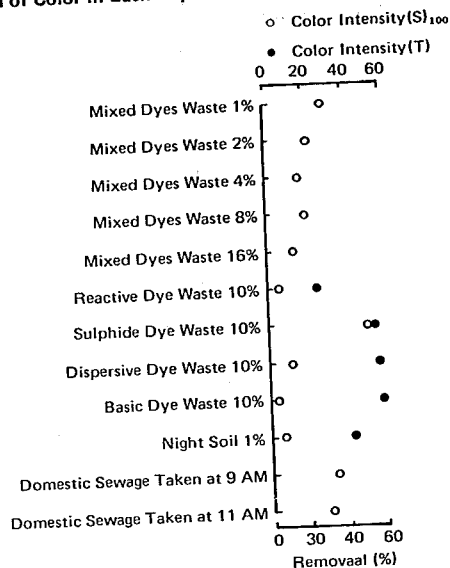
The upper figures are the average values and the lower figures show the range.

Fig.-5 Removal of Turbidity, SS and COD in Each Experimental Run of Activated Sludge Treatment



The removal of color intensity in each experimental run is summarized in Fig. 6. Since color intensity is not a linear index, the concept of removal may not be appropriate. But for convenience sake the removal was defined as the ratio of the difference of color intensities of the feed water and the treated water to the color intensity of the feed water. The removal of color intensity (T) of runs of mixed dyes waste and domestic sewage are not listed owing to malfunctioning of measuring devices.

Fig. 6. Removal of Color in Each Experimental Run of Activated Sludge Treatment



The removal of color intensity (S)₁₀₀ was about 30 to 40% for runs of domestic sewage. But when textile wastewater was mixed, the removal was about 20% with regards runs of mixed dyes waste and below 10% concerning runs of specific dye waste excluding that of sulphide dye waste. With regards sulphide dye waste, substances classified as dissoluble were predominantly in the form of colloid particles and were absorbed by the activated sludge, thus giving higher removal. Furthermore, it is noteworthy to mention that sewage added with night soil was very low in removal compared to sewage containing only domestic sewage.

Also, concerning removal of color intensity (T), it was about 60% for the hydrophobic dispersive and sulphide dyes with the apparent color by suspended matters considered totally removed. Naturally, the removal of color intensity (T) for the hydrophilic reactive dye waste water was as low as 25%. With regards basic dye waste water which is also hydrophilic, the removal of color intensity (T) was extremely high owing to the reasons mentioned before that actual waste water from textile plant was not used. In short, as it was a synthetic wastewater by artificially dissolving dyes in water, the dyestuffs were adsorbed by the SS or activated sludge in the water and thus the apparent removal rate was considered to be high. When actual wastewater from textile plant is used, it is assumed that the removal of color intensity (T) is extremely small.

To further study on the removal of color caused by dissolved substances, chromaticity diagrams were made for samples of filtered feed water and treated water (0.45 μ membrane filtration). Figures 7 to 10 show the chromaticity diagrams for each experimental runs of sewage containing only domestic sewage, sewage with 16% mixed dyes waste, sewage containing reactive dye and sewage

added with dispersive dye.

Fig.-7. Change in Color through Activated Sludge Process: Influent is the domestic Sewage

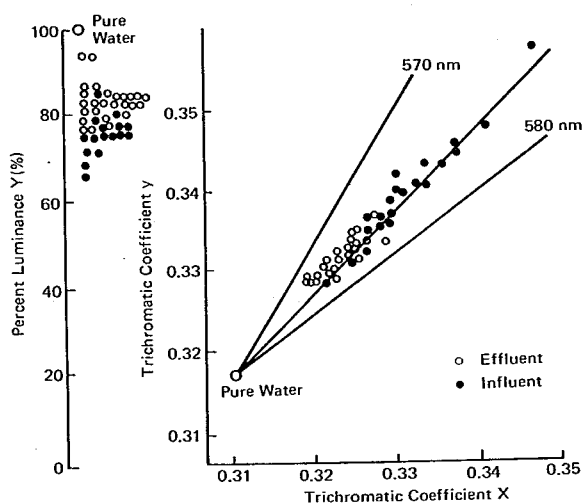


Fig.-8 Change in Color through Activated Sludge Process: Influent is the Sewage containing 16% of textile waste

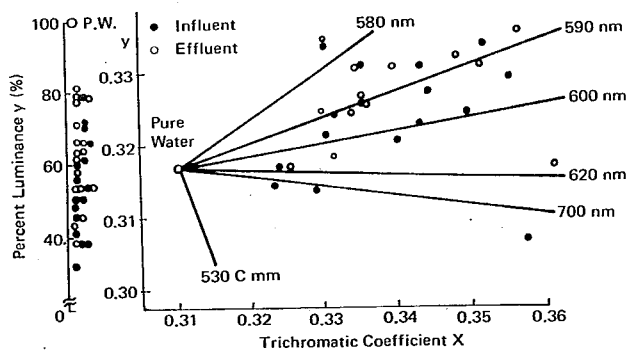


Fig.-9 Change in Color through Activated Sludge Process: Influent is the Sewage containing 10% of reactive dye waste

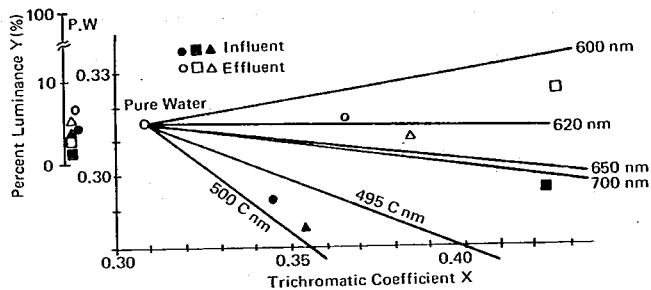


Fig.-10 Change in Color through Activated Sludge Process: Influent is the Sewage Containing 10% of dispersive dye waste

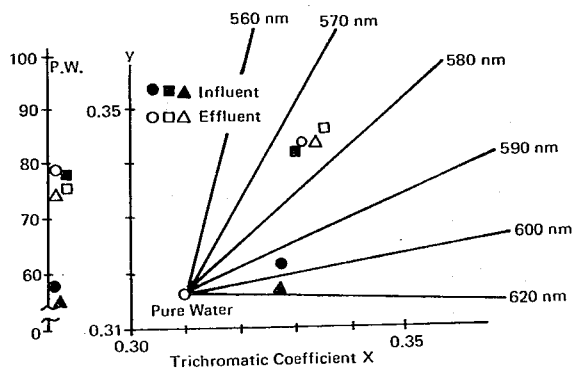


Figure 7 shows that the dominant wave length for both feed water and treated water containing only domestic sewage was 57t nm (yellow). And by applying the activated sludge process, the excitation purity has decreased while the luminance has increased, testifying to the fact that decoloring was evident.

On the other hand, Figure 8 shows that the luminance followed a trend of increase with regards sewage containing 16% of mixed dyes. And also the excitation purity followed a similar trend. In this experimental run, considering the fact that 80% of the sewage was domestic sewage, color by dissolved substances of the dyestuffs is considered to be strengthened by the activated sludge process. With regards this point, Figures 9 and 10 on reactive and dispersive dyes make the matters clear. Concerning the run of reactive dye waste, the hues of red and purple are treated and converted to red color in the neighborhood of 620 nm. The excitation purity, too, increased slightly. Furthermore, in case of the run of dispersive dye waste, even when the hue of feed water is either red or yellow, the hue of treated water changes to yellow (about 575 nm) with the excitation purity increasing greatly.

When processing sewage containing only domestic sewage, the excitation purity drops when treated by the activated sludge process. But as mentioned above, with regards sewage mixed with dispersive dye, although domestic sewage occupies about 80 to 90 % of the total, the excitation purity increases when treated by the activated sludge treatment. Also as the hue changes, the dyestuffs are considered to undergo changes owing to the activated sludge process and show stronger color.

Although the chromaticity diagram for sewage containing 1% of night soil is similar to that of sewage containing only domestic sewage, the rate of drop in excitation purity is smaller. And as understood from the comparisons made in Fig. 6, by the addition of 1% of night soil color removal drops to about 1/4 of the sewage containing only domestic sewage. Therefore, the color of domestic sewage that can be removed by activated sludge process is considered to be only that of miscellaneous drainage and not night soil.

Although not illustrated, the chromaticity diagram of the run of sulphide dye waste is nearly identical to that of domestic sewage, proving that sulphide dye can be removed by the activated sludge process.

4. REMOVAL OF COLOR FROM SECONDARY EFFLUENT BY PHYSICAL CHEMICAL PROCESS

When treating sewage containing textile wastewater by the activated sludge process, removal of color caused by suspended matters is quite effective. But, on the other hand, removal of color caused by dissolved substances is poor and sometimes color is strengthened by the treatment. Therefore, in order to effectively remove color by such substances, tertiary treatment may be necessary. Thus studies were made to examine the color removal by ozonation, activated carbon adsorption and chemical coagulation processes.

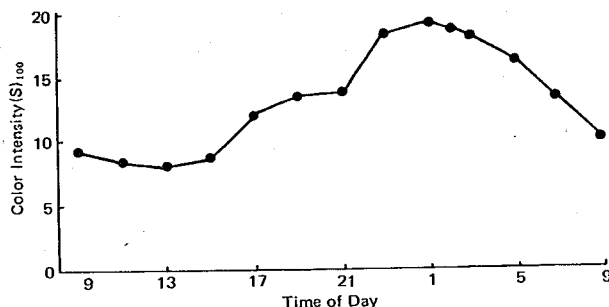
4.1 EXPERIMENTAL METHOD

4.1.1 Samples Used for the Experiments

Similar to the activated sludge process experiment, the experiments were conducted by preparing samples containing various types of dyes altogether and containing only specific dyes. As the former samples the secondary effluent (before chlorination) at the Chubu Sewage Treatment Plant in Hamamatsu city were used, and treated water from the activated sludge experiments was used for the latter samples.

As mentioned previously, about 20% of the influent at the Chubu Plant is wastewater from textile plants (about 13% when only colored wastewater), thus the effluent is considerably colored. Fig. 11 shows an example of the daily variation of color intensity (S_{100}) of the secondary effluent. Since visual color evaluation of river water mentioned before showed that a rough boundary between 'dirty' and 'clean' is about 2.5 in color intensity (S_{100}), the secondary effluent of the plant is colored to a good extent. The dominant wave length of light absorption was between 570 and 600 nm with the hue being yellowish orange.

Fig.-11 Diurnal Variation of Color Intensity(S_{100}) of the Secondary Effluent of the Chubu Sewage Treatment Plant



4.1.2 Experimental Method

(1) Ozonation process

The experiment was based on the batch test with an ozone generator of maximum capacity of 0.9 g/hour. One-liter of sample was used for each experiment, and the reacted ozone was calculated from the following equation:

$$\text{Reacted ozone (mg/l)} = [\text{Ozonation per unit time (mg/min)} \times \text{Elapsed time (min)}] - \text{Excess ozone (mg)}$$

The measurement of ozone contained in the water was conducted by titration of sodium thiosulfate.

(2) Activated carbon adsorption

The decolorization experiment by the activated carbon adsorption process was conducted by both the adsorption isotherm test and the continuous column test.

The experimental process of the isotherm test was as follows:

The activated carbon was crushed in the mortar, and only those passing through the 100 mesh sieve were taken and dried for 2 hours in the drying oven adjusted at 105 – 110°C. 0.01, 0.025, 0.075 and 0.15 grams of the activated carbon were placed in different 500 ml Erlenmeyer flasks with stopper, respectively. Then the flasks were added with the water sample which had been filtered through 1 μ membrane filter, and then thoroughly shaken to be placed in a 20 C constant temperature room overnight. The color intensity (S_{100}) of the water sample was measured prior to and after the adsorption test, and the difference was regarded as the color intensity adsorbed by the carbon. The adsorption test was repeated four or five times using the same water sample, and the arithmetical mean was obtained.

The activated carbons used in the adsorption isotherm test with the secondary effluent of the Chubu Plant were 12 types of 7 manufacturers. Concerning other secondary effluents, three types of activated carbons were used. The selection of three types of carbons were based on the test results with the Chubu plant effluent, and one type of carbon was chosen from each category evaluated as 'good', 'normal' and 'poor'. The 12 types of activated carbon were all of coal type of which

four were spherical carbons and the rest granular carbons.

The activated carbon column used in the continuous test was made of acrylic resin with an inner diameter of 34 mm and length 2 m. The operation of the carbon column was of a pressurized down-flow type. The continuous test was held only on the filtered secondary effluent of the Chubu treatment plant.

First, to examine the influence of contact time, a single type of activated carbon was selected. And tests were conducted by setting the condition at LV 100 (m/day) and SV at 2, 4, 6, 8, 10, and 12 (1/hour). Next, the color removal by activated carbon was compared of the 12 types at conditions of LV 100 (m/day) and SV 4 (1/hour).

(3) Chemical coagulation process

The following chemical coagulants were used in the tests: Four types of metal coagulants including alum, polialuminum chloride (PAC), ferric chloride and lime. Twelve types of polymers including eight cationic and four anionic coagulants.

All tests were conducted by jar tests, using coagulants independently and in combination. The mixing were conducted in three different speeds as follow: rapid mix (150 rpm), medium mix (80 rpm) and flocculation (40 rpm). When single coagulant was used, the mixing time was 1.5 minutes for rapid mix, 0.5 minutes for medium mix and 3 minutes for flocculation. And when the coagulants were combined, the time was 3, 1 and 6 minutes respectively.

4.2 EXPERIMENTAL RESULTS AND DISCUSSION

4.2.1 Ozonation

Ozone's ability to remove color caused by organic substances is well known. In this experiment, it was also confirmed that the color removal by ozone of secondary effluent colored by textile wastewater produced extremely good results. Fig. 12 shows the relationship between the amount of reacted ozone and the color intensity (S_{100}) removal. Here too, the removal is defined as the ratio of the difference in color intensity of the feed water and the treated water to the color intensity of the feed water for convenience sake.

Fig.-12 Removal of Color by Ozonation: Samples are filtered secondary effluent of the Chubu Sewage Treatment Plant

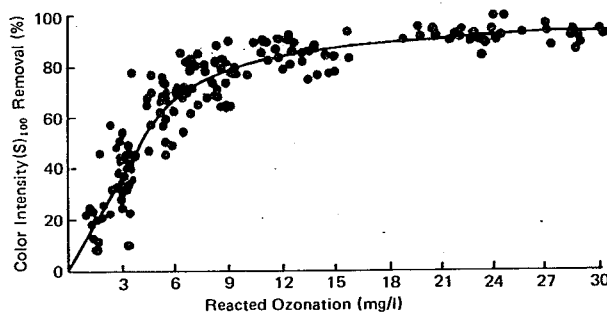


Fig. 13 similarly shows the change in color by ozonation on the chromaticity diagram. It shows that with the increase in reacted ozone, the luminance increases and the excitation purity decreases proving that decolorization is progressing. Also, the dominant wave length changes from 588 nm to 577 nm, and the orange hue of the feed water changes to a yellowish hue.

Fig.-13 Change in Color by Ozonation; The sample is filtered secondary effluent of the Chubu Sewage Treatment Plant. Figures in the parentheses show reacted ozone in mg/

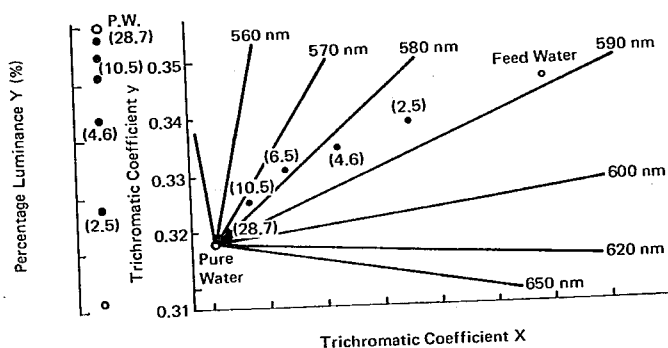
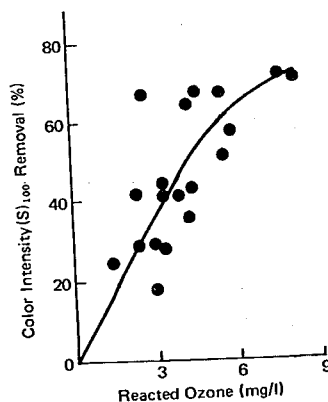


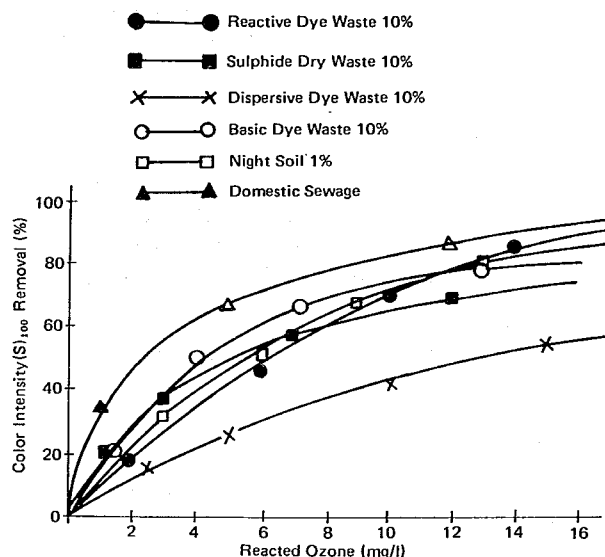
Fig. 14 shows the relationship between reacted ozone and color intensity (S_{100}) removal with regards non-filtered secondary effluent of the Chubu Sewage Treatment Plant. It shows similar results as shown in Fig. 12, and when ozone of low concentration is dosed to the secondary effluent of this level of SS (roughly 20 mg/l), ozone consumption or its decoloring effect will not be much affected. Also concerning removal of color intensity (T), similar results were obtained although the deviation of data were a little larger.

Fig.-14 Removal of Color by Ozonation: Samples are non-filtered secondary effluent of the Chubu Sewage Treatment Plant



As to the results of the runs of specific dyes, the relation between reacted ozone and removal of color intensity (S_{100}) was as shown in Fig. 15. In Fig. 15, results of runs of 1 percent night soil addition and domestic sewage alone are also shown for comparison. The figure indicates that except for the extremely poor decoloring effect of dispersive dye, there were no significant differences observed of other dyes. However, they seem to be slightly inferior when compared with secondary effluent of domestic sewage.

Fig.-15 Removal of Dissolved Color by Ozonation: Samples are secondary effluents obtained by treatment of sewage containing specific kinds of dye and others



Although not illustrated, relationship between color intensity (T) removal and reacted ozone was found to be similar to that shown in Fig. 5. In this case, however, not only dispersive dye but also sulphide dye had a poor color removal. Perhaps, this is reasoned to the fact that as both dyes are hydrophobic, oxidation by ozone is not effective in removing color caused by suspended matters.

From Figures 12, 14 and 15, it can be commonly said that decolorization progresses roughly in proportion to the amount of reacted ozone until the removal reaches 60 or 70 percent. The color remaining after ozonation, as an example of which is shown in Fig. 13, is yellowish in most case with the dominant wave length being in the neighborhood of 575 nm. It is well known that yellowish color often remains when wastes of high concentration is treated by ozone. Therefore, the residual color after ozonation of secondary effluent might be caused by oxidation products of dissolved dye. However, since similar color remains in the ozone treated effluent when domestic sewage, or domestic sewage and night soil were handled

it was considered that remaining color was caused mainly by night soil.

4.2.2 Activated Carbon Adsorption

The adsorption at equilibrium state of dissolved organic substances by activated carbon may be expressed by the following Freundlich Equation:

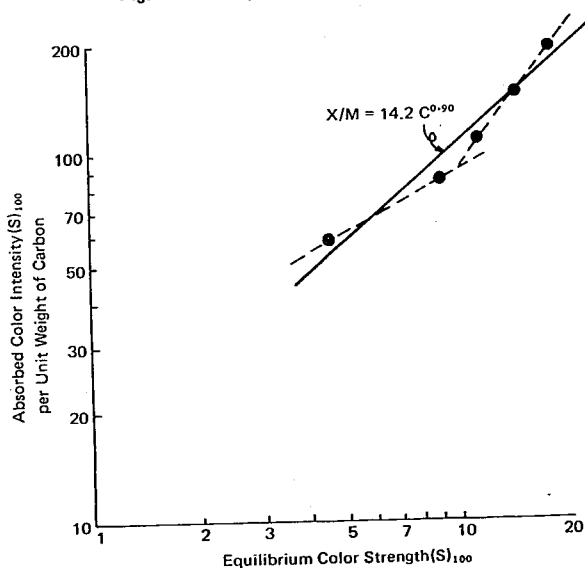
$$X/M = KC$$

Here, X is the amount of adsorbed substances. M is the amount of activated carbon. C is the equilibrium concentration after adsorption. And K and n are constants.

When applying adsorption of color in the equation, concentration of the color causing substances or a parameter which has a linear relationship with the substance should be used. But since there is no proper means of measuring the concentration of color causing substances, the color intensity $(S)_{100}$ was incorporated to obtain approximate values.

Adsorption isotherm tests were carried out using the secondary effluent of the Chubu sewage treatment plant and 12 types of activated carbons, A to L. In some cases, straight lines were obtained. In most cases, however, knicks appeared and two straight lines gave closer approximation than single line. An example is shown in Fig. 16. As mentioned before, this is caused by the fact that the adsorption expressed by color intensity is not in proportion to the concentration of the color causing substances and also the substances different in adsorption characteristics were present.

Fig.-16 Adsorption Isotherm, Carbon A



However, to make rough comparisons, it was judged that single line was possible for approximation, and, thus, K and $1/n$ values of the equation were calculated from the data obtained by the experiments using the secondary effluent of the Chubu Plant. The result is shown in Table 7. It indicates that the adsorption ability differs greatly depending on the types of carbons. Activated carbons H, E, J, I and G have shown high decoloring efficiency while carbons L, K and B were poor.

Table-7 Constants in Freundlich Equation: Adsorption of Color from Secondary Effluent containing Mixed Dyes

Name of Carbon	K	$1/n$
A	14.2	0.90
B	6.8	1.20
C	12.2	0.75
D	12.0	0.80
E	62.0	0.45
F	4.4	1.10
G	45.0	0.60
H	100	0.40
I	46.0	0.55
J	64.0	0.50
K	11.0	0.90
L	2.9	1.20

Based on the assumption that the average color intensity $(S)_{100}$ of the feed water is 22 from Fig. 11 and that 80 percent of this is to be removed, the necessary quantities of carbon with the largest adsorption capacity and with the smallest adsorption capacity differ about 10 times.

Adsorption isotherm tests with secondary effluent of the sewage containing 10 percent of textile wastewater of specific dyes and the sewage containing one percent of night soil were also conducted by using carbons E, H and L. K and $1/n$ values obtained from the tests are shown in Table 8. The difference in activated carbons had similar effect to those obtained from the tests using secondary effluent of the Chubu treatment plant. However, it should be noted that the adsorption characteristics differed greatly dependent on the difference in dyes. Reactive dyes were adsorbed comparatively easily while basic dyes proved most difficult to adsorb of all tested dyes.

Table-8 Constants in Freundlich Equation: Adsorption of Color from Secondary Effluent containing Specific Types of Dye and Others

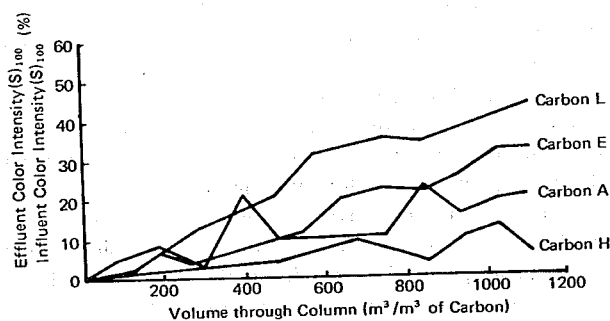
Name of Carbon Name of Dye	K			1/n		
	E	H	L	E	H	L
Reactive	123	177	0.45	0.21	0.18	1.51
Sulphide	22.2	38.0	0.25	0.89	0.70	0.72
Disperse	9.7	26.6	0.14	1.19	0.87	2.48
Basic	26.0	22.2	0.83	1.28	1.48	1.61
Night Soil	52.0	62.0	8.0	0.42	0.48	0.78

The effect of contact time was investigated by continuous column test using the carbon A. The filtered secondary effluent of the Chubu Plant was used as the feed water. As a result, as far as color intensity removals at the same feed water volume applied to carbon volume was concerned, the removal rate was obviously large when SV = 2 (1/hour, hereinafter the same). However, within the SV range of between 4 and 12, there was no significant difference.

Furthermore, to confirm the results obtained from the adsorption isotherm tests, continuous tests were conducted on all activated carbon employed in the experiment by using the filtered secondary effluent of the Chubu Plant as feed water.

In this instance, the LV was set at 100 (m/day) and SV at 4 (1/hour). The results of the selected activated carbons are shown in Fig. 17.

Fig.-17 Comparison of Adsorptive Capacities of Test Carbons for Color Strength(S_{100})
Influent is the secondary effluent of the Chubu Sewage Treatment Plant



From the adsorption isotherm test, activated carbon E was superior in adsorption characteristic to carbon A. However, data shown in Fig. 17 are not so. There were this kind of minor differences in the results of both tests, but as a whole, continuous column tests gave the similar results to those obtained from the adsorption isotherm tests.

The difference in adsorption capacity owing to the difference in activated carbons was compared with the characteristics of the carbons themselves. Table 9 shows the characteristics of activated carbons given by each manufacturer. The blank space in the Table is due to lack of information. Although the values listed in the Table are not so precise, the activated carbons having greater transitional pores can be judged to have higher adsorption capacity. Therefore, dyestuff substances that have undergone biological treatment are likely to be adsorbed in the transitional pores.

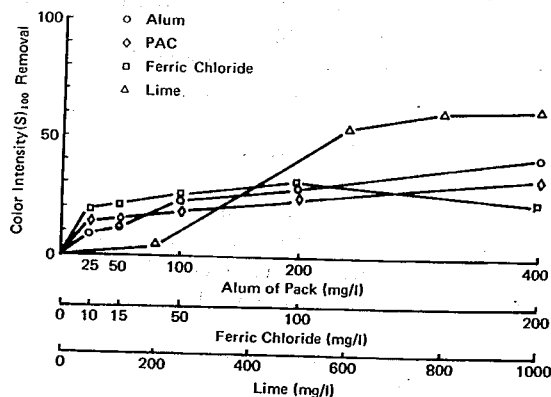
Table-9 Properties of Test Carbons

Test Carbon	A	B	C	D	E	F	G	H	I	J	L	K
Apparent Density g/cc	0.48	0.44	0.45 +0.5	0.45 -0.5	0.4 -0.45	0.43	0.44	0.41	0.40	0.4 -0.5	0.49 -0.51	0.44 -0.51
Hardness %			>98	>98	>90	97	90	91	99	>93	>99	88 -92
Ash %	<8.0	<8.5				3.1	6.4	7.2		<10	15 -16	3 -5
Iodine Adsorption Cap. mg/g	>900	>1000	900 -1150	900 -1150	>350	1080	924	785	1014	>1000	990	1000 -1100
Methylene Blue Ads. Cap ml/g											160	200 -220
Benzene Ads. Cap %												
Specific Surface Area m ² /g	>950	1000 -1100	900 -1200	900 -1200	900 1200	11001	1070	750		>1000	900	
Approximate Pore Size Distribution	20 Å cc/g	0.12										
	20-10 ³ Å cc/g	0.22				0.24	0.85	0.92	0.92		0.15	0.20
	10 ³ -10 ⁴ Å cc/g					0.48	0.43	0.48	0.30		0.32	0.27

4.2.3 Chemical Coagulation Process

Various chemical coagulants were used in the jar tests of the secondary effluent of the Chubu Plant to investigate on the decoloring efficiency. In general, only unsatisfactory results were obtained. As an example, the test results employing metal coagulants are shown in Fig. 18. The most effective was lime. However, in order to conduct effective removal, extremely high dose was needed proving impractical to serve only for color removal.

Fig.-18 Relationship between Coagulant Dose and Color Strength(S)₁₀₀ Removal: Samples are the secondary effluent of the Chubu Sewage Treatment Plant



With regards polymer, anionic coagulants were virtually ineffective. However, cationic coagulants, when added with over 10 mg/liter, more than 50% of color caused by dissolved substances was removed, but such a high dose was beyond practical use. Poor flocc settlability is another defect.

Any combinations of metal salts and polymers did not give satisfactory result too.

5. Summary and Conclusion

(1) As a result of examining the existing measurement methods of color, particularly color due to industrial wastewater, it is considered most appropriate to express color by color difference with pure water. This can be done by measuring the normal transmittance value of the filtered sample with regards color by dissolved substances, and by measuring the total transmittance value with regards suspended matters. The former is referred to as color intensity (S) and the latter color intensity (T).

Color intensity of river water and visual impression obtained by looking at the river were compared. Although the figures are rough, the limits that did not make people feel uncomfortable or repugnance was 2.5 in color intensity (S)₁₀₀ and 0.7 in color intensity (T), respectively.

(2) Experiments on activated sludge treatment of sewage containing about 10 percent of textile wastewater were carried out. The removal of color caused by suspended matters was quite effective, but removal of color caused by dissolved substances was generally poor, and color was sometimes strengthened.

Color caused by dissolved substances in domestic sewage was removed 30 – 40 percent by activated sludge process. However, 1 percent of night soil addition to the domestic sewage, decrease color removal rate considerably.

(3) Experiments on ozonation of secondary effluent was conducted to remove residual color due to textile wastewater. Color caused by dissolved substances was effectively removed by ozonation. About 60 and 70 percent removal was obtained at a dose of less than 10 mg/l. Removal of color was roughly proportional to dose up to this level. However, when it exceeded this level, the removal of color per unit of reacted ozone decreased considerably.

Color caused by suspended matters was not effectively removed by ozonization. Rather, the suspended matters in secondary effluent was irrelevant to ozone consumption.

(4) Similarly, experiments on activated carbon adsorption of color remaining in secondary effluent were conducted.

Adsorption by activated carbon depended greatly on the types of activated carbons and the types of dyes present in water. It was found that activated carbons with greater transitional pores were particularly effective to remove residual color. Within the range of the dyes experimented, color by reactive dye was comparatively well removed by activated carbon.

(5) Chemical coagulation was considered to be inadequate process when the purpose is only to remove residual color in the secondary effluent.

CHAPTER 5 DEVELOPMENT AND EVALUATION OF AUTOMATIC WATER QUALITY MONITORING EQUIPMENTS

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CHAPTER 5

DEVELOPMENT AND EVALUATION OF AUTOMATIC WATER QUALITY MONITORING EQUIPMENTS

I. CURRENT STATE OF THE DEVELOPMENT OF AUTOMATIC WATER QUALITY MONITORS FOR HAZARDOUS SUBSTANCES IN WASTEWATER

1. INTRODUCTION

When a public sewage system receives industrial wastewater, provisions should be taken to prevent possible adverse effects on facilities or treatment function. It should not cause any difficulty in meeting the effluent standards applied to the treatment plant, nor create particular difficulty in treatment and disposal of sewage sludge. For these purposes, ordinances concerning pretreatment standards are provided to regulate the quality of wastewater being discharged into a sewerage system. Especially with regards to hazardous substances, pretreatment standards can be, and in most cases are, as stringent as the effluent standards applied to industrial wastewater discharged directly into public bodies of water.

To effectuate such ordinances and regulations, it is important not only to thoroughly guide and supervise the pretreatment facilities of the factories but also to establish a system to monitor water quality of industrial wastewater being discharged, which the municipalities across the nation are presently endeavoring. However, by a manual monitoring system, there are limits in the frequency of city officials inspecting all of the industrial plants, and there are danger of overlooking the discharge of harmful wastewater either by accident or on purpose. On the other hand, the current status of automatic monitors is that there are only few automatic monitors put to practical use to check wastewater being discharged. And even those put to practice are complicated in structure and require considerable manpower for operation and maintenance. Therefore, installation of these equipments, if they are installed, are limited to the places such as sewage treatment plants and pumping stations. However, automatic monitors that are most desirable to be developed are those highly reliable and free from maintenance, for example, similar to flight recorders mounted on aircraft and those which can readily be installed in sewers or outlets of industrial wastewater into sewers. For the past few years, the Ministry of Construction have entrusted the Association of Electrical Engineering to conduct researches to boost development of such automatic water quality monitors for hazardous substances.

This report summarizes on the present situation of the development of automatic water quality monitors for hazardous substances and related problems.

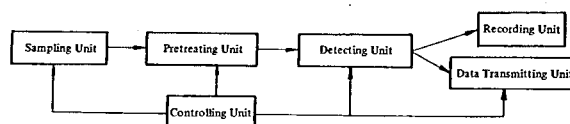
2. PROBLEMS RELATED TO THE DEVELOPMENT OF AUTOMATIC MONITORS

2.1 OUTLINE

An automatic water quality monitoring device can be divided into several units as shown in Fig. 1. The structure and system of each unit differ depending on the characteristics of water handled and substances to be monitored, thus the

problems involved are varied. Even when water is comparatively clean and the constituents are relatively simple, automatic measurement of hazardous substances is not easy. Since sewage contains wide variety of substances, most of which interfere the measurement, and have the characteristics to easily develop biological slime, automatic monitoring of harmful substances in sewage is quite difficult.

Fig.-1 Schematic Configuration of Automatic Water Quality Monitor



Major problems involved are as follows:

a) Suspended solids

The sampling pumps and valves in the piping are easily subjected to clogging in continuous operation as wastewater contains a good amount of suspended solids and floating substances. Normally, the substances to be measured in wastewater like heavy metals are contained in suspended solids. However, the method to detect and analyze substances is generally only possible when the substances are in dissolved form. Therefore, a process to dissolve substances contained in suspended solids becomes necessary. Even when this dissolving process is unnecessary, there are many instances requiring pulverization of suspended solids to obtain stable data.

b) Interferences

As substances found in wastewater are diversified and varied, when analyzing hazardous substances such as heavy metals, it is necessary to either eliminate interferences or mask them. Accordingly, the automatic monitoring devices must be equipped with a mechanism to eliminate the interferences. These mechanisms are hard to automate, and even when automation is possible the mechanical structures will be extremely complicated.

c) Biological slime

Wastewater usually contains a large amount of organics making it ideal for microorganisms to grow. Therefore, slime easily develops in the inner walls of the equipment coming in contact with the sample. Slime not only causes clogging of piping but also obstructs measurement by developing at the surface of the detector. Also, substances contained in water are often adsorbed on the slime to change quality of water, or slimes are often detached from the wall to interfere measurements.

2.2 SAMPLING UNIT

The engineering methods and equipments are available to take samples of wastewater directly from a sewer either in large rate continuous flow system or batch system. However, concerning sampling of extremely small continuous flow, the available methods and equipments are not considered satisfactory, since suction inlet and piping are liable to clog easily. Submersible pumps (with cutter) and air-

lifts are employed for sampling continuous large rate discharge while vacuum suction sampling or air lifts are used for batch sampling. Generally, strainers of suction inlets are not useful and at times are harmful by accelerating clogging.

In general, there are two types of automatic monitors, that is, continuous type and batch type. In case of the continuous type, sampling of large rate flow is taken at first. And then the necessary amount of sample is supplied to the monitoring device via a branch tube directly from the main piping or through a head tank. In this way, the shape of the inlet of a branch tube receiving small rate of flow can be formed to hydraulically make it difficult to clog. Also it is possible to shorten the length of tubing with the small rate flow. However, even though employing such method, it is difficult to maintain a constant flow over a long period of time without maintenance. Therefore, when quantitative accuracy is demanded, it is necessary to conduct an appropriate pretreatment before supplying sample to the measuring equipment.

In case of batch type monitoring device, sample volume is measured at each detection, thus there is almost no problems on the quantitateness of the sample. Therefore, as far as the sampling unit is concerned, the batch type is easier to operate and maintain.

2.3 PRETREATMENT UNIT

The role of a pretreatment unit differs depending on the substances to be analyzed and detection methods. But generally, the purposes of a pretreating unit are (a) to prevent formation of slime, (b) to dissolve substances contained in suspended solids, (c) to remove or mask interferences, and (d) to adjust samples to best conditions for measurements.

Hazardous substances, particularly heavy metals, in wastewater, are in most cases present in the form of suspended solids. Whatever analytical method is taken, the substances must once be put in a dissolved form. And when the analysis is conducted manually, samples are pretreated by wet oxidation with sulfuric-nitric acids or nitric-perchloric acids to oxidize and decompose substances. However, as it is structurally and materially difficult to incorporate such powerful oxidizing process in the automatic monitoring units, pretreatment to merely lower pH of the sample by dosing acid is normally done. When compared to wet oxidation, mere lowering of pH values can not be considered a perfect pretreatment method. But it is effective to a certain degree to dissolve the heavy metals in suspended solids.

Figures 2 ~ 6 show the results of experiments on solubilization of heavy metals in suspended solids by pH adjustments and heating. Samples are raw sewages taken at 4 to 8 sewage treatment plants. These samples were added with a hydrochloric acid for pH adjustment and then filtered. To examine the effect of heating, a part of the sample was heated prior to the filtration. The concentrations of metals in the filtered solutions were analyzed and the dissolved fraction of each metal was calculated. 300°C hot plates were used for heating at about 95°C of water temperature for five minutes. The analysis was conducted by the atomic absorption spectrophotometry (direct aspiration) after wet oxidation of the sample. In case when the metal concentrations in raw sewage was too low to analyze, return sludge was added

to the sample to raise the concentrations.

Fig.-2 Solubilization of Heavy Metal in SS in Wastewater by pH Adjustment —Chromium

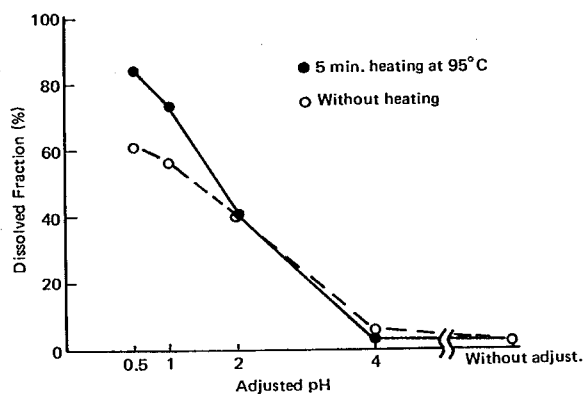


Fig.-3 Solubilization of Heavy Metal in SS in Wastewater by pH Adjustment —Copper

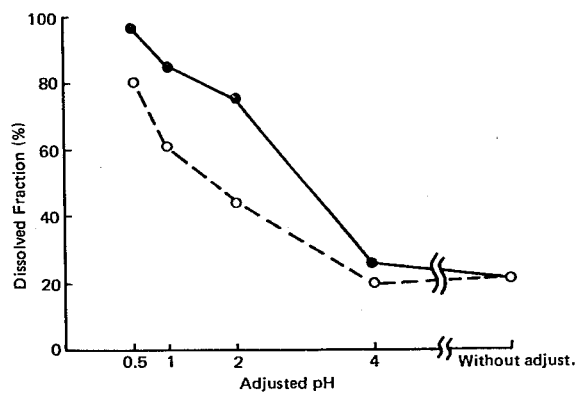


Fig.-4 Solubilization of Heavy Metal in SS in Wastewater by pH Adjustment —Iron

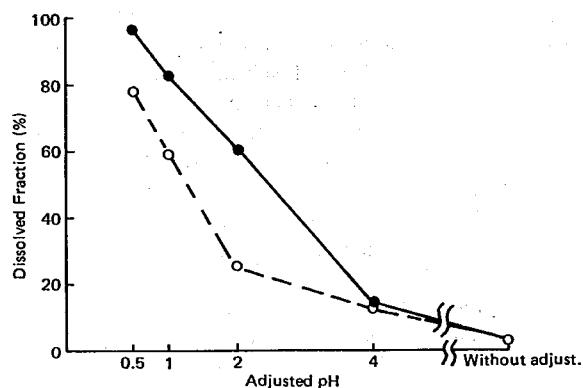


Fig.-5 Solubilization of Heavy Metal in SS in Wastewater by pH Adjustment —Zinc

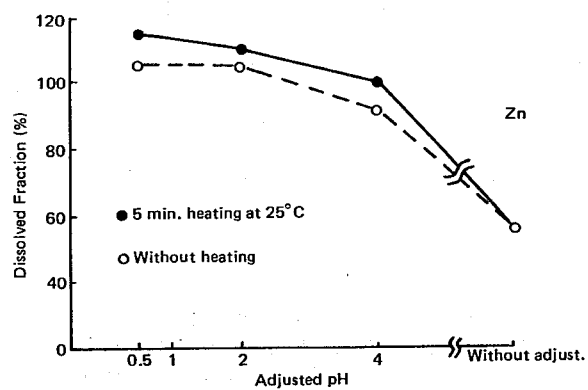
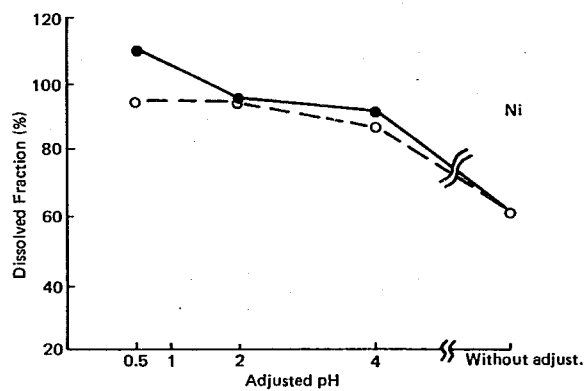


Fig.-6 Solubilization of Heavy Metal in SS in Wastewater by pH Adjustment —Nickel



As understood from the data of the samples without pH adjustment in these figures, a good portion of metals in the sewage was contained in the suspended solids. Especially, dissolved fractions of chromium and iron in the unadjusted samples were quite small. Although the dissolved fractions of zinc and nickel were comparatively high, they were about 50 percent. The lowering of pH is effective to increase the dissolved fraction as shown in the figures. At pH value of 2, zinc and nickel were almost totally dissolved. But with regards chromium, copper and iron, only 80 percent of them were dissolved even when pH value was lowered to 0.5. Heating together with the lowering of pH was found to be effective, and the dissolved fractions of chromium, copper and iron increased to about 90 percent at pH 0.5. Incidentally, the values shown in the figures are average values, and there were deviations of data between 10 and 30 percent expressed in standard deviation. The relationship between pH and dissolved fraction might be dependent on characteristics of wastewater. Therefore, in the process of dissolving substances in suspended solids, measurement errors to some degree would be produced.

Concerning prevention of slime formation, since disinfection is conducted by both acid addition and heating, pretreatment for dissolution of metals can prevent formation of slime.

As to removal of interferences, methods may differ depending on the parameters to be measured and methods of measurement, thus making it difficult to generalize the methods. However, as far as the analysis of heavy metals are concerned, organics are the common interferences. Since it is not wise to automate wet oxidation process for automatic monitors, the activated carbon adsorption may be only process to be acceptable. The adsorption of heavy metals contained in the sample to activated carbon was very small under acidic condition.

2.4 DETECTING UNIT

Measuring methods for automatic water quality monitors for hazardous substances include automated colorimetry, ion selective electrodes and polarography. Atomic absorption spectrophotometry, high frequency plasma spectrography and X-ray fluorometry may be included, although they are too sophisticated in mechanism and considered unsuitable for on-site automatic measurement. The possibility of application of each method is listed in Table 1.

Table-1 Analytical Methods and Their Applicability to Automatic Monitor

Substances Methods	CN	Cd	Pb	As	Org-P	R-Hg	T-Hg	Cr(VI)	T-Cr	Phenols	Cu	Zn	D-Fe	D-Mn	F
Automated Colorimetry	○		△	△				○	○	○	○	○	○	△	△
Ion Selective Electrode	○	○	○								○				○
Polarography	○	○	○								○				
Atomic Absorption		○	○	○		△	○	△	○		○	○	○	○	
Others	High Frequency Plasma Spectrophotometry and X-ray Fluorometry for Metals, and UV Absorption for Cr (VI)														

Notation ○ : Possible, △: difficult

2.4.1 Automated Colorimetry

The most orthodox detecting method in automatic monitoring is automated colorimetry. When strict quantitative analysis is required, pretreatment is indispensable. However, for actual application, it is considered difficult to develop a monitoring device having complicated functions, such as wet oxidations, solvent extraction and so on. Therefore, the analytical methods for monitors are limited to those with relatively simple procedure, yet giving reasonably accurate results.

The following methods are some examples: Bathocuproin method for copper, diphenylcarbazide method for chromium, 4-aminoantipyrine method for phenol, isonicotinic acid-pyrazolone method of cyanide, etc. Even with these methods it is necessary to perform pretreatment, such as oxidation of trivalent chromium for analysis of total chromium, reduction of trivalent iron for measurement of total iron, reduction of divalent copper for appraisement of total copper, and distillation of cyanide for valuation of total cyanide.

When employing automated colorimetry, the problems involved are troubles caused by using wet chemicals and danger of resulting large measurement errors due to lack of complete pretreatment procedure to eliminate interferences. However, the latter is a common problem to any measurement method.

Since it is difficult to totally remove suspended solids, the device must have a mechanism that can correct the sample blank. Although sample blank correction can be done by the double beam system and others for continuous type monitors, the batch measurement is easier in this respect.

2.4.2 Ion Selective Electrodes

Ion selective electrodes available on the market are those for cadmium, lead, copper, cyanide and fluoride measurements. Fluoride electrode has high selectivity and less interferences. However, as regards other electrodes, they are many and serious interferences. The well known ones are Hg^{2+} , Ag^+ , Fe^{3+} and S^{2-} for cadmium, lead and copper electrodes, and S^{2-} for cyanide electrode. It is not that difficult to insert in the unit a process of dosing masking agents or other processes to eliminate the interferences by these inorganic ions. The greatest problem is the interferences caused by organics present in the wastewater. Table 2 shows the selectivity coefficients of selected organic substances. The Table shows that ionized organics cause extremely large interference. Actually, when measurements are done without removing the organics, for example using cadmium electrode, the measured values sometimes are lower by one order than the true concentration. Accordingly, when employing ion electrodes for the detecting unit, it is imperative to remove organics by activated carbon and soon.

Table-2 Selectivity Coefficients against Selected Organic Substances

Electrodes Substances	Cadmium	Copper	Lead
Ethyl Alcohol	$10^5 <$	$10^5 <$	$10^4 <$
Glucose	$10^4 <$	$10^4 <$	$10^4 <$
Sucrose	$10^5 <$	$10^5 <$	$10^4 <$
Acetic Acid	2.1	0.6	1.2
Succinic Acid	1.9	28	7.2
Tartaric Acid	21×10^2	84	54
Citric Acid	2.2×10^3	57	2.1
Linoleic Acid	$10^4 <$	$10^4 <$	$10^4 <$
Oxalic Acid	0.27	1.1	2.8
L-Ascorbic Acid	4.8	64	21
L-Gultamic Acid	2.2	$10^3 <$	4.0
Casein	3.1×10^2	8.4	54
Peptone	2.4	4.9×10^{-2}	15
Dextrin	1.6×10^2	6.1	2.3×10^2
Powdered Cream	18	2.1×10^3	34
Urea	7.0×10^4	1.8×10^2	90

Note : Figures in the table are the averages of the selectivity coefficients at cadmium concentrations of 0.01, 0.1 and 1.0 mg/l for the Cd electrode, at copper concentrations of 0.3, 3.0 and 30 mg/l for the Cu electrode, and at lead concentrations of 0.1, 1.0 and 10 mg/l for Pb electrode, respectively.

2.4.3 Polargraphy

Ordinary polargraph with dropping mercury electrode is occasionally used in the automatic monitors for rivers. But owing to the difficulty in coping with interferences such as organics, reducing substances, iron and other interfering substances, and the difficulty in maintaining proper condition of the dropping mercury electrodes, ordinary polargraph are considered unsuitable for monitors for wastewater. However, as the anode stripping voltimetry, which is one type of polargraphy, allow the use of mercury electrodeposited graphite electrode or glassy carbon electrode, it has a possibility for being applied in automatic monitoring devices.

There are three heavy metals possible for measurements at the same time by the anode stripping voltimetry – cadmium, lead and copper. According to a test employing a mercury electrodeposited graphite electrode, it was possible to obtain comparatively high precision measurements of lead and copper by dissolving these metals by acid addition followed by filtration and removal of dissolved oxygen. Organics contained in wastewater did not cause strong interference. However, with regards to cadmium measurements, when measurements were conducted in a sample pretreated in the above mentioned way, the characteristics of the electrode deteriorated tremendously thus the removal of organics was considered necessary.

The anode stripping voltimetry has given rise to such problems as expensive maintenance cost due to electrodeposition of electrodes at each 100 or 200 times of measurement and complicated data processing due to the necessity of obtain integral values instead of peak values of output electric current.

2.4.4 Atomic Absorption Spectrophotometry

The atomic absorption spectrophotometry is the most popular method in conducting manual analysis of heavy metals in wastewater. And the development of automatic monitors with this method as detecting unit is advancing to a certain stage. Especially with regards to mercury analysis, the flameless atomic absorption spectrophotometry was regarded as the only practical measurement method.

When measurements are conducted by the cold vapor atomic absorption method, the analysis of inorganic mercury is said to be effectively done by performing pretreatment of dosing ammonium chloride and heating. It is also reported that the measurement of total mercury was effectively conducted only by the oxidation with potassium permanganate under acidic condition.

Concerning other heavy metals, when the flame atomic absorption spectrophotometry and the flameless atomic absorption spectrophotometry are compared, it is considered that the flameless method is more appropriate from the view points of removing interferences by organics and the possibility of on-site installation. However, in case of the flameless method, it is difficult to automate the sample injection to the carbon atomizer. At this stage, atomic absorption spectrophotometry is considered to be too sophisticated and complicated for monitors being installed on-site.

2.4.5 Others

When ignoring complexity of the equipments, difficulty in operation and maintenance, and economy, the high frequency plasma spectrography and the X-ray fluorometry would be good methods since they have less interferences than other methods and have the merits of measuring various elements at the same time. However, the possibility of putting these methods to practical use at the present stage is dim.

Hexavalent chromium can be measured by ultraviolet absorption. This method utilizes the property of hexavalent chromium in alkaline solution that exhibits ultraviolet absorption at about 370 nm wave length, while trivalent chromium does not adsorb UV in the area of this wave length. The measurement of the hexavalent chromium concentration is seeked from the difference in the absorbance before and after the hexavalent chromium is reduced to trivalent in the sample. The greatest interference is ferric ion. When the ferric concentration is high, the it must be removed.

3. CURRENT STATUS OF DEVELOPMENT

On consignment from the Ministry of Construction, the Association of Electrical Engineering has organized a committee composed of users and manufacturers within its framework and has so far tried to develop and improve automatic

monitoring devices for total cyanide, total chromium, hexavalent chromium, cadmium and copper. In performing these works, specifications of the devices, such as accuracy of measurement, which are considered achievable, are determined, and long term field tests are to be conducted to confirm that the specification are met.

Of automatic monitoring devices, the total cyanide monitor, for the time being, has been developed, and its standard specifications were already published. However, concerning others, they are presently under development and are slated for commencement of field tests by the end of this year.

3.1 TOTAL CYANIDE MONITOR

In the development of total cyanide monitor, the most important thing is to remove interference by sulfur ion and others. As a result of laboratory and field tests on the methods of pretreatment, it has been decided to adopt the method to oxidate sulfur ion by potassium permanganate under acidic condition prior to distillation and the method to remove sulfur ion by granular lead peroxide after distillation. The measurement of cyanide is conducted by the cyanide electrode.

The field tests were conducted for about two years at an ordinary municipal sewage treatment plant and at a treatment plant handling industrial wastewater mainly consist of metal finishing wastes. And improvements of the devices were made during the field test. It was found that some kinds of organics could be transferred into the distillate during distillation and could interfere the measurement. Therefore, activated carbon column is necessary to remove organics in the distillate when occasions demand. Through these tests, it was confirmed that the accuracy of measurement was between the range of -0.15 pCN and 0.25 pCN provided that there were no unforeseen interferences contained in the sample. The larger error on the positive side was due to the fact that the influence of interferences acted more strongly on the 'plus' side.

There are three types of monitoring devices designated by the standard specifications: one batch type and two continuous types. Concerning the details, refer to the "Standard Specifications of Automatic Total Cyanide Monitoring Devices" issued by the Association of Electrical Engineering in March 1978.

3.2 TOTAL CHROMIUM MONITOR

A few types of automatic total chromium monitors based on the diphenyl-carbazide method are already being put on the market. However, it is doubtful whether these monitors can be used for the measurement of chromium in wastewater which contains organic reducing substances in high concentration. Therefore, based on the hitherto laboratory tests, a series of field tests to improve and modify the monitoring devices presently marketed will begin from late this year. The major purposes of the field tests are to study the effects of preliminary aeration prior to addition of potassium permanganate and the possibilities of using other oxidizing agents such as sodium hypobromite instead of potassium permanganate. Based on the results of these field tests, standard specifications are to be made.

3.3 HEXAVALENT CHROMIUM MONITOR

With regards to the measurement of hexavalent chromium, a few types of automatic monitoring devices employing the diphenylcarbazide method are also on the market. But when these monitors are used for the measurement of Cr (VI) in the sewage, sample blank becomes extremely large and it often exceeds the range of automatic correction. Furthermore, direct measurement of Cr (VI) by the diphenylcarbazide method in samples containing a large amount of reducing substances may be doubtful, thus gives rise to studies of introducing the aforementioned ultraviolet adsorption method in the monitoring devices. However, the ultraviolet adsorption method, too, faces interference by iron. Ferric hydroxide formed in the alkaline solution absorbs ultraviolet, and 10 mg/l of ferric ion gives the interference equivalent to about 1.5 m/l of chromium. Therefore, when this method is applied to water sample containing a large amount of ferric ion it must first be removed.

3.4 CADMIUM MONITOR

Concerning cadmium measurement, as there is no appropriate colorimetric analyzing method for automatic monitoring, studies are presently being advanced to develop an automatic monitoring device with a detecting unit using ion selective electrodes. However, as mentioned previously, cadmium electrode has an increasing large number of interferences. According to the hitherto basic experiments, results show that interferences by organic were removed to some extent by passing the sample through activated carbon column under acidic conditions and that interferences by inorganic ions were eliminated by addition of proper masking agents. Masking agents to remove metal ions, for example, are phosphates to remove Pb^{2+} , Ag^{2+} , Fe^{3+} , etc.; L-ascorbic acid as against Cu^{2+} and oxidizing substances; and sodium tetraphenyl borate to cope with Ag^{2+} and Cu^{2+} . For others, by utilizing the nature of cadmium that it is adsorbed to anion exchange resin under acidic condition with hydrochloric acid, extraction of cadmium from the sample is being studied.

With regards to studies of cadmium monitoring devices, field tests are slated to commence at the end of this year to conduct comparasions of effects of the above mentioned pretreatment methods and to decide on the apt mechanical structures of the devices considered most appropriate for practical application.

3.5 COPPER MONITORING UNIT

The bathocuprion method with extremely few interferences is a colorimetric analyzing method of copper and serves as an excellent detecting method for an automatic monitor. Concerning copper monitoring units employing the bathocuprion method, field tests are expected to begin from the latter part of this year. And surveys will be conducted on measurement precision, operation and maintenance of the devices.

3.6 OTHERS

Besides cooperating in developmental studies of various monitoring devices on consignment by the Ministry of Construction, manufacturers have their own development projects. As mentioned before, mercury monitoring devices employing the

frameless atomic absorption spectrophotometry are presently marketed, and also a monitoring device for heavy metals having flame atomic absorption spectrometry detecting units is on the market. However, as these devices are not always designed for application to wastewater that contains a large number of interferences, there are many problems involved when they are to be used for wastewater monitoring.

Presently, automation of X-ray fluorometry and high frequency plasma spectrophotometry has advanced to a stage of developing laboratory type automatic instruments. And, depending on the requirement of the users, there is a possibility of these methods being adopted as detecting units in automatic monitoring devices in the future.

4. CONCLUSION

The current status of the development of automatic water quality monitoring devices for hazardous substances in wastewater and its related problems have been discussed in this report. At the present stage, the only reliable monitoring unit that has been completed is that for cyanide measurement. As regards chromium, cadmium and copper, the outlook for developing monitors for these substances is bright.

The strenuous efforts until now has been exerted to develop monitors to give as accurate data as possible in practical sense. However, generally speaking, as the measurement accuracy requires complicated mechanism, the accuracy required and the cost as well as difficulty in operation and maintenance are in a counteracting relation. Therefore, studies should be made on the 'software' of the monitoring system, such as the role of automatic monitors in the total monitoring system and cost benefit relationship. And the results of these studies should be forwarded as a feed-back information to set the targets to develop automatic monitoring devices.

II. EVALUATION OF CONTINUOUS WATER QUALITY MONITORING EQUIPMENTS FOR SEWAGE TREATMENT

INTRODUCTION

Since 1972, the Public Works Research Institute of the Ministry of Construction has conducted a series of research activities on advanced waste treatment using a pilot plant constructed at the existing sewage treatment plant in three cities, Shitamachi plant in Yokosuka, Toba plant in Kyoto and Nishiyama plant in Nagoya, with full collaboration from respective municipalities. These researches also cover the applicability test on the continuous water quality monitoring equipments available on the market which are indispensable for effective operation and control of the advanced waste treatment at the said plants.

The evaluation of continuous water quality monitoring equipments is tested mainly at Kyoto plant and Nagoya plant. Kyoto plant, which is intended to treat secondary effluent, is provided with the functions essential for that specific purpose such as chemical precipitation, sand filtration, activated carbon adsorption, and break point chlorination. Nagoya plant, on the other hand, is an actual plant designed to upgrade the functional aspects of the existing plant by adding coagulant, and it also has sand filters for experimental purposes.

This paper introduces some of the monitoring equipments installed at the two plants which are generally applicable for advanced waste treatment, with specific reference to their performance and problems in their actual operation.

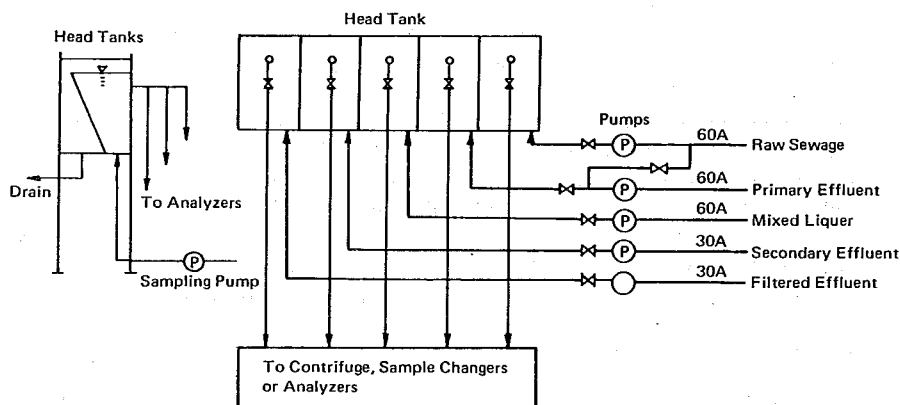
1. SAMPLING PROCEDURE

In automated water quality analysis of sewage, the sampling procedure or the method of leading sample sewage to the terminal water quality monitoring equipments (hereinafter referred to as the "water quality analyzers" or "analyzers") bears very closely upon smooth and accurate measurement. This is due to the inherent characteristics of sewage, especially raw sewage, which contains lots of solids and organic matters. The solids are prone to be accumulated in the pipes and the organic matters are liable to cause slime formation, so that the piping system is easily clogged up and changes in water quality are liable to occur. Particularly in the case of raw sewage which contains lots of coarse solids, sampling must be carried out constantly to maintain sample continuity and the whole configuration of the sampling system must be designed with care taken in the selection of sampling pumps and valves.

Kyoto plant is a tertiary plant intended mainly to treat secondary effluent, so that its sampling system is less influenced by the above mentioned characteristics of sewage than at secondary treatment plants. In addition, as the conveyance distance is short, it is not confronted with any specific difficulty in leading sample from each specified sampling point to the analyzer by making use of the head in the conveyance route or by means of exclusive sampling pumps.

In the case of Nagoya plant, however, the applicability test was conducted by making use of the actual plant, so that it was necessary to drive all effluents, ranging from raw sewage to final effluent, to the shed designed exclusively for water quality analysis. For this reason, raw sewage and effluents were pumped up continuously from each sampling point to specially designed head tanks, and thence to respective analyzers through pipelines with a suitable head. Further, a centrifuge (8,000 rpm) run by an industrial motor was installed immediately beneath the head tank to send the sample free from suspended solids to those analyzers whose performance could be degraded by the inflow of sample containing the solids. A sample changer with an electromagnetic valve was also used for measurement of a plural number of samples by a single analyzer. The flow chart of sampling at Nagoya plant is shown in Fig. 1.

Fig.-1 Flow Chart of Sampling (Nagoya)



By reason of their functional and structural characteristics, pH meter and sludge density meter were installed at each measuring point outside the sampling system described above.

The sampling pumps were of self-contained volute type, with a suction port diameter of 60 A for raw sewage and primary effluent and 30 A for other effluents, and the flow from them to the head tanks was adjusted by means of delivery regulating valves to maintain an optimal rate of overflow from the head tanks.

After about two and a half years' operation of the above sampling system, the following problems were brought to the fore.

- 1) Scums were formed in the head tanks, and their admixture in the sample caused dispersion of measured values. This drawback could be coped with by cleaning the head tank every morning for most effluents but not for raw sewage which contained lots of solids. Thus, the system proved to insufficient for sampling raw sewage.

- 2) A diversity of troubles were encountered in the pumping of raw sewage. To cite an example, the strainer of ordinary suction pipe became clogged up rapidly due to the inflow of paper, debirs and dirts contained in raw sewage, often causing overload of the pump. By introducing a large stainless steel basket type strainer (400 x 400 x 550 mm, 5 mm square), this trouble was mitigated to a substantial extent, but it was still necessary to carry out screening once a week or so.
- 3) As the raw sewage sampling pipeline installed at Nagoya plant was long (approx. 70 m), it was subjected to frequent clogging, causing gradual decline of the pump delivery rate. Four solution of this problem, the delivery side piping of primary effluent pump was connected with the said raw sewage sampling pipeline to flush is at suitable intervals with the primary effluent as backwash water.
- 4) Pretreatment by the centrifuge for removal of solids had to be conducted every 5 to 7 days to remove concentrated solids caught inside the rotor. Neglect of this pretreatment caused the decline of SS removal rate, which resulted in the decomposition of concentrated solids and emission of an offensive odour in summer.

2. PERFORMANCE OF ANALYZERS, AND PROBLEMS IN THEIR MAINTENANCE

2.1 TURBIDIMETER

The turbidimeter used for water quality monitoring is of the type designed for measuring scattered lights on the free water surface formed on top of the flow cell by the overflow of sample effluent. This meter is generally considered to be suited to the measurement of sewage turbidity for two reasons: it does not come in direct contact with sewage, and sample volume is usually abundant.

At Kyoto plant, 10 units of this turbidimeter are installed for the purpose of continuous water quality monitoring of secondary effluent, chemical clarifier effluent. At Nagoya plant, 6 units are installed for turbidity measurement of raw sewage, primary effluent, secondary effluent, and filtered effluent. All the 16 units are operated at a high rate of nearly 100%.

As turbidity is not the only or a sufficiently credible index in sewage treatment, it is important to clarify the turbidity vs. SS relationships which are shown in Figs. 2 ~ 4 for the two plants. Fig. 2 shows the relationships at Kyoto plant between the turbidity of secondary and filtered effluents and their SS concentration obtained by manual analysis. Fig. 3 also shows the turbidity-SS relationships between effluent. As seen in the two figures, secondary and subsequent effluents present a marked correlation between turbidity and SS concentration, indicating that SS concentration can be estimated by turbidity measurement. Fig. 4 shows the turbidity-SS relationships between raw sewage and primary effluent at Nagoya plant. This figure indicates that raw sewage does not present any notable correlation between turbidity and SS concentration, suggesting that it cannot be justified to represent SS by turbidity. This is assignable to the working principles of the turbidimeter which does detect settleable solids of relatively large size.

Fig-2 Turbidity ~ SS (Secondary Effluent and Its Filter Effluent)

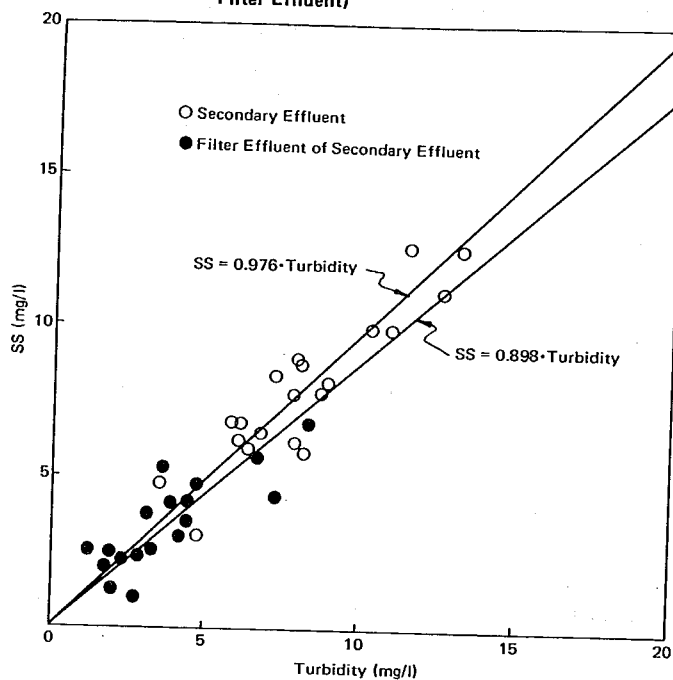


Fig-3 Turbidity ~ SS (Alum Precipitation Effluent and Its Filter Effluent)

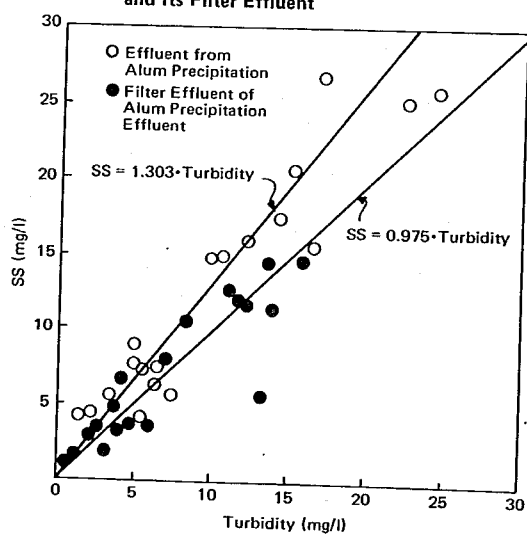
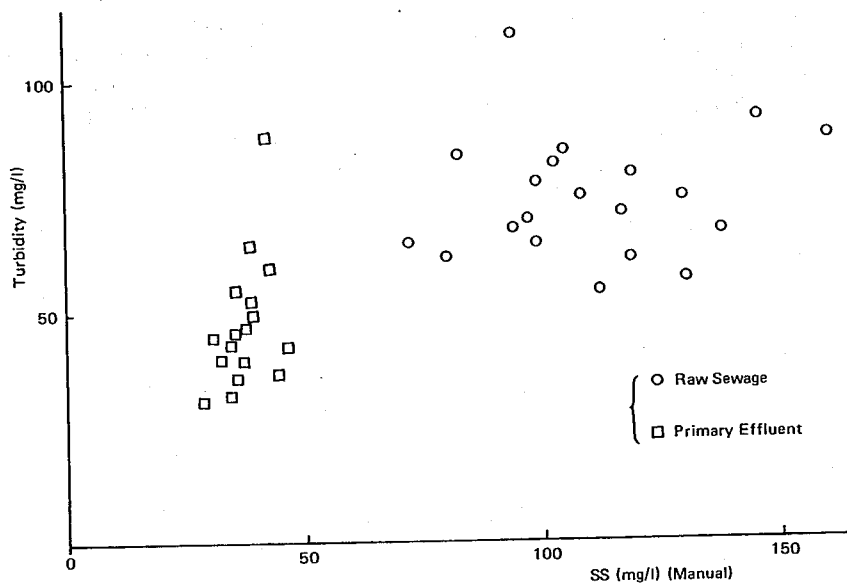


Fig.-4 Turbidity vs. SS (Nagoya)



From the experience obtained at the two plants, the follow proposition can be advanced in connection with continuous turbidity monitoring.

- 1) Secondary effluent, chemical clarifier effluent and filtered effluent present a comparably high correlation between turbidity and SS concentration. In so far as these effluents are concerned, therefore, it is feasible to obtain SS concentration from the measured values of turbidity with a fairly high accuracy. However, as the relationships between these two factors vary according to sample quality, it is necessary to establish the relationships for each effluents.
- 2) As for raw sewage, the validity of estimating SS concentration from measured turbidity values is questionable. At both plants, turbidimeters were used for quality monitoring of backwash waste of filters which had a higher SS concentration than raw sewage. In the case of this backwash waste, the correlation was rather high, which may be ascribed to the fact that activated sludge flocs which are relatively uniform in size constitute the greater part of suspended solids of backwash waste.
- 3) The effluent flow velocity on the surface of flow cell is limited to an extent by reason of the system's working principles. Hence, raw sewage containing lots of coarse solids formed a debris film covering the flow cell surface, which caused dispersion of measured values. Formation of this film was so rapid that it was not possible to prevent the dispersion by cleaning it away once a day or so. The debris film was also formed on the flow cell surface of primary effluent and secondary effluent, making it imperative to clean the cell at least once a day for stabilized measurement.

- 4) Certain minor differences in measured values were observed between respective turbidimeters, which are likely to have been noted among other analyzers. Specifically, there were cases where the turbidity of the same sample differed from turbidimeter to turbidimeter. This is because even if a number of meters are calibrated all at the same time, the measured value inevitably involves a deviation from the correct value varying in degree for each meter with the lapse of time. This fact must be taken into careful consideration when measured values of low turbidity effluents such as filtered effluent and carbon effluent are to be used for absolute turbidity comparison between such effluents. Nevertheless, this trouble can be averted by measuring the turbidity of a number of samples with the same turbidimeter by means of the aforementioned sample changer.

2.2 UV (ULTRA VIOLET) PHOTOMETER

The absorbance in the neighbourhood of extinction of 254 mm beam in water containing organic matters is known to have a certain correlation with the organic matter concentration measured in terms of COD and BOD. In general, UV photometer is basically designed for measuring absorbance through a flow cell, and it is simple in structure and easy for maintenance. Where the organic matter concentration in sewage or treated effluent can be represented by UV absorbance, its measurement can be greatly facilitated by the use of UV photometer.

The UV photometers installed at the two plants are capable for measuring the absorbance of an extinction of 254 mm beam using a mercuric lamp, and can effect correction to the influences of turbidity of taking the ratio of transmitted light intensities of ultraviolet rays and visible rays.

At Kyoto plant, 2 units of UV photometers are combined with the sample changer for continuous quality monitoring of secondary effluent, chemical clarifier effluent, filter effluent and carbon effluent. At Nagoya plant, on the other hand, 1 unit is installed for combination with the sample changer for measurement of primary effluent, secondary effluent, and filtered effluent.

Although a period of about one and a half years has elapsed since the commencement of the measurement, a very high operational rate is exhibited by all the three photometers. In the earlier stage of measurement, however, the following problems were experienced.

- 1) Measured values showed fluctuations due to temperature changes in the neighbourhood of the flow cell.
- 2) Ozone is generated near the mercuric lamp, emitting its peculiar smell.

The former trouble was solved by improving the measuring unit so as to maintain a constant temperature (40°C), and the latter by inserting activated carbon in the measuring unit to adsorb ozone.

Fig. 5 shows the relationships between COD (permanganate) and UV absorbance as obtained by measurement conducted for about half a year (December to June) at Kyoto plant on effluents at different stages of treatment. The figure presents the general tendency that both COD and UV absorbance decline with the progress of sewage treatment from secondary effluent to chemical clarifier effluent, and further

to carbon effluent, but indicates the difficulty in estimating COD from UV absorbance.

Fig.-5 UV vs. COD

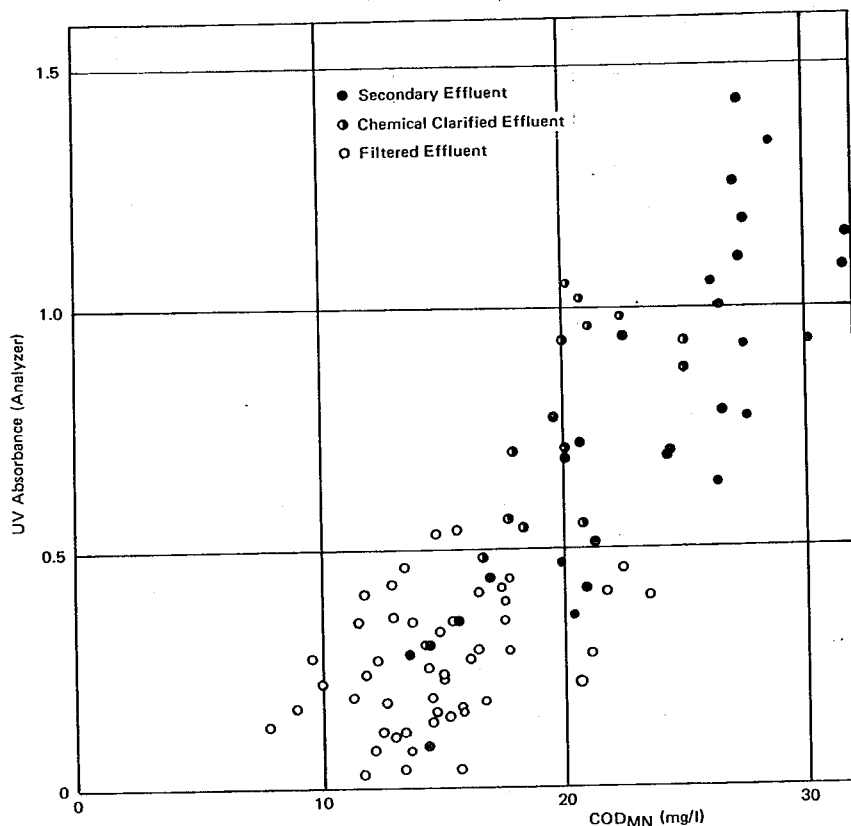


Fig. 6, which illustrates the COD vs. UV absorbance relationships as obtained by measurement in a period differing from that mentioned above, indicates that COD and UV absorbance presenta marked correlation with each other if the survey period is the same, but the correlation changes if the survey period is not the same.

Fig. 7 shows the relationships between the absorbance measured by the UV photometer at Nagoya plant and TOC (value measured by continuous TOC meter). The figure indicates that UV absorbance vs. TOC relationships vary according to the treatment stage just as the absorbance-COD relationships mentioned above, and also makes it clear that when TOC is higher, its value is vulnerable to a large fluctuation even by a slight difference in UV absorbance. It seems that there exists no clear correlation between the turbidity measured by turbidimeter and the UV absorbance, and that turbidity correction was effected without any hindrance.

Fig.-6 UV vs COD (Seasonal Change)

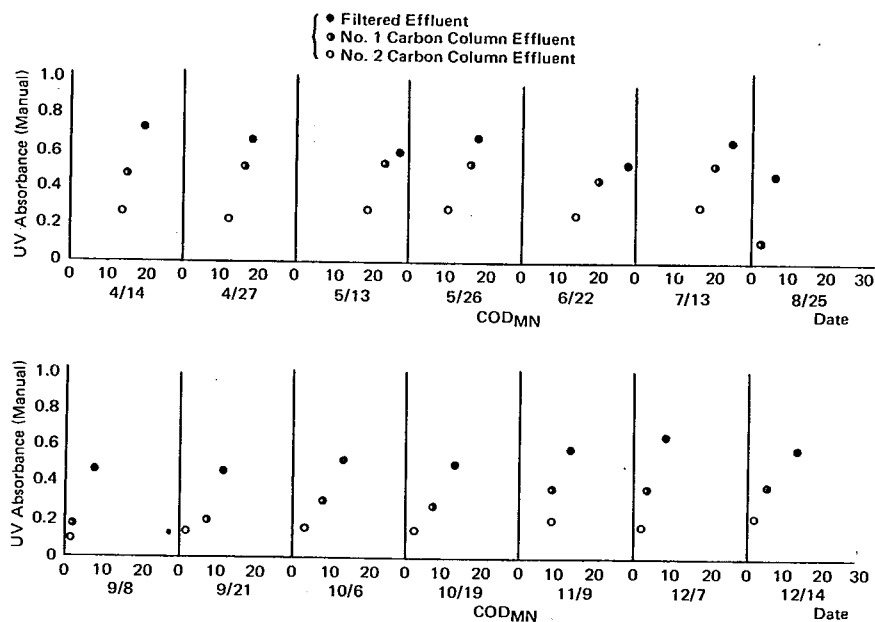
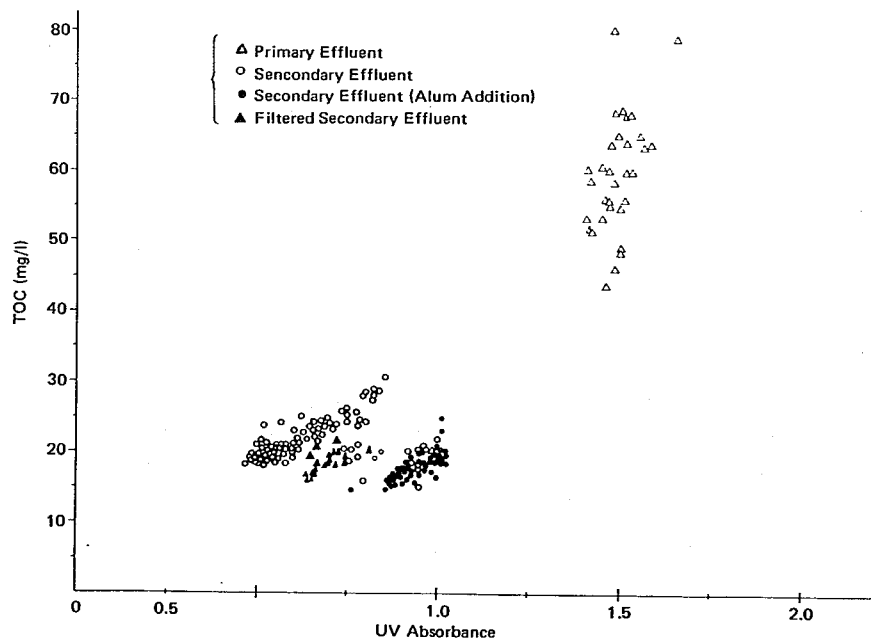


Fig.-7 Relationship between UV Absorbance and TOC (Automatic Analyzer)



From the results introduced above, it appears questionable to obtain the absolute values of organic matters from UV absorbance by continuous water quality analyzers, although the absorbance may be used in setting the control point within a certain limit, e.g., the point of breakthrough of carbon effluent.

As described already, maintenance of UV photometer is very easy and calls only for the replacement of the mercuric lamp (one thousand and several hundred hours) and routine inspection services.

2.3 AUTOMATED COLORIMETRIC ANALYZER FOR PHOSPHORUS AND AMMONIA NITROGEN

Detailed description on the captioned analyzer is given elsewhere in this report.

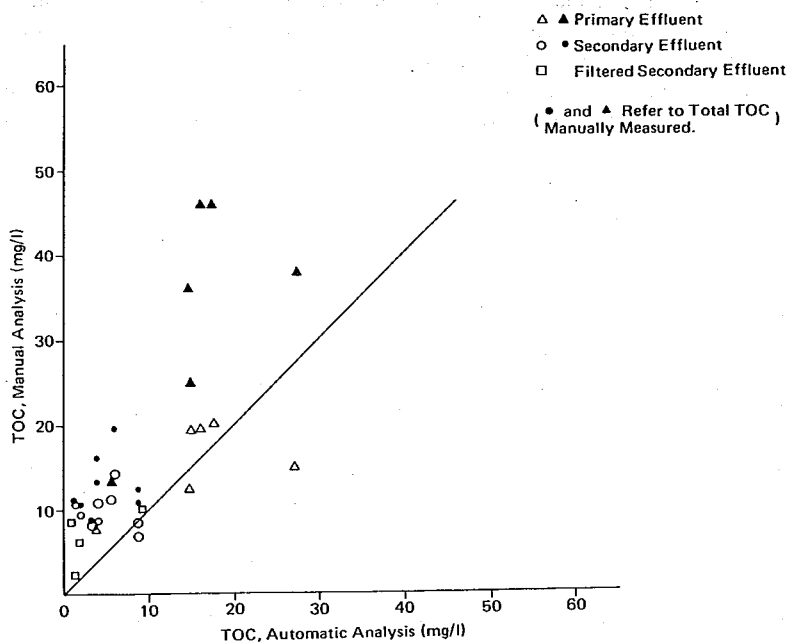
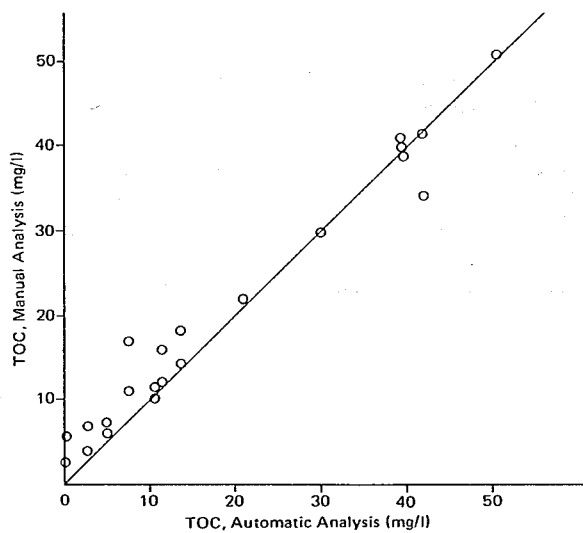
2.4 TOC METER

The TOC meter used at the two plants is of the type designed to drop pH value of continuously supplied sample by adding hydrochloric acid, purge inorganic carbon therefrom by bubbling in an exclusive scrubber, and then obtain TOC by measuring CO_2 with an infrared analyzer after incinerating the sample at a temperature of about 800°C . CO_2 -free air is used as carrier gas.

By reason of its working principle, TOC meter presupposes instantaneous incineration of sample, so that the sample must be very small in volume and the pipeline must also be small in diameter. This makes it inevitable for the meter to be subjected to strong influences of suspended solids such as the large fluctuation of measured value resulting from the infiltration of suspended solids into the furnace, and the deflection of measured value of total TOC which is caused when part of suspended solids is introduced in the pipeline running from the sampling point through the analyzer. Fig. 8 is a comparison between TOC values of primary effluent, secondary effluent and filtered effluent as obtained by manual analysis (on samples collected from the outflow point of head tank) and the readings of continuous analyzer recorded at the same time. In the manual analysis, values of both total TOC and soluble TOC were obtained. As seen in this figure, the values obtained by continuous analyzer are close to those of soluble TOC, suggesting that a considerably portion of suspended solids is removed in the sampling line downstream of the measuring point.

Fig. 9 is a comparison between the TOC values obtained by manual analysis on the sample collected from the scrubber and the readings of continuous analyzer recorded at the same time. As can be seen in the figure, the two show a fair conformity to each other, indicating that the measured values of continuous analyzer become stabilized after suspended solids have been removed to some extent.

Fig-8 Comparison of TOC, Manual and Automatic Analyses

Fig-9 Comparison of TOC, Manual and Automatic Analyses
— Samples taken at the Outlet of the Scrubber in the TOC Monitor —

Prior to its actual application, the TOC meter mentioned above was considered to be superior to all other continuous TOC analyzers currently available on the market for the purpose of analyzing samples containing suspended solids. Judging from the test data, however, it does not seem fully applicable to continuous measurement of total TOC including suspended solids. At Nagoya plant, this problem is coped with by pretreatment using a continuous centrifuge.

Although the following operational troubles and maintenance troubles were encountered in the past, none were so serious as to invite suspension for a long time and the TOC meters exhibited a high operating rate.

- 1) Pipelines developed frequent thermal deterioration especially in the neighbourhood of cell of infrared analyzer where the pipe replacement can be done only by the manufacturer.
- 2) The carrier gas line was often clogged up due to moisture. Although an electronic cooler was installed behind the cooling condenser to remove moisture, water collected in the dust filter and often clogged up the carrier line. This trouble was coped with by modifying the shape of dust filter so as to be able resist the collection of water to an extent.
- 3) Dehumidifying silica gel had to be replaced frequently due to the high relative humidity of ambient room air used as carrier gas.
- 4) The scrubber for removing inorganic carbon has a shape which makes its cleaning difficult, and the pipeline supplying sample from the pump to the scrubber is subjected to frequent clogging.
- 5) The furnace needs to be replaced in less than two years due to its corrosion, and the breaking of heater wires must also be assumed to take place after the lapse of just about the same period.

2.5 pH METER

The pH meters used are of dual sensor type with augmented internal liquid volume (total length : approx. 2 m).

At Nagoya plant, 5 pH meters of this type are installed in the aeration tanks and primary effluent delivery lines.

By calibrating these pH meters once a week, measured values are stabilized at present. The sensor surface becomes soiled considerably in a single day if the meter is installed directly in the aeration tank, but excessive soiling could be prevented by cleaning it once a week and it did not affect the measured values. By reason of its functional characteristics, the pH meter needs an amplifier to be fitted near the extreme end of its sensor. As there were no adequate measures to reduce the humidity near the amplifier, satisfactory measured values could not be obtained from some meters. To cope with the high humidity resulting from the tanks being installed indoors, silica gel filled in a box is replaced at suitable intervals.

2.6 SLUDGE DENSITY METER

Ultrasonic type sludge density meters are installed in designated places in the pipeline at both plants; for density measurement of primary sludge and waste activated sludge at Nagoya plant and alum sludge at Kyoto plant. The density meter itself is a virtually maintenance-free instrument, but attention must be directed to the following points in order to obtain accurate measured values.

- 1) As the declining rate of ultrasonic wave varies according to the changes in sludge properties resulting from the development of bulking and addition of coagulant, it is necessary to carry out calibration frequently. In the density measurement of waste activated sludge conducted at Nagoya plant, it was discovered that 20 dB decline at FS 3% when SVI stood around 100 in summer had to be adjusted to 33 dB decline at FS 3% in winter when SVI rose to about 200 (pipe diameter: 150 mm).
- 2) The declining rate is high especially for primary sludge. The measured density of primary sludge once showed a value about 1.5 times as large as that obtained by manual analysis even near the uppermost limit of adjustable range (FS - 8%, 45 db decline) (pipe diameter : 300 mm). As primary sludge is subject to little fluctuation of properties and consequently presents a high density correlation between manual analysis and density meter measurement, a predetermined coefficient is adopted at Nagoya plant to obtain the primary sludge density.
- 3) As the density meter gives the most reliable value around the centre of the measuring range, it is not advisable to set the measuring scale extending unnecessarily far beyond the density range of measured sludge. This caution needs to be observed particularly for waste activated sludge as its density changes largely with the lapse of time.

3. CONCLUSION

In the foregoing pages, the continuous water quality monitoring analyzers installed at Kyoto plant and Nagoya plant have been introduced in outline, together with the problems entailed in their maintenance as disclosed from the record of their past operation.

All the analyzers selected for elucidation in this report exhibited a satisfactory operating rate. Considered from the viewpoint of reliability, however, they can be divided into two groups, those producing fairly stabilized measured values and those liable to produce misleading values unless operated with full understanding of functional and structural characteristics. In terms of maintenance services, too, some are nearly maintenance-free, others call for simple maintenance only, and still others demand complicated maintenance services.

The dominant cause of troubles related to the maintenance of all analyzers was, as anticipated, the clogging of flow lines in the sampling system and measuring system ensured from the inherent characteristics of sewage. Especially those lines conveying a small volume of sample were found to be prone to be clogged up readily because of the limited flow velocity and insufficient sectional area. These lines must be made as large in diameter as possible up to the measuring point so as to be able to carry abundant sample, and should also have a structure promising easy flushing operation. The sampling lines at Nagoya plant are commendable in this respect up to the head tanks, but all lines at subsequent treatment stages are not immune from maintenance troubles. If the sampling pipelines are provided with a suitable automatic flushing mechanism, it will certainly contribute to sizable labour-saving.

Continuous water quality monitoring analyzers are often required to be installed in unfavorable conditions such as high humidity or liability to water intrusion. It was found that the tested analyzers were not necessarily installed with due regard to these unavoidably adverse factors, so that they developed not only electrical troubles but also disjoining of pipes which caused the flow cell to be filled with water. In prevention of such troubles, the layout of internal components of measuring unit rack must be designed with special care. Furthermore, for the purpose of easier and quicker routine inspection, all parts to be checked every day or at short intervals should be gathered on the front of equipment. It was noted that maintenance was made difficult by multitubular piping and by inadequate design, shape or layout of equipment which force the worker to move around it for calibration or inspection, and this gave rise to the occurrence of another troubles. Although improvement of all equipment for completely maintenance-free operation may not be possible, it certainly appears possible to reduce manpower requirement by effecting suitable improvement to various equipment. For easier maintenance and inspection services and quicker detection of troubles, it is advisable to affix a rough sketch showing pipelines, measuring methods, signals and power source on the front surface of each equipment. For all these improvements, cooperation of manufacturers is indispensable and solicited.

To maintain all analyzers in perfect service condition, it is recommended to appoint those with some experience in water quality analysis as exclusive operators of analyzers because nearly all analyzers installed at the two plants call for routine maintenance and inspection services, and the amount of such services is by no means small considering the number of analyzers. The changes in water quality of sewage generally depict the same pattern every day, so that the service condition and malfunction of each analyzer can be checked with ease from the daily observation record if it is operated by an exclusive operator. The need for such exclusive operator. The need for such exclusive operators can also be justified by the fact that some analyzers cannot be operated satisfactorily without the delicate knock which only the exclusive operators can gain through accumulation of skills.

Maintenance cost of analyzers is by no means small even if personnel cost is excluded. NH_3 analyzer, for example, incurs an annual cost of more than 150 thousand yen merely for consumables such as chemicals and tubes. As another conspicuous example of high maintenance cost, it may as well be mentioned that COD analyzer using the acid process is known to require an annual expenditure of more than a million yen only for chemicals.

Utilisation of continuous water quality monitoring equipments in sewage treatment produces immeasurable benefits for overall operation and maintenance of sewage treatment plant in that it makes it possible to know the water quality of raw sewage and effluents at any time. It is to be noted, however, that such benefits can be expected not by simply installing necessary automatic analyzers but by operating each individual analyzer with full understanding of its characteristics and keeping it in perfect fault-free service condition under a well-planned and integrated system of routine inspection and maintenance services.

III. DEVELOPMENT OF AUTOMATED CONTINUOUS P-D, HYDRO AND NH₃ ANALYZERS

Pilot or demonstration studies concerning advanced waste treatment are conducted by the Public Works Research Institute of the Ministry of Construction in Kyoto, Nagoya, and Yokosuka.

Of the three plants, studies are conducted on the practicability of Automated Continuous Water Quality Analyzer together with development of advanced water treatment processes in Kyoto and Nagoya.

This report mentions the studies conducted at the plants in Kyoto and Nagoya on colorimetric P analyzers (hereinafter referred to as "P analyzer") and colorimetric NH₃ analyzer (hereinafter referred to as "NH₃ analyzer").

The P analyzers installed in Kyoto and Nagoya are both products of K company. However, the P analyzers and the NH₃ analyzers installed in the Kyoto plant are the products in the developing stage.

Especially, the P analyzers are the first model ever made. On the other hand, as the P analyzers and also the NH₃ analyzers installed in Nagoya in 1976 are improved versions of those in Kyoto, this report will mention the analyzers in Nagoya. However, with regards operating conditions of the analyzers, the report will refer to both Kyoto and Nagoya.

1. P ANALYZER (PHOTO 1)

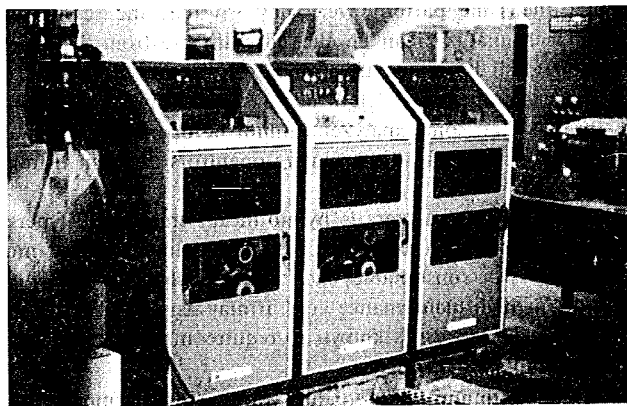
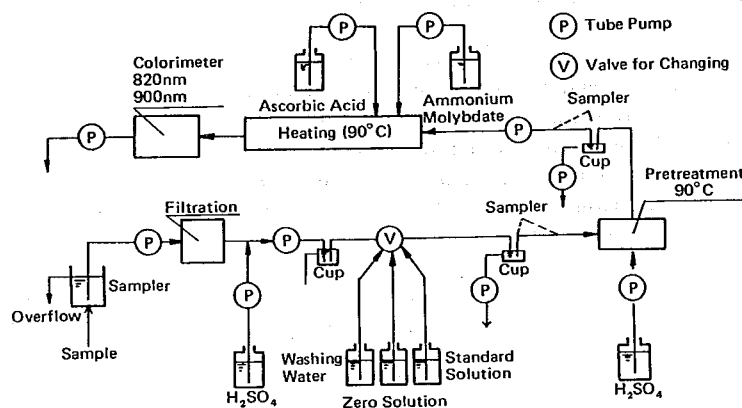


Photo-1 P Analyzer (Nagoya)

The flow sheet of the P analyzer is as shown in Fig. 1. This analyzer is a mechanized version of the manual analyzing method of P-D, hydro. The analyzer can be divided into three stages: Sample filtration, Pre-treatment and Color absorbance measuring stages.

Fig.1 Flowsheet of P Analyzer



In the Sample filtration stage, the insoluble matters in sample are removed by filter paper. The rolled sheets of filter paper, after filtration, is continuously wound after being dried at about 100 degrees centigrade. And the winding speed is adjustable between 1 and 10 mm per minute depending upon the properties of the insoluble matters. A roll of filter paper is 30 meters long. Therefore, one roll lasts between 2 and 21 days. Then sulfuric acid is injected into the filtrate to prevent contamination of the flow passage.

At the Pretreatment stage, the sample from inside a cup is collected by a vertical movement of a sampler with air which partitions it. Then sulfuric acid is injected into the sample. After mixing polyphosphate and part of organic phosphorous contained in the sample, is subjected to hydrolysis in an incubator maintained at 90 degrees centigrade.

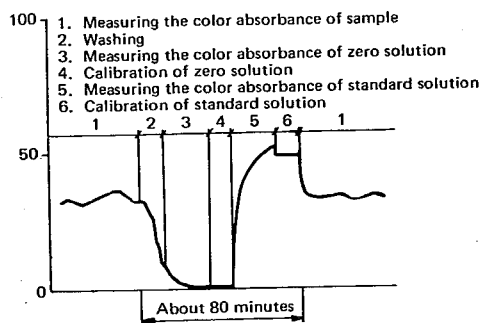
At the Color Absorbance Measuring stage, after releasing air in the pretreated sample from the cup, the sample is again subjected to the vertical motion of the sampler. In a mixing coil, ammonium molybdate is added, and the sample is rolled and mixed. Then in the 90°C incubator, coloring occurs depending upon the ortho-phosphate contained in the sample. After complete coloring, the sample is colorimetrically analyzed in the flow cell. This unit utilizes the two wave type method to prevent interference caused by color and turbidity in the sample. The P-D, hydro in the sample, measured in such a manner, is sent to either the controller or the recorder by the output of 4 ~ 20 mA or 0 ~ 10 mV.

The response time from the Filtration Stage to the Color Absorbance Measuring Stage is about 30 minutes. The maximum concentration can be set at three ranges of 2.5, 5 and 10 mg·p/l. Washing of the flow passage and calibration are automatically conducted at designated time by a 24-hour timer. Fig. 2 shows the method. After washing, zero solution containing no phosphorous is injected into the piping. And when the indicating value becomes stable, the value is electrically set to "0". This is followed by injection of standard solution containing phosphorous of

50% full scale concentration, and when the indicator shows a stable value, the value is electrically set to 50% of full scale. The time required for washing and calibration is about 110 minutes. About 30 minutes from the start show the sample's measurement values. When a facility is controlled automatically based on output from the analyzer, and when washing and calibration is in progress, the output shown immediately before the operation remains unchanged and are transmitted to the control unit. In case of any abnormality such as dropping of water level in sampling tank, ripping of filter paper, or scaling out, the measurement process is suspended and the alarm is sound. The alarm is sound even when it exceeds the minimum values set in advance.

Daily inspection of flow passage, once weekly reagent replenishment, once or twice weekly filter paper changing, and once in between every 2 weeks and one month tube changing are necessary to maintain them.

Fig-2 Automated Washing and Calibration



The above mentioned P analyzers in Nagoya are improved versions of those in Kyoto as follows:

- 1) Filter paper feeding system has become continuous due to simplification of winding mechanism.
- 2) The filtering direction changed from upflow to downflow to solve the problem of sulfuric acid backflow, injected to prevent contamination of flow passage.
- 3) The air injection method to divide the sample has been changed from the glass tube utilization method to the sampler vertical motion method. As a result, the intervals between the sample and air became consistent and stable.
- 4) The colorimeter has been altered from the double beam type to the two wave type analyzing method, and thus the cell has become single instead of double. Then the response time has been shortened.
- 5) The addition of the Automated Washing Equipment has stabilized measurements. At Kyoto, manual washing is conducted on a twice weekly basis by using a syringe.
- 6) The flow passage that ran back and forth in the front and rear of the equipment has been grouped together in the front of the unit.

Fig. 3 compares the measurement values of the P analyzer and the manual

method (After filtration with No. 5 C filterpape-paper, the P-D, hydro was measured). Sampling was conducted on an once weekly basis during continuous operation of the P analyzers, and measurements were taken for six-months. On the whole, the P analyzer results has shown slightly larger values than the manual method. One of reasons cited can be the sulfuric acid injected to prevent contamination of flow passage after filtration. Fig. 4 shows the results when identical sample was flown into two P analyzers of which only one was injected with sulfuric acid. The Fig. shows that the values of the P analyzer injected with sulfuric acid were higher. This is reasoned to the fact that a part of the injected sulfuric acid has reached the filtration stage and dissolved part of the insoluble phosphorous on the filter.

Fig. 5 shows an example of the automated continuous measurement results of the P analyzer.

Fig.-3 Comparison between P Analyzer and Manual Analysis (Kyoto)

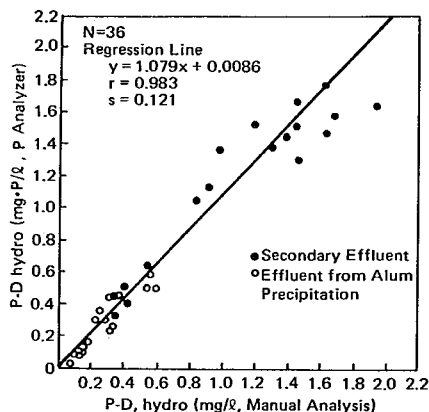


Fig.-4 Effect of H_2SO_4 for Cleaning on Measuring

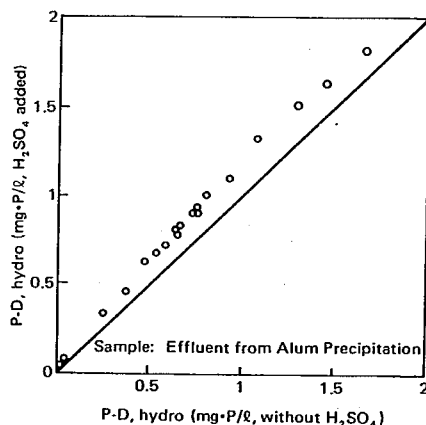
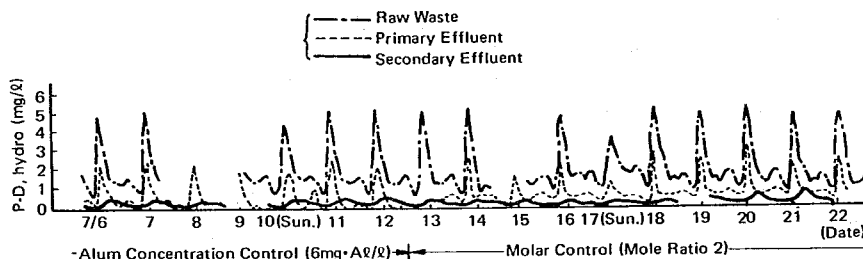


Fig.-5 Variation of P-D, hydro (Alum was dosed into the primary clarifier., Nagoya)



The hitherto developed troubles are as follows:

- 1) The residual flock containing phosphorous in the alum precipitation effluent was not removed thoroughly by the original filter paper (20μ), and thus the filtrate contained a reasonable amount of insoluble phosphorous. And when supplying paper, the filter paper sometimes was torn. By improving the paper quality and adjusting the pore size to about 1μ , the problems were solved. (Kyoto)
- 2) Because exchanging and cleaning of tubes at each part were not easy, proficiency of the facility was deteriorated. However, efforts were made by exchanging the flow passage to ease cleaning work. (Kyoto)
- 3) At first, persulfuric solution was used as a washing agent to clean the pipelines, etc. However, as persulfuric was scattered onto the skin and clothes during manual washing, it was dangerous. Therefore, the washing agent was changed to phosphorous free detergent. The new agent has been bringing about good washing results. (Kyoto)

On the other hand, in Nagoya, the original design required the use of hydrogen peroxide. However, when using only hydrogen peroxide in washing, it was not able to remove scale in the mixing cell immediately before the flow cell. As it was shown that the scale was removable by an alkaline solution, a caustic soda solution was used as a washing agent alternating with hydrogen peroxide solution every week. When using the caustic soda solution, it caused abnormal coloring (especially when phosphorus concentration was high) until being totally discharged and sounded the alarm to suspend operation. (Nagoya)

- 4) Troubles frequently developed in the filtration stage. And virtually all of the troubles were eliminated by improving the filtration system. Troubles developing in the filtration stage were as follows:
 - (1) Improper feeding of filter paper. (Kyoto)
 - (2) Tearing of filter paper. (Kyoto, Nagoya)
 - (3) Leaking of sample into the filtrate. (Nagoya)
 - (4) A hole was made in the filter paper due to backflow of sulfuric acid.

(Nagoya)

Those were the troubles, but, presently, a total of 5 P analyzers are operating in good conditions both in Kyoto and Nagoya.

A single person can service several P analyzers although it takes about a month for him to be accustomed in handling the units.

Table 1 shows the maintenance costs of the P analyzer and the NH_3 analyzer that are explained later.

Some problems that remain unsolved are as follows:

In case of continuously measuring phosphorous as water quality monitoring, it is necessary to measure not only soluble phosphorous but also insoluble phosphorous. To perform this, development of a unit enabling the measurement of insoluble phosphorous is necessary. Though as the ratio of organic phosphorous contained in the total phosphate in wastewater is small, the hydrolyzable phosphorous is nearly equal to total phosphorus, organic phosphorus can not necessarily ignored in surface water, so development of a unit enabling measurements of organic phosphorous is necessary.

Table-1 Maintenance Costs of P and NH_3 Analyzers (YEN/month·unit)

Item	P Analyzer	NH_3 Analyzer	Remarks
Tube	8,200	8,000	A exchange/two weeks
Filter	1,200	1,200	A exchange/one weeks
Reagent	1,100	2,800	
Total	10,500	12,000	

2. COLORIMETRIC NH_3 ANALYZER (PHOTO 2)

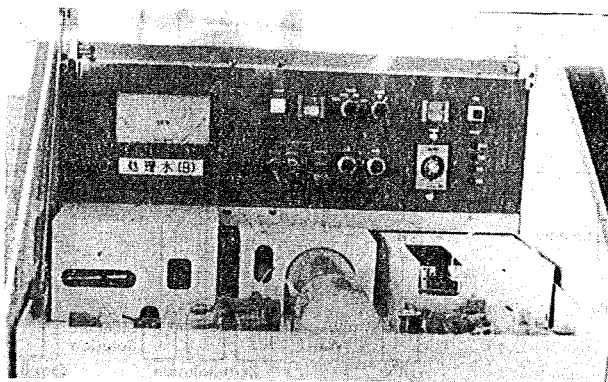


Photo-2 NH_3 Analyzer

The measurement principle of this unit is as follow:

After adding salicylic acid to the sample, when the alkaline isosalic acid is applied, the sample turns green in color. As the degree of the green is proportionate to the ammonia-nitrogen concentration in the sample, by measuring the absorbance of the green color the ammonia-nitrogen concentration in the sample can be determined. By this method, besides ammonia-nitrogen, mono-chloroamine can also be

determined.

The flow sheet of the NH_3 analyzer installed in Nagoya is shown in Fig. 6.

The filtration method, washing and calibration methods, and absorbance measuring method in the NH_3 analyzer are the same as the P analyzer. However, as pretreatment stage is not required in the NH_3 analyzer, the response time is only about 15 minutes, or nearly half of that of the P analyzer.

At maximum measurement concentration of $20 \sim 30 \text{ mg}\cdot\text{N/l}$, similarly with the P analyzers, the full scale can be switched into 3 stages and it is possible to operate even at $1/2$ or $1/4$ of the maximum concentration. When ammonia-nitrogen concentration is more than $20 \text{ mg}\cdot\text{N/l}$, a straight calibration line is not obtained. Therefore, when operating in full scale of over $20 \text{ mg}\cdot\text{N/l}$, the two fold dilution equipment is employed. The daily routine operation is the same as that of the P analyzer.

Fig. 7 compares actual measurement results of the NH_3 analyzers and the manual method (Indophenol blue method). Fig. 7 shows the measurement results during 18 months of operation, using samples collected at once weekly rate.

Fig. 8 shows an example of continuous measurement results.

Fig.-6 Flowsheet of NH_3 Analyzer

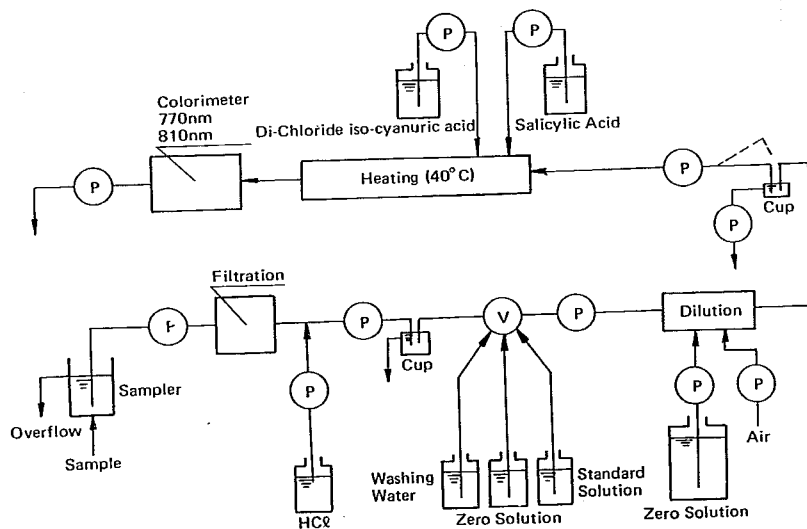


Fig.-7 Comparison between NH_3 Analyzer and Manual Analysis (Kyoto)

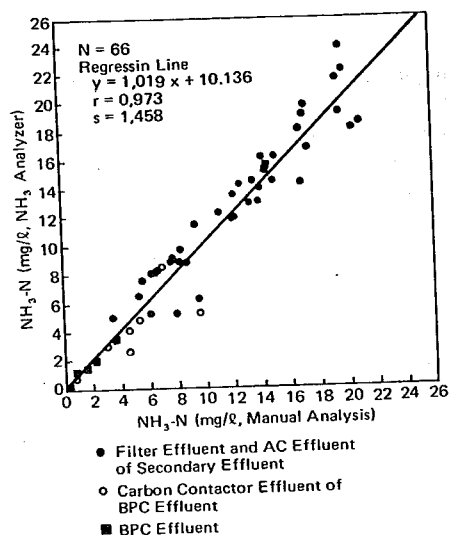
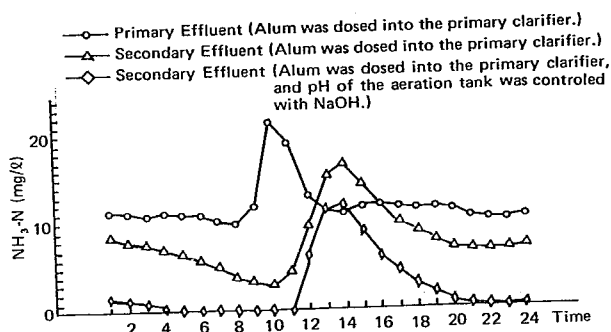


Fig.-8 Variation of NH_3



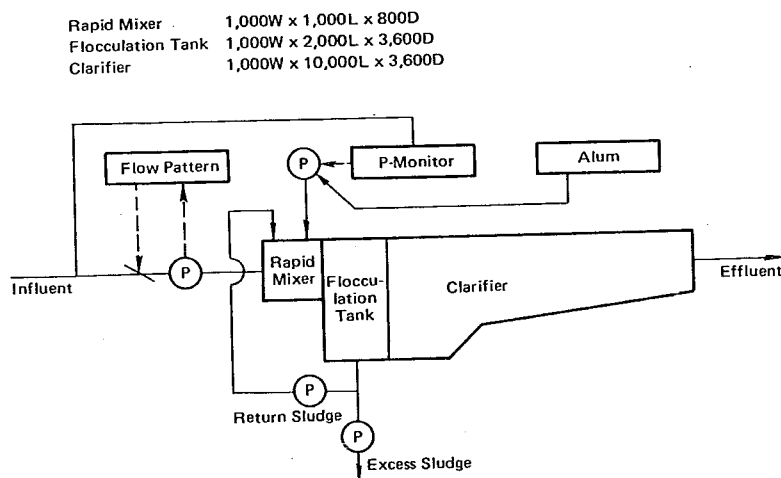
Trouble developed until now are as follows:

- 1) The sodium nitroprusside added to expedite reaction of coloring reagent of salicylic acid was instable when pH exceeded 8. This deteriorated the measurement accuracy gradually. However, by adjusting the pH correctly, the problem was solved. (Kyoto)
- 2) As the open type standard solution preservation container was used, the water in the standard solution evaporated. There were times when the 10 mg·N/l standard solution condensed to 13 mg·N/l 10 days later, sealed type containers are now used. (Kyoto)
- 3) Also there were problems similar to those in the P analyzers. Presently, a total of 6 NH_3 analyzers are functioning normally at the plants in Kyoto and Nagoya. Table 1 shows the daily maintenance costs.

IV. ALUM DOSING METHOD IN ALUM PRECIPITATION

At the Kyoto pilot plant, experiments were conducted to compare the alum constant dosing method with the molar control method, that is, alum is dosed into the influent in proportion to the dissolved phosphorous concentration (P-D). The flow diagram of the precipitation facility is as shown in Fig. 1. And the experimental conditions and results are as shown in Table 1. The influent was effluent from conventional activated sludge. The influent flow was 300 m³/day (in case of fluctuations in flow, the daily average influent). The overflow rate of the clarifier was 30 m³/day.

Fig.-1 Flow Diagram of Alum Precipitation



EXPERIMENTAL CONDITIONS — See Table 1 —

Experiment numbers 1 ~ 3 were constant dosing method, and experiment numbers 4 ~ 6 were molar control method.

The amount of alum dose in the constant dosing method was set at 5.9 mg·Al/liter. In case of molar control method, based on the phosphorous monitor output that continuously measured P-D of the influent, the alum dosing pump was regulated to maintain the molar ratio at 6 of Al against P-D of the influent.

The experiments on the constant dosing method and the molar control method were diversified as follows:

- Experiments 1 and 4: Constant influent flow without return sludge.
- Experiments 2 and 5: Constant influent flow with return sludge.
- Experiments 3 and 6: Varying influent flow with return sludge.

Table -1 Experimental Conditions and Results of Alum Precipitation at Kyoto P.P.

Number of Experiment		1	2	3	4	5	6
Item							
Conditions	Flow	Constant	Constant	Varying	Constant	Constant	Varying
	Alum Dosing Method	Constant	Constant	Constant	Molar Control	Molar Control	Molar Control
	Sludge Return Rate (%)	0	4.2	5.1	0	4.0	4.9
	Excess Sludge Rate (%)	0.6	0.7	0.7	0.7	0.7	0.7
	Alum Dosing (mg-Al/l)	5.9	5.9	5.9	7.1	7.3	6.8
	Mole Ratio (Al/P-D)	4.8	4.6	5.7	6	6	6
P (mg-P/l)	Influent	1.69	1.83	1.44	1.50	1.51	1.44
	Effluent	1.01	1.08	0.80	0.80	1.08	0.79
	Excess Sludge	26.7	74.7	35.8		23.9	37.2
	Mixed Liquor		9.40	6.27		3.20	4.95
	Removal (%)	40.2	41.0	44.5	46.7	28.4	45.1
P-D (mg-P/l)	Influent	1.40	1.48	1.18	1.36	1.39	1.30
	Effluent	0.44	0.32	0.23	0.30	0.25	0.26
	Excess Sludge	0.19	0.39	0.22		0.29	0.27
	Mixed Liquor		0.87	0.47		0.66	0.32
	Removal (%)	68.6	78.4	80.5	77.9	82.0	80.0
SS (mg/l)	Influent	9.7	7.7	12.6	6.1	5.8	8.9
	Effluent	24.8	17.6	16.2	13.3	19.7	15.2
	Excess Sludge	1690	2190	1740		640	1450
	Mixed Liquor		188	155		74	112
pH	Influent	7.2	7.1	7.0	7.1	7.1	7.1
	Effluent	6.9	7.0	6.9	6.9	6.9	6.9
M-Alkalinity (mg-CaCO ₃ /l)	Influent	159	145	150	144	143	144
	Effluent	135	129	117	123	113	118
Temperature	Effluent	20.5	16.1	19.1	15.1	13.4	16.7

By performing the above mentioned experiments, studies were made on alum dosing methods, effect of return sludge, influence of variation of influent flow. The experiment results as shown in Table 1 are average values for each experiment. Also, the analysis of influent and effluent was conducted by using the composite samples of each day. Other samples were collected at 10 in the morning everyday.

EXPERIMENTAL RESULTS AND DISCUSSION

According to Table 1, the removal rate of phosphorous (P) was low ranging between 40 and 45%, except for Experiment 5. In contrast, the P-D removal rate was about 80%, and in all cases SS in the effluent was higher than SS in the influent. From these facts, the lowliness of the phosphorous removal rate can be considered to be caused by the lowliness of the insoluble phosphorous removal rate. Therefore, it is necessary to conduct studies on the improvement of the clarifier.

Results of P-D removal are shown in Fig. 2 concerning Experiments 1 ~ 3, and in Fig. 3 concerning Experiments 4 ~ 6.

Fig.-2

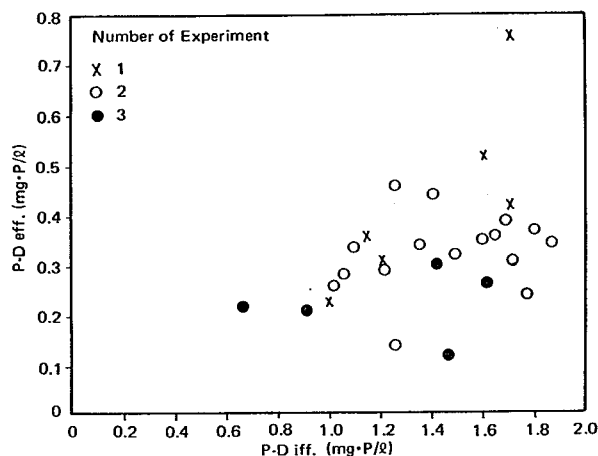
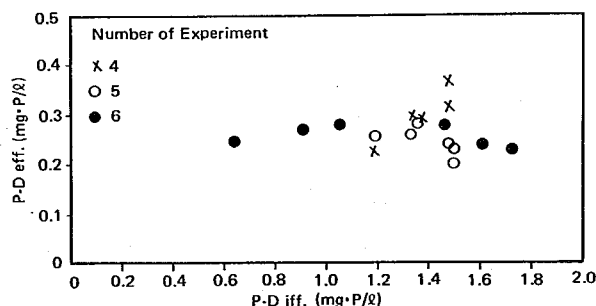


Fig.-3



From Table 1, Fig. 2 and Fig. 3, the followings can be considered concerning the P-D removal:

- 1) In both the constant dosing method and the molar control method, it was possible to lower P-D concentration in the effluent by the return sludge. Also, it lessened the fluctuations of P-D concentration in the effluent. This is because the alum sludge still had the ability to remove phosphorous. In Table 1, Mixed Liquor is a combination of influent and return sludge before alum dosing. In other words, Table 1 shows that between 40 and 75 percent of P-D in the influent were removed by the return sludge. Accordingly, the return sludge lowered the P-D concentration in the influent, and as variations became smaller, it lowered P-D concentration in the effluent to further minimize fluctuation.
- 2) The molar control method prevented variation of P-D concentration in the effluent by either daily average (Fig. 2, 3) or continuous measurement (Fig. 4, 5) than the constant dosing method even when sludge was returned. However,

according to Fig. 2, 3, the daily average value of P-D concentration in the effluent did not show any clear differences between the two alum dosing methods. The molar ratio of P-D/Al in the constant dosing method was 6 when P-D concentration of the influent was 1.13 mg·p/l. When the P-D concentration was about 1.13 mg·p/l, the P-D in the effluent was a little less than 0.3 mg·p/l in both methods.

- 3) Both alum dosing methods with return sludge did not cause increase of the P-D loading in the effluent owing to the variation in influent flow. (See Table 1 and Fig. 4, Fig. 5) Although this was considered quite natural in the molar control method, it was worth mentioning in the alum constant dosing method. So, it can be concluded that with regards P-D removal in alum precipitation, there is no need to conduct molar control method when sludge is returned.

Fig. -4

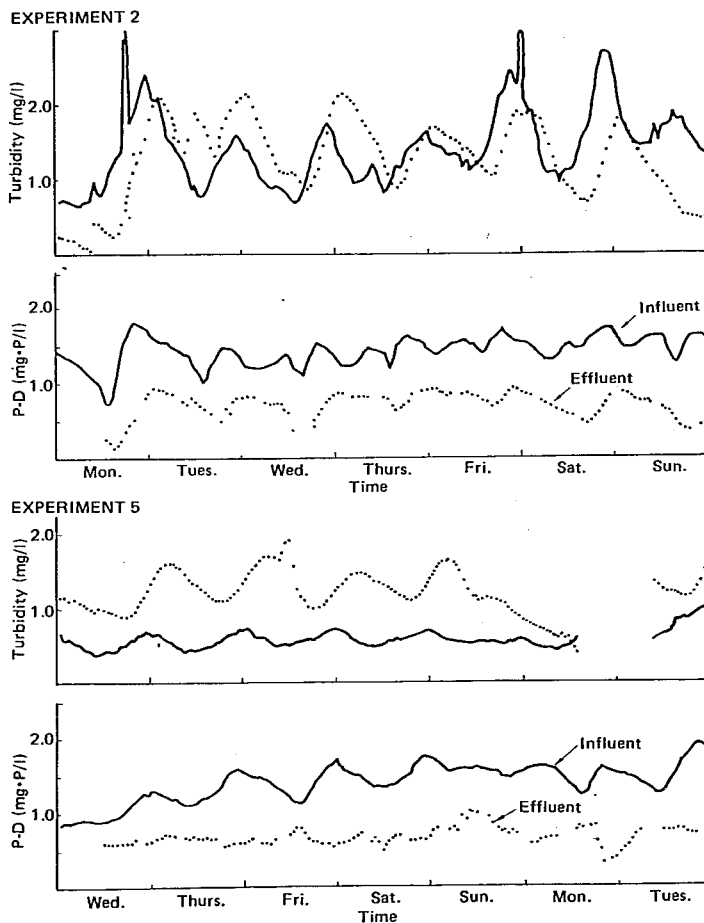


Fig. -5

