

**A CORROSION MECHNISM OF CONCRETE IN A SEWAGE TREATMENT FACILITY
USING AN OXYGEN AERATION ACTIVATED SLUDGE PROCESS**

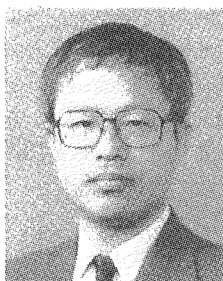
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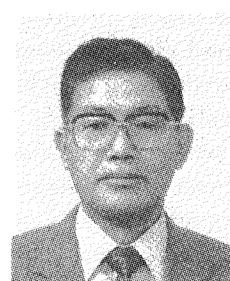
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In order to study the corrosion and deterioration mechanisms of concrete, concrete prism specimens were immersed in the final sedimentation tank and troughs of an oxygen-aeration activated sludge facility at a sewage treatment plant. Over the years, changes to the roughened surfaces, mass loss and a decreasing relative dynamic modulus of elasticity were observed. After 10 years, the bending performance of conventional concrete specimens immersed without a lining was lower in comparison to specimens with a lining. Microstructure and chemical analyses showed that surface samples underwent more obvious changes than interior ones, with the degree of change depending on the concrete mixture and whether or not the surface had been coated with a lining. The production of erosive free carbon dioxide was influenced by the quality of the sewage water, while the activity of bacteria and protozoa affected corrosion and deterioration of concrete more than sulfuric acid in sewage treatment water. Corrosion and deterioration of concrete progressed through chemical reaction and ion transport in concrete and sewage treatment water flows. A method for estimating the corrosion/deterioration of concrete in this sewage facility is proposed from the results and a calculation of free carbon dioxide.

Key Words: *corrosion of concrete, sewage treatment facility, free carbon dioxide, mass loss, dynamic modulus of elasticity, pore distribution, chemical analysis*

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1. INTRODUCTION

The corrosion of concrete in sewage facilities varies with sewage quality, the type and quantity of microbes present, the sewage treatment environment, and other factors. The main cause of sewage-pipe corrosion is thought to be acid (sulfuric acid) corrosion, and this is affected by the activity of bacteria such as sulfate reduction bacteria in the liquid phase and sulfur oxidation bacteria in the gas phase. Recent work has gradually clarified that such corrosion occurs as a result of bacterial activity and chemical reactions[1],[2],[3]. Thus, to protect sewage facilities from corrosion, the mechanisms at work must be clarified [4],[5]. Examination of corrosion occurring early on concrete surfaces in sewage treatment facilities has been traced to erosive carbon dioxide through analysis of the water quality and the corroded concrete [6],[7]. Thus, the mechanism was different from the sulfuric acid corrosion of sewage pipes. To further examine such mechanisms, experiments have been done on bacterial metabolism and concrete deterioration [8],[9]. With the increasing demand for qualitative and quantitative improvements in the water supply after wastewater treatment, there is a great need to obtain basic information on which to base countermeasures against corrosion in concrete sewage facilities.

In this ten-year study, 13 types of concrete test specimen with different mix proportions were placed at three locations in a final sewage treatment facility for an examination of corrosion mechanisms. Over the 10 years, measurements were conducted to evaluate changes in the specimens. This report presents our findings with respect to concrete corrosion and deterioration mechanisms. The main focus of this study was to nondestructively measure the degree of deterioration under the differing conditions of each immersion location. Over the 10 years, the test specimens were subjected to visual inspections and also to measurements of changes in mass and dynamic modulus of elasticity. After this 10-year period, some of the test specimens were examined physically for bending performance, water absorption, carbonation depth, and pore distribution and were also analyzed chemically by electron probe microanalysis, X-ray fluorescence analysis, and X-ray powder diffraction.

2. CAUSE OF EROSIIVE CARBON DIOXIDE

The material balance in a sewage treatment facility, as in all environments where natural reactions take place, depends on various cyclic processes such as decomposition, linkage, and immobilization, and there are complex interactions among them. Various organic and inorganic materials are present in the water, composing elements such as hydrogen, oxygen, carbon, nitrogen, sulfur, and phosphorus. Another factor affecting decomposition and immobilization in the material balance is the energy metabolism of the bacteria in sewage, and the growth/decline of their populations as kept in balance by the predatory mechanism of protozoa.

The activated sludge process is commonly used for aerobic and anaerobic treatment, and the quantity of aerobic bacteria, anaerobic bacteria, or facultative anaerobes in each system depends on the concentration of organic substances, the amount of dissolved oxygen, and other conditions. In aerobic treatment, organic substances are

decomposed to carbon dioxide, water, nitric acid, phosphoric acid, sulfuric acid, and other inorganic substances using the oxidative characteristic of bacteria metabolism[10]. In anaerobic treatment, organic substances are decomposed to methane and carbon dioxide depending on the metabolism mechanism of the bacteria. Both treatment methods were examined, with the oxygen aeration activated sludge process using pure oxygen, termed the "oxygen process", and the conventional activated sludge process with air, termed the "air process". In the first sedimentation tank of both systems, the occurrence of hydrogen sulfide and corrosion were minimal in the process leading up to a final product, since this stage of the process does not involve holding the sludge, although anaerobic activity is observed. With aeration, the activity and proliferation of facultative anaerobes cause nitrification, denitrification and phosphorus removal, so there is little possibility of the formation of hydrogen sulfide and sulfuric acid (Fig.1).

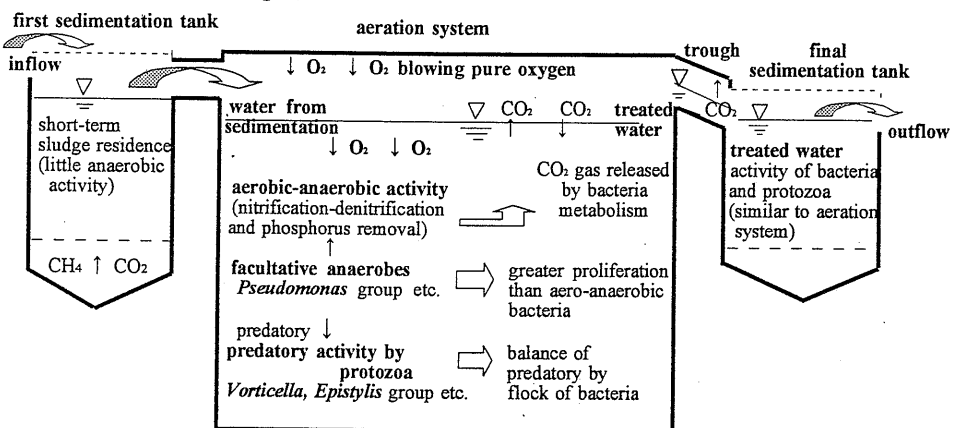


Fig.1 Outline of oxygen activity sludge treatment system

Identifying the main corrosion factor among nitric acid, carbonic acid, and others, including hydrogen sulfide and sulfuric acid, is difficult because many factors are at work in a complicated system such as found in sewage treatment facility. For instance, the corrosion mechanism taking place in sewage-pipe is influenced primarily by the process of sulfuric acid formation. However, other contributing factors include hydrogen sulfide and sulfuric acid. Carbon dioxide occurs in gas and liquid phases at aeration points, according to the results of existing measurements [7]. As for the occurrence of carbon dioxide in the oxygen process, corrosion is more obvious than in the air process. However, there are no significant differences with respect to other corrosion factors between the oxygen and air processes. Therefore, at the immersion locations in the facility used for these experiments, erosive free carbonic acid from carbonic acid in the liquid phase, is likely to be the primary cause of corrosion. The carbon dioxide is formed by the bacterial metabolism and the conditions of its growth or decline are affected by the oxygen demand. If the concentration of organic substances in the sewage is high, the sewage load becomes high, and much carbon dioxide is formed in the liquid phase. The sewage load in the oxygen process is higher than in the air process, and the concentration of carbon dioxide rises to a high level in the liquid phase. Also, the carbon dioxide concentration in the liquid phase increases between the aeration system and the final sedimentation tank, as carbon dioxide diffuses to the gas phase from the liquid phase and dissolves into the liquid phase.

All the dissolved carbonic acid in the liquid phase is called the "free carbonic acid", referring to the carbon dioxide remaining after linkage of carbonic acid with calcium, magnesium, and other cations. Of the free carbonic acid, the equilibrium level of dissolved carbonic acid is called the "dependent free carbonic acid", and the remainder is called the "erosive free carbonic acid" [11] (Fig.2). Although the carbon dioxide content of water is affected by the partial pressure and temperature of the water, after dissolution, the carbonic acid assumes various forms such as CO_2 , H_2CO_3 , HCO_3^- and CO_3^{2-} ; which vary in proportion with changes in pH.

Free carbonic acid, and especially the erosive free carbonic acid, is affected most by changes in the inflow load, bacteria metabolic activity, alkalinity, and pH of the liquid phase or the system environment. In the oxygen process in large treatment facilities, concrete corrosion may be largely due to the formation of carbon dioxide rather than of hydrogen sulfide and sulfuric acid, because of greater bacterial metabolic activity than in a sewage-pipe.

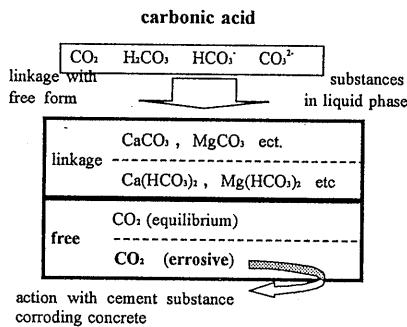


Fig.2 Formation and action of carbonic acid

Table 1 Materials

Material		Note
Cement		O.P.C
Aggregate	Coarse	Crushed stone
	Fine	Beach sand
Admixture	Water-reducing agent	Lignin sulfonic acid type
	High water-reducing agent	High condensation triazine type
	Air-entraining agent	Natural resin acid type
	Polymer	SBR latex
Lining	Epoxy resin	Condensation compound of bisphenol A and epichlorohydrin
	Tar-epoxy resin	Tar denatured component of epoxy resin

Table 2 Mix proportion factors

	Non-lining concrete						Lining concrete				Non-lining concrete		
	Conventional concrete						Epoxy (resin) lining concrete	Tar-epoxy (resin) lining concrete	Mortar lining concrete	Flow concrete	Polymer-cement concrete		
Specimen No.	1	2	3	4	5	6	7(1) ^{*1}	7(3) ^{*2}	8(1) ^{*1}	8(3) ^{*2}	9	10	11
Water-cement ratio (%)	50	55	60	50	55	60	55					51	
Sand percentage (s/a, %)	44						42				48	42	
Unit cement weight (kg/m ³)	300						330						

(1)^{*1}: one coating (lining thickness of 400-600 μm)

(3)^{*2}: three coatings (lining thickness of 600-1000 μm)

3. EXPERIMENTAL OUTLINE

3.1 Immersion Conditions

The main location selected for immersion of the test specimens was the trough of the final sedimentation tank in the oxygen treatment process. The water depth in the trough was 13~32 cm. The flow speed was about 96 cm/sec at a depth of 4.5 cm. For comparison, other immersion locations, such as the final sedimentation tank of the oxygen process and the trough in the air treatment process, were also selected. The water level in the trough of the air treatment process system was 14~21 cm and the flow speed at a depth of 6 cm in the center of the trough was about 80 cm/sec [12].

3.2 Test Specimen Factors

The materials and mix proportion factors are shown in Table 1 and Table 2. Ordinary Portland cement was used with sea sand (specific gravity: 2.56; F.M.: 2.79) and crushed stone (specific gravity: 2.71; F.M.: 6.92) as aggregates. The water-cement ratio was set at the largest amount of water acceptable for AE concrete based on durability as given in the sections on "water-tightness concrete" and "mix proportion" of the Japan Society of Civil Engineers Standards at the time of experiment planning. As a result, three water-cement ratios of 50, 55, and 60 %, and two unit cement weights of 300 and 330 kg/m³ were chosen ("conventional concrete"; specimen number in Table 2 : 1~6). The slump and air volume of all concrete specimens were, respectively, 8±1 cm and 4±0.5 %. In addition to these six types of concrete, specimens with different coating ("lining") specifications ("lining concrete"; specimen number: 7(1) and 7(3) ("epoxy lining concrete"), 8(1) and 8(3) ("tar-epoxy lining concrete"), and 9 ("mortar lining concrete")), flow (high slump; "flow concrete"; specimen number: 10) and polymer-cement concrete ("polymer-cement concrete"; specimen number: 11) were also prepared. The basic mix proportions of the base concrete for the lining specification, unit cement weight and water-cement ratio, were respectively 330 kg/m³ and 55 %. The slump of flow concrete was 18±1 cm. The polymer cement ratio of the polymer-cement concrete was set at 10 % and the water-cement ratio at 51 %. For the lining, two kinds of resin and one kind of mortar were used. Each epoxy resin and tar epoxy resin were used as resin for lining. The epoxy resin was combined with paint or other materials to form condensation compounds of bisphenol A and epichlorohydrin. The denatured aliphatic polyamine was used as a hardener component. Also, the tar-epoxy resin was made with a denatured component of tar, which was mixed with bitumen material to form epoxy resin. The thickness of the resin lining applied to the concrete was 400-600 μm or 600-1000 μm. The thickness of 400-600 μm represents one coating (specimen number : 7(1) and 8(1)) and 600-1000 μm represents three coatings (specimen number: 7(3) and 8(3)). The mortar for the mortar lining concrete was made with a 34 % water-cement ratio ; sand : cement = 2 : 1 ; and a flow value of 183. The lining quantity was measured from the difference in test specimen mass before and after the lining was applied. The lining thickness was calculated as the mean value by using the unit mass of the lining material and the test specimen surface area. Furthermore, there was a possibility that a lining primer would impregnate the concrete and change its physical properties. Therefore, no primer was used.

The concrete materials were mixed using a 50-L tilting mixer. The concrete was cast in accordance with JIS A 1132. All test specimens were cured in water for two weeks and then under atmospheric conditions for two weeks. Test specimens were subjected to an immersion test after which the concrete surface was coated with the lining or subjected to other forms of processing.

3.3 Test Specimens and Tests

Test specimens measuring 10×10×40 cm were immersed in the sedimentation tank while those in the trough measured 5×10×40 cm. Thinner test specimens were used for the trough tests to allow easy installation, to minimize disruption to the flow, and to prevent the loss of the test specimen due to flooding or other reasons. The test specimens were placed in a stainless steel net and immersed in the sedimentation tank.

There was a possibility that test specimens immersed in the trough could be washed away by the water flow. Therefore, they were attached by metal fittings to a stainless steel chain stretched in the flow direction of the trough. Test specimens were measured after being raised from their location and washed. Three test specimens were prepared for each factor. Each test specimen was also inspected visually in its immersion location (roughness of surface, swelling, peelings and cracks in the lining layer), change in mass and measurement of the resonance number of vibrations (JIS A 1127) by the deflection-vibration method. One test specimen for each factor was subjected to a bending performance test (JIS A 1106).

After the test specimen had been ruptured by the bending performance test, it was subjected to visual section inspection and measurement of carbonation depth (phenolphthalein method), water absorption rate, pore distribution (mercury intrusion method) as well as electron probe microanalysis, X-ray powder diffraction analysis, and X-ray fluorescence analysis. Multiple test specimens were examined in cases where the resin lining showed significant swelling and peeling. An overall outline of this research is shown in Fig.3.

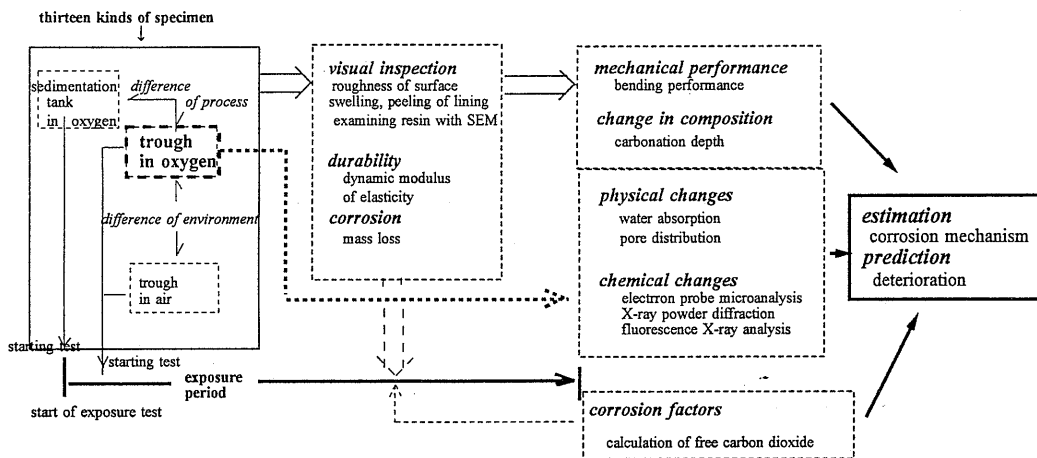


Fig.3 Outline of study

4. RESULTS AND CONSIDERATION

4.1 Change in Specimens with Exposure Period

a) Visual inspection

All test specimens without surface lining treatment (conventional concrete) showed a change in color (oxygen process) at an early stage (3 months after immersion), while those with a 60 % water-cement ratio immersed in the trough showed a loss of corners. Erosion proceeded gradually. After more than 10 years, the surface was very rough, with exposure of coarse aggregate as shown in Photo 1. For specimens with a cement ratio of 50 %, some mortar remained among the coarse aggregate on the surface. However, for specimens with 55 % and 60 % water-cement ratios, the surface mortar

had almost all eroded away and only coarse aggregates were seen. Even this was often lost. Therefore, we concluded that immersion has a stronger erosive effect as the water-cement ratio increases, with more mortar falling away from the surface and erosion occurring at the interface between coarse aggregate and mortar.

For 3 months after immersion had begun, specimens with lining showed no color change or other changes except in one case where swelling of the surface occurred. As the exposure period increased, the lining of some test specimens began to swell and peel. Almost all tar epoxy resin linings peeled from the concrete surface leaving a rough concrete finish. With the epoxy resin linings, swelling occurred over almost the entire surface with cracking and peeling of the single-application resin layer (400-600 μm). In cases where the lining had been applied three times, swelling was observed in some specimens. In the case of the mortar lining, long-term immersion caused loss of corners and exposure of the fine aggregate. However, the concrete did not become exposed, because the mortar was 1 cm thick and had a low water-cement ratio. With specimens, the flow concrete and the polymer-cement concrete showed the same degree of roughness on the surface as the conventional concrete. No advantage of the flow concrete and the polymer-cement concrete in comparison to the conventional concrete was observed visually.

Environmental differences had a greater effect on erosion in the oxygen processing system than in the air processing system. The degree of erosion differed with both the processing system and the specimen location. The most severe erosion occurred with specimens placed in the trough of the oxygen process. This is because these test specimens were influenced by the difference in the content of the immersion solution as well as the mechanical action of the processing water flow. In all environments, the damage with the mortar lining and the three-layer epoxy lining was less than with a one-layer epoxy lining and a one- or three-layer tar-epoxy lining.

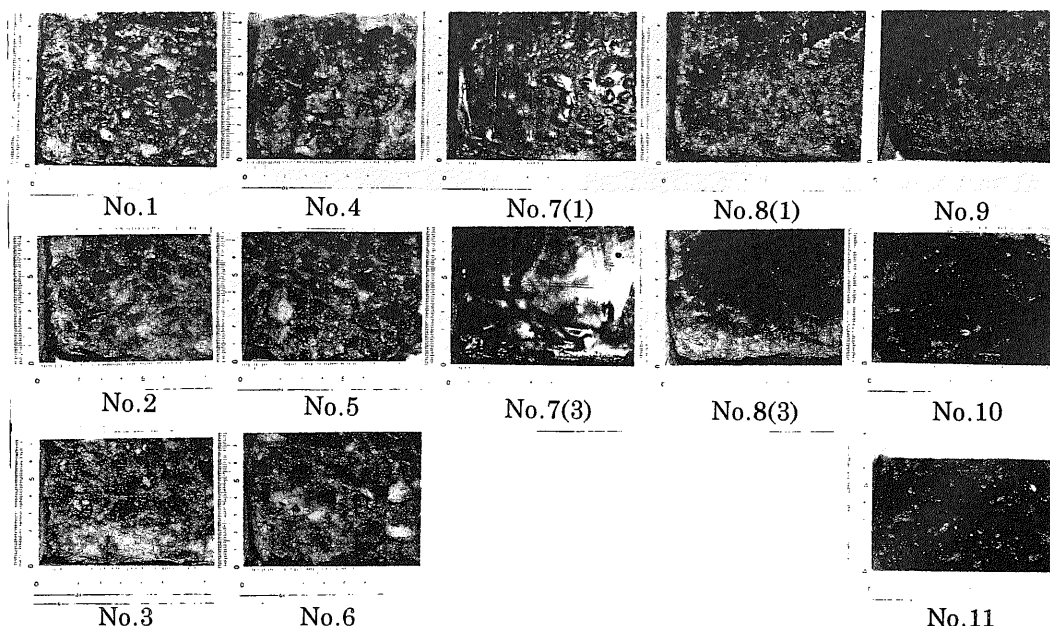
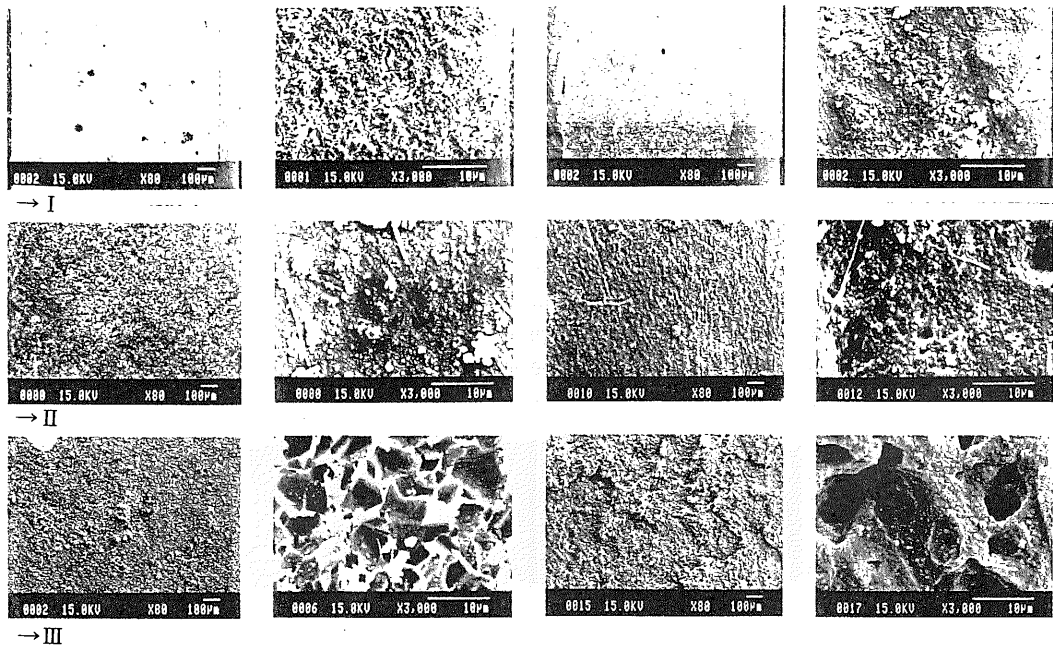


Photo 1 Results of visual inspection (trough in oxygen process)

b) Corrosion of resin

To examine the resin lining, it was peeled off from test specimens and observed with an electron microscope. Photo 2 shows representative results. These samples were the three-layer epoxy and tar-epoxy linings from specimens which had been immersed in the troughs of the oxygen process for about 13 years. Low-magnification images of the cross section show many bubbles of about 100 μm in the epoxy, but few in the tar-epoxy lining. However, high-magnification images show the epoxy lining to be almost uniform while the tar-epoxy lining is not. Both types of lining were coated with matter which had been floating in the processing water. The high-magnification images of the surface also revealed that there were almost no faults in the epoxy lining but pinholes of 1~10 μm over the whole of the tar-epoxy lining. The difference between the two linings was evident. Examination of the back surface of the lining showed clear traces of cement hydrates in the case of the epoxy. This indicated that the epoxy resin had adhered well to the concrete. However, in the case of the tar-epoxy, swelling/peeling was observed in many places, and the hydrates of cement or the resin itself had eroded.



(1) Low-magnification (2) High-magnification (1) Low-magnification (2) High-magnification
 (a) Epoxy resin lining (b) Tar-epoxy resin lining

Photo 2 SEM micrographs of resin lining (trough in oxygen process,
 I : section, II : surface, III : reverse)

c) Nondestructive testing

Changes in the relative dynamic modulus of elasticity during the exposure period are shown in Fig.4. In the case of the sedimentation tank in the oxygen process, the relative dynamic modulus of elasticity was high until 1 year in all cases. However, the value decreased for some resin-lining test specimens and for most non-lining specimens immersed in the trough of oxygen process. Most non-lining specimens aside from the polymer concrete one immersed in the troughs of the air process showed values above 100 % with a peak at 3 months. On the other hand, for some resin-

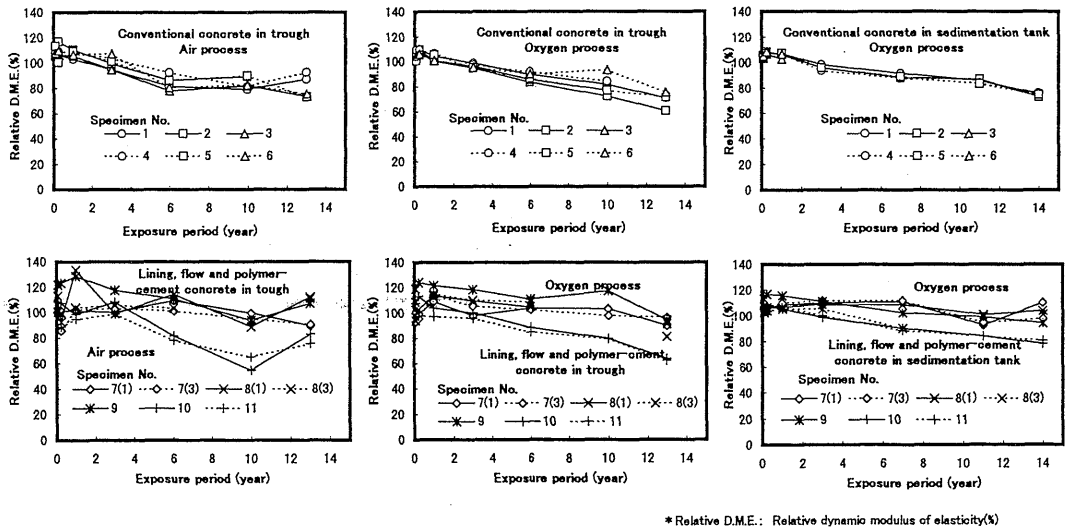


Fig.4 Change in relative dynamic modulus of elasticity

lining test specimens, the value fell below 100 %. The results for the three environments differed as a result of the variations in processing water quality, mechanical action of water, and the period of hydration of the immersed concrete. For example, a comparison of specimens from the sedimentation tank of the oxygen process and the trough of the air process shows that the former had a more detrimental effect on the concrete. However, in the sedimentation tank of the oxygen process almost no erosion due to mechanical action occurs, in contrast with the trough of the air process. Also, the differences in the degree of hydration among the test specimens themselves led to differences.

Based on these findings, the differences were considered to arise from the environment and depend on the moisture condition, caused by immersion (non-lining test specimens), the environment during the drying before lining, and the lining (the resin-lining test specimens). Therefore, test specimens immersed for 1 year were considered to have undergone a complex process including improvement of the physical properties due to the progression of hydration, which was then offset by the chemical action of the processing water or the physical action of the trough water flow. The relative dynamic modulus of elasticity of conventional concrete in the trough of the oxygen process decreased by around 5 % between 1 year and 3 years. However, except for the tar-epoxy lining specimens, most others showed values above 100 %. Differences in relative dynamic modulus of elasticity were also found to arise due to variations in the unit weight of cement and the water-cement ratio. The rate of decrease in relative-dynamic elasticity modulus of the conventional, flow and polymer-cement concrete in each environment were comparatively large as the exposure period increased, but very small for the resin-lining test specimens.

The conventional, flow and polymer-cement concrete showed decreases in relative dynamic modulus of elasticity of 10~30 % at the end of the exposure period in the air process. Some of the lining specimens showed about a 10 % decrease, but most showed almost no decrease even after long exposure. Many specimens immersed in

the oxygen process could not be measured due to the roughness of the specimen surfaces. Thus, it is difficult to compare the effects of the sedimentation tank and the trough. However, most of the lining specimens in the sedimentation tank indicated no decrease, except for the 5 % decrease found for the mortar lining. For the trough specimens, the decrease was about 5~20 %. The value of non-lining specimens in the sedimentation tank decreased about 20 % (flow and polymer-cement concrete)~25% (conventional concrete), and the value of non-lining specimens in the trough decreased about 35 % (flow and polymer-cement concrete) and also about 25~40 % (conventional concrete). Therefore, the influence of the trough in the oxygen process was greatest among the three environments. In general, decreases in the relative dynamic modulus of elasticity of the conventional, flow and polymer-cement concrete specimens were more obvious than for the lining concrete. Comparison of the environments shows that the decrease in the air process was of the same degree or larger than in the sedimentation tank in the oxygen process, and was largest in the trough in the oxygen process. The decrease began within a year for the conventional, flow and polymer-cement concrete. With the lining concrete, almost no decrease was noted under these exposure environments for 10 years or more. This led us to conclude that lining concrete can offer protection for a long period.

d) Mass change

The change in mass over the exposure period is shown in Fig.5. Almost all specimens showed loss of corners and other changes after 3 months of immersion. Nevertheless, their mass increased due to absorption because the initial mass value was the dry value before immersion. The specimens were affected by erosion in the immersion liquid, mechanical erosion from the water flow and other causes of mass loss. However, the mass loss was small until 1 year because absorption and hydration exceeded the influence of erosion. Mass loss of specimens in the air process and in the sedimentation tank of the oxygen process was not observed until 1 year. On the other hand, all specimens of lining concrete in the trough of the oxygen process had decreased in mass after 1 year. This result shows that the trough environment in the

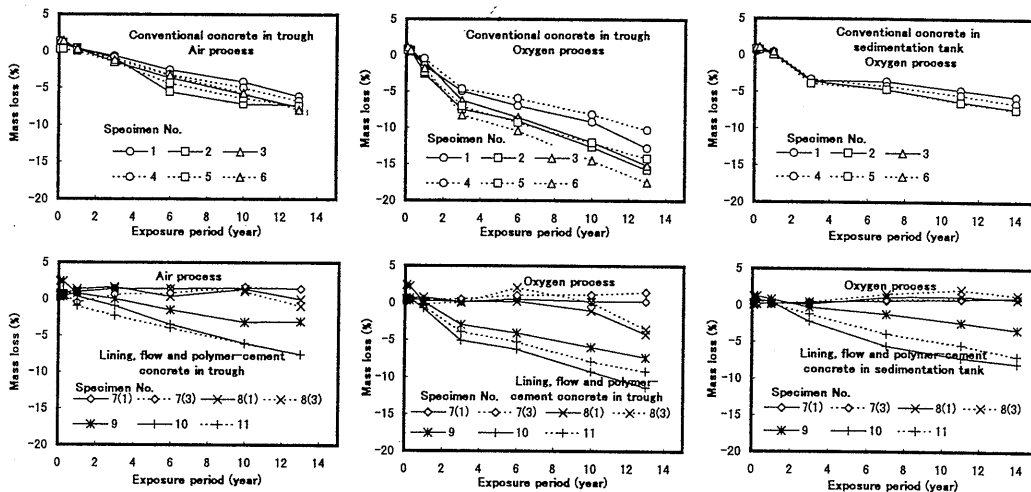


Fig.5 Changes in mass in each system

oxygen process system is severer than the other environments. Until the third year, the non-lining specimen immersed in the air process decreased in mass about 3 %, and there was a 3~7 % mass loss after that period. A higher unit weight of cement gave some protection against mass loss. The mass loss of specimens with a water-cement ratio of 50 % was less than that of 55 % or 60 % specimens. Therefore, in non-lining concrete, low water-cement ratio and high unit-cement weight was useful for corrosion resistance. Although mass loss was not observed for most lining specimens, the mortar lining specimen showed a few percent mass loss. The flow and polymer-cement concrete was in the loss range of conventional concrete and decreased by about the same degree.

The ultimate mass loss at the end of the exposure period was as follows. In the air process, non-lining concrete specimens decreased by 6~10 % and the lining ones 0~2 % (resin) and 4 % (mortar). Also, in the sedimentation tank of the oxygen process, the mass losses of non-lining ones were 6~8 % and those of lining ones were 0 % (resin)~3.5 % (mortar). Furthermore, in the trough of the oxygen process, the mass loss of the non-lining specimens was 9~16 % and that of the lining ones was 0~5 % (resin) and 8 % (mortar). The relative surface area of the test specimens in the trough of the oxygen process was large, about 1.4 times that in the sedimentation tank of the oxygen process. Even if this is considered, the mass loss of the non-lining specimens in the trough of the oxygen process was the largest. There was no obvious difference in mass loss with unit weight of cement, though there was influence with the water-cement ratio in mass loss. These results show the need for a low water-cement ratio and a high unit weight of cement to ensure concrete durability. The mass loss of non-lining specimens in the trough of the oxygen process was 15 % or more, and the mass loss of the lining specimens was near that of the non-lining specimens in the air process and in the sedimentation tank of the oxygen process. From these mass change results, again the trough of the oxygen process is shown to have the severest environment.

4.2 Physical and Chemical Properties

a) Bending strength

Bending strength tests were done in conformity with JIS A 1106. The bending section of the test specimens in the trough had a width of 10 cm and a bending height of 5 cm. The bending test specimens were divided into three equal 30-cm spans at loading. Measurements were done for one conventional, flow and polymer-cement concrete specimen without the resin lining and mortar lining for each factor. For the lining concrete specimens in the trough of the air process and the oxygen process, all specimens with a single epoxy coating and a single or triple tar-epoxy coating showed obvious swelling/peeling on the surface, and all the lining specimens except those with a mortar lining in the sedimentation tank of the oxygen process were measured individually.

Loading in the bending test, was done in the casting direction. Because the erosion of the test specimen surface was severe, accurate comparison of cross section measurements could not be done. Instead of bending strength, the maximum load results were compared. These results are shown in Fig.6. As noted earlier, the section

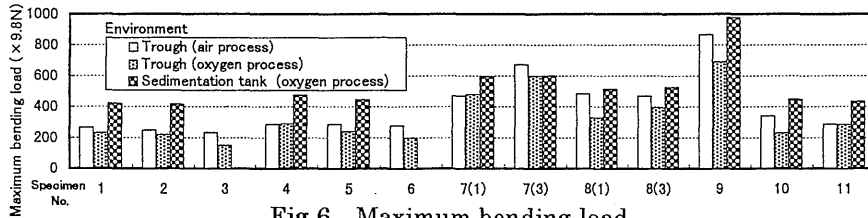


Fig.6 Maximum bending load

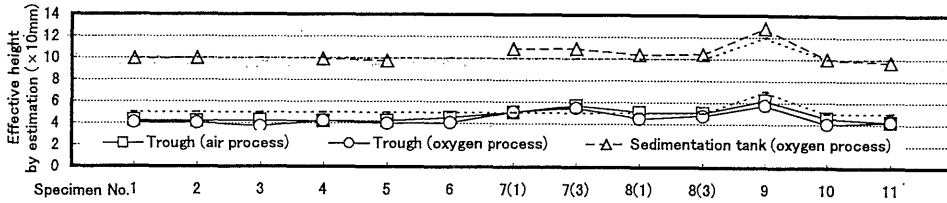


Fig.7 Effective section height by estimating maximum bending load

height of the test specimens in the sedimentation tank of the oxygen process was twice that of the test specimens in other environments. Considering this, the measured values of bending strength for test specimens in the sedimentation tank of the oxygen process would be 4 times greater. Therefore, these maximum loads are multiplied by a factor of 1/4 in Fig.6. Since most of the measured values are from a single test specimen only, a considerable variance is conceivable. However, as a whole, the maximum load determined from bending tests on test specimens in the trough of the oxygen process is lower than that in the trough of the air process. Therefore, the results clearly show the differences between the influence of the environment in the trough of the air and oxygen process. Thus, these test results suggest that a test specimen in a particular environment is influenced by the unit cement weight, water-cement ratio, and lining on the surface. Therefore, durability increases with a high unit cement weight, low water-cement ratio, and a lining. All the test specimens were subjected to destruction within the bending span in the bending test. The maximum bending load depend on mix proportion factors and the system environment.

The effective section was estimated using the calculation formula $f_b = PL/bd^2$ for the bending strength based on the compression test results at the start of exposure, where P is the maximum load on the test specimen, L is the span, b is the width of failed section, and d is the height of the failed section. Estimation of the effective section was based on the following relationship. The specimen exposed in the sedimentation tank of the oxygen process showed the relation of $d \approx b$ and also the relation of $d \approx b/2$ in the trough of the oxygen and air process. The f_b used was 1/7 of the value of the 28-day compressive strength at the time the test specimen was cast. The value of d estimated using this assumption is shown in Fig.7. Comparison of the estimated values showed the effective section of the non-lining test specimens to decrease more than the epoxy resin lining ones. Also, looking at the difference in environments, the effective section of the oxygen process specimens decreased more than that of the air process specimens. If the effective section of the resin lining specimen estimated to be larger than the standard value before immersion was taken as equal to the standard value, the ratio of the effective section of each test specimen would be as shown in Fig.8. However, the estimated effective section was calculated from the standard value of the bending strength of the concrete based on the compressive strength for the

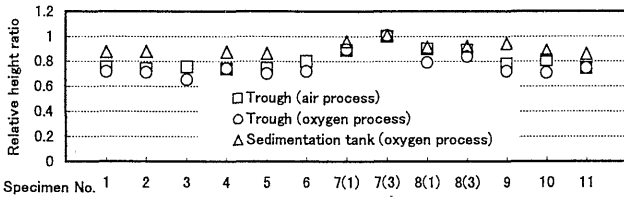


Fig.8 Relative height ratio (effective height of resin lining concrete: 1)

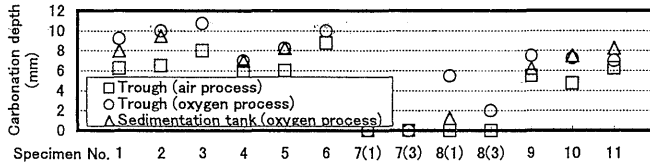


Fig.9 Mean value of carbonation depth

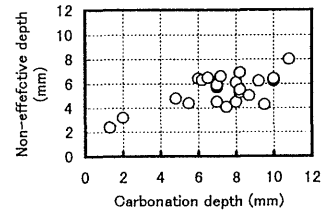


Fig.10 Relationship between carbonation depth and non-effective depth

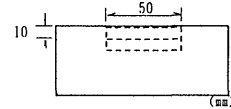


Fig.11 Geometric section of specimen at cutting

compressive test specimen cured for 28 days. Therefore, the estimated effective section may have been too large. Also, the d value of the lining test specimens shows a larger value in Fig.7 than the standard value, may have been possible the influence by the lining. Further consideration of this influence is needed.

b) Carbonation

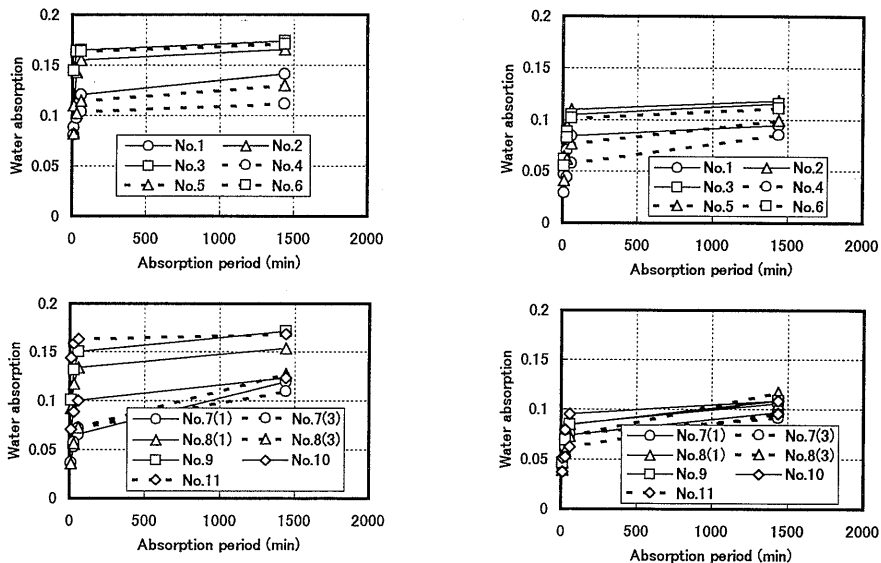
A 1% of phenolphthalein solution was sprayed on the section tested for bending performance and the depth of color change was observed. The specimen was observed to have three regions from the outside to inward. The outside periphery of a few to 10 mm was a faint brown, the next about 1 mm was white, and the innermost section was gray. Spraying with phenolphthalein, the innermost gray portion changed to red while the outer brown and white sections did not change. Therefore, the outer brown and white regions had undergone carbonation while the inner section had not. The inner-gray region may not have been chemically affected by erosion. It was difficult to judge whether the white region between the outermost and innermost regions was due to direct chemical action of the immersion liquid or the secondary action of equilibrium reactions maintaining the chemical balance between outside and inside. The carbonation depth can be compared if the specimen is not damaged by chipping. However, the degree of erosion of the cross section differs with test specimen and it is difficult to compare carbonation depths. Carbonation depth was estimated to save extent from the initial face of specimen before immersion by assuming that even the part eroded and washed away passes through the process of carbonation \rightarrow dissolution \rightarrow outflow. All conventional, flow and polymer-cement concrete specimens showed carbonation depths of about 4 mm to 10 mm, while most the lining specimens showed no carbonation, as can be seen from Fig.9. Also, differences were apparent according to the type of concrete and the environment. Therefore, the non-effective depth was taken to be half the height of the section (the standard section) before corrosion minus the height of the estimated effective section in Fig.7. Comparing the non-effective depth and carbonation depth showed the latter to be larger, as can be seen in Fig.10. Thus, the part of carbonation region contributes to the mechanical performance. However, as mentioned above, if the effective section of the resin lining specimen is assumed to be the basic effective section, the section of each non-lining test specimen decreases, and non-effective depth approaches the carbonation depth.

c) Water absorption and pore distribution

The test specimen used for the bending performance test were examined for absorption and pore distribution characteristics. The test specimens were those from the trough in the oxygen process and which were thought to have been exposed to the most severe corrosion. To eliminate influence from the edge face, the specimen was cut about 100 mm along the long axis, and about 50 mm along the short axis and at about 10 mm sections from the surface to the depth shown in Fig.11. The specimens were then divided into samples for pore distribution, chemical analysis, and absorption studies. Before measurement, all samples were dried in a vacuum and then immediately subjected to measurements.

Water absorption depends on the physical properties of the hardening substance and the absorption time. However, it was assumed that water absorption does not depend on time and that the moisture distribution gradient within the sample was zero in this case because of its thinness. Fig.12 shows the relation between water absorption rate and time. This is compared with absorption over 24 hours as the standard value (the final value). Water absorption in the early period approaches the final value. This tendency is especially evident at the surface region of sample. In most samples, the water absorption rate near the surface at 10 minutes was about 7/10~8/10 of the standard value. On the other hand, when there was a resin lining (except for the single coating with tar-epoxy), the interior samples had a the 10-minute absorption of about 3/10~5/10 of the standard value. Therefore, the physical properties of the surface without a lining differ from those of the interior.

The water that comes into contact with concrete reaches close to saturation in the pores near the surface. Water penetration can be thought to advance inside via smaller pores. The pore distribution near the surface can be considered to change as the pore size increases through contact with the eroding liquid. Therefore, the pore distribution structure near the surface changes from the original pore distribution, which is depend on the water- cement ratio and the unit weight of cement.



(a) Surface region

(b) Inside

Fig.12 Changes in water absorption

Pore size of 6 nm to 200 μm was measured by the mercury intrusion method. The total pore volume of the surface region and the interior is shown in Fig.13 (a) and the ratio of each to the total pore volume in Fig.13 (b) (surface) and (c) (interior). The total pore volume of the surface region is larger than that of the interior. With the exception of samples with a resin lining, the difference in total pore volume between the surface region and interior is large. These total pore volumes differ with mix proportion factors, unit weight of cement and water-cement ratio. The total surface pore volume of the mortar lining sample is larger than that of other samples because the surface mortar region contains many fine aggregate particles with a large relative surface area. Therefore, the interfacial zone attacked by the eroding liquid is greater in the mortar than in the concrete [13]. In the resin lining samples, the difference in total pore volume between the surface region and the interior may be caused by the dry curing carried out prior to lining.

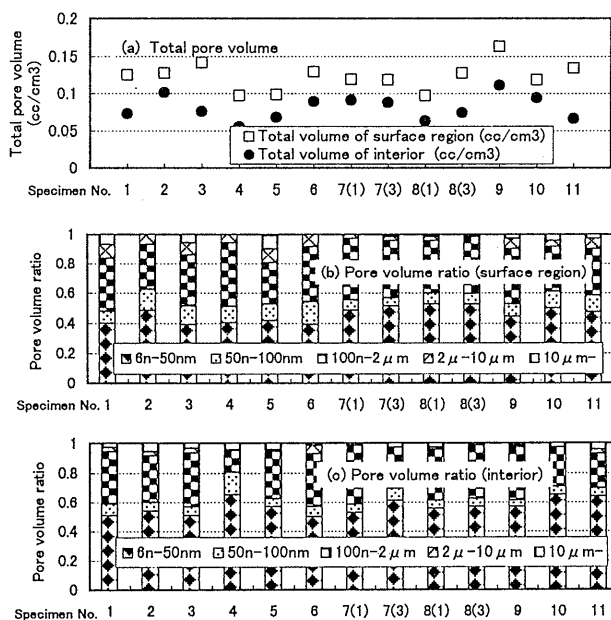


Fig.13 Total pore volume and pore volume ratio

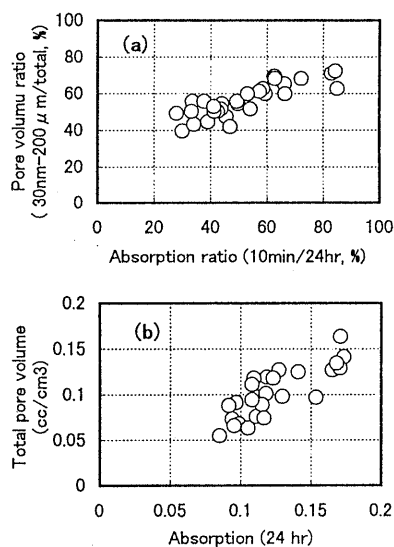


Fig.14 Relationship between water absorption and pore volume

Comparing the various pore volumes in the surface region shows that pores of 2 μm ~ 10 μm are present in conventional concrete, although they were thought not to exist. The surface region is thought to be more influenced by corrosion because pores of 2 μm ~ 10 μm are rare in interior. The pore distribution was divided into small (below 20 nm ~ 30 nm) and large (over 20 nm ~ 30 nm). Fig.14 (a) shows a correlation between absorption over 10 minutes and the absorption over 24 hours as well as between the ratio of pore volume over 30 nm to total pore volume. There was also a correlation between the ratio of absorption over 24 hours and the total pore volume (Fig.14 (b)). In the early period, absorption is thought to be influenced largely by the capillary pores, including those in the interfacial zone between aggregate and cement paste. Also, although the final absorption ratio exceeded the total pore volume, this difference was large for interior of the specimens. This result is mainly influenced by gel pores less than 6 nm and shows that the gel pores of interior were not attacked by the eroding liquid.

d) Electron probe microanalysis (EPMA)

The surface of a vertical section taken toward the axis of the sample were subjected to elemental analysis. The main measurement conditions were as follows: acceleration voltage, 15 kV; absorption current, 2.5×10^{-7} A; and probe diameter, 10~200 μ m. Point analysis of neighboring corroded parts was also done. Fig.15 shows about a 20-mm width section from the middle of a cross section subjected to the bending test (Photo 3) with a probe diameter of 200 μ m (Fig.15 (a)). The elements in the corroded part included carbon, calcium, silicon, and even sulfur. There were many cases in which the carbon was concentrated mainly at the corroded surface and decreased toward the inside, while there was little calcium at the surface but much further inside. These results show that carbon (main corrosion factor) and calcium (main component of cement) show concentration gradients which change with specimen depth. These results show that carbon (main corrosion factor) and calcium (main component of cement) show concentration gradients which change with specimen depth. No calcium concentration gradient was observed in the sample with the resin lining, though gradients including one for calcium were confirmed in conventional, flow and polymer-cement concrete. Thus, the coating with resin lining appears to protect against or reduce the effect of the erosion factors at the surface. Therefore, the possibility is great that erosive carbon dioxide originates from carbon, although sulfur can also be suspected.

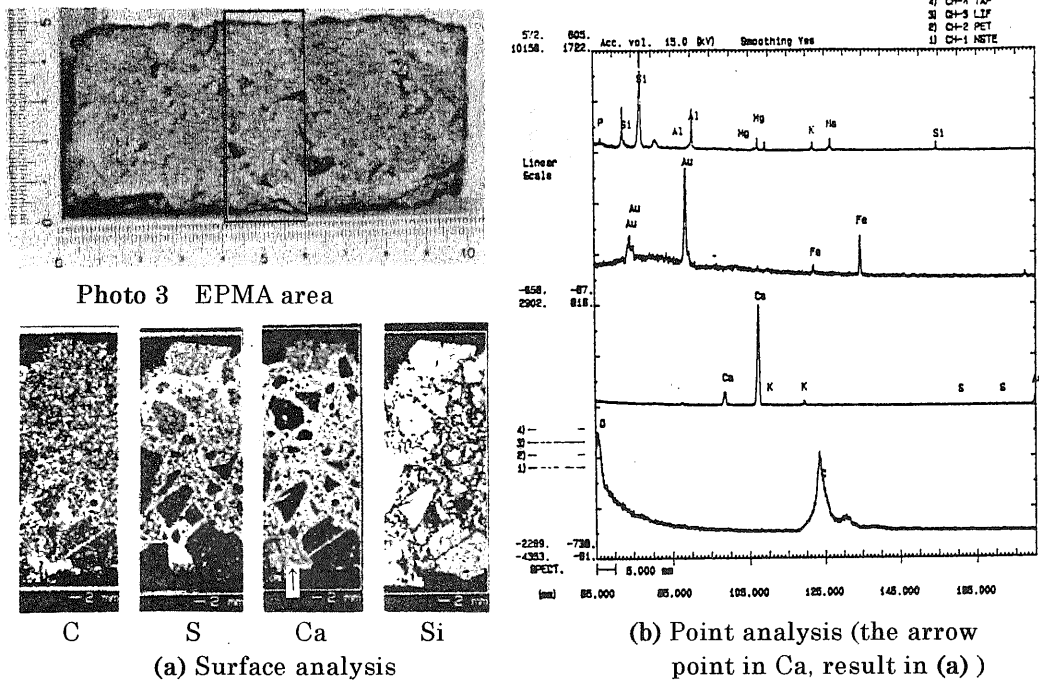


Fig.15 Typical results of EPMA (No.5 sample in trough of oxygen process)

e) Fluorescence X-ray and powder X-ray diffraction

Each sample described in 4.2 c) was analyzed by X-ray fluorescence and diffraction at the three points: the softening part, the surface, and the inside. Each sample was prepared by removing the coarse and fine aggregates with a sieve. The measurement conditions for X-ray fluorescence analysis were as follows: anticathode, Rh; applied voltage-current, 50 kV-50 mA; analyzer crystal, RX-60, TAP, GE, LiF; and detector, PC, SC. Also, the powder samples of constant mass were molded into thin disks of less

than 1 mm to decrease measurement errors by Compton scattering. On the other hand, the measurement conditions for X-ray powder diffraction were: target, Cu-K α ; applied voltage-current, 40 kV-80 mA; and slit system, 1 degree-1 degree -0.15 mm. Standard samples were several types of Portland cement of NBS (National Bureau of Standards) and Standard Reference Material.

The principal component elements of cement and carbon were analyzed by X-ray fluorescence. However, the concrete-attaching carbon was judged to be difficult to obtain with good precision in comparison with other elements because it is a light element and gave 10 or fewer measuring counts even in the softening part and surface portion. Also, every effort was made to prevent contamination of the test specimen even by fine aggregate, but the major elements were not considered and the focus was directed mainly at calcium and magnesium. Fig.16 shows the count ratios of calcium or magnesium in the softening part, surface, and inside of each sample. The count ratio of calcium is about 0.8 to 1.0 in the inside, although the ratio fluctuates. The ratio in the softening part was shown to be about 0.2 irrespective of mix proportion factors, although this value is very low in comparison with the inside. The ratio for conventional, flow and polymer-cement concrete is lower than that for lining concrete, although the ratio of the lining series is almost 1.0, and this result shows a characteristic different from the softening part and the inside. This result demonstrates that calcium decreased due to dissolution and ionization in the surface region in comparison with the inside, where there is much calcium hydrate from the cement, and shows that little calcium is present in the softening part. The lack of calcium may be due to its dissolving out of the sample. This agrees with the concentration gradient of calcium determined from surface analysis. On the other hand, for magnesium, the relative concentration is large inside each sample compared with the surface and the softening part. The difference between the amount of calcium and magnesium may arise due to the calcium concentration before corrosion being greater than that of magnesium or due to the magnesium not dissolving because of its higher solubility product. The sulfuric acid, nitric acid, carbonic acid, and other components suggested as corrosion factors are present in sewage treatment water.

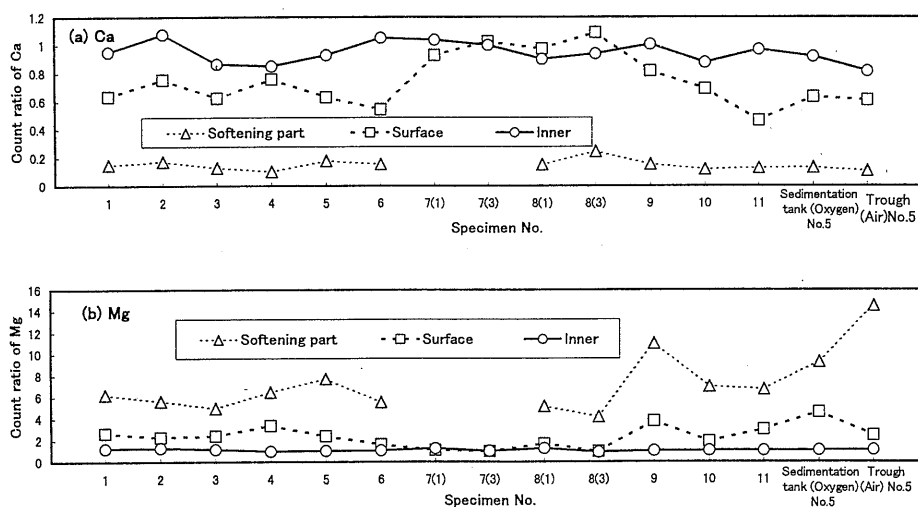


Fig.16 Count ratio (No.7(3) specimen count: 1) by fluorescence X-ray analysis

Acid-attacking hydration products of cement, such as calcium hydroxide, ettringite, and calcium silicate hydrate, react with acid and decompose, although the extent of the reaction differs with the acid. Calcium hydroxide was not found in the softened part and the surface of samples without lining, and even in the lining samples the amount of calcium hydroxide was small. On the other hand, calcium hydroxide clearly existed in the interior, which remained in better condition as it was not affected as much by corrosion in comparison with the surface. Although sulfur was detected at the surface by surface analysis, no gypsum was found in the softening part and at the surface by X-ray diffraction [14]. Therefore, it is likely that almost no corrosion due to sulfuric acid occurred. Identification of the components was done by referring to a report on a similar deterioration case [6]. The main peak of calcium hydroxide and calcium carbonate and the peaks of the quartz and feldspar groups included in the aggregate and other materials were identified. Magnesium compounds were also identified but at a very low level in comparison with the other components. However, they could not be ignored in forming a hypothesis. The results are presented in Fig.17. The headings used in the figure are those given by JCPDS (Joint Committee on Powder Diffraction Standards) and thus some may not have been present in the actual samples.

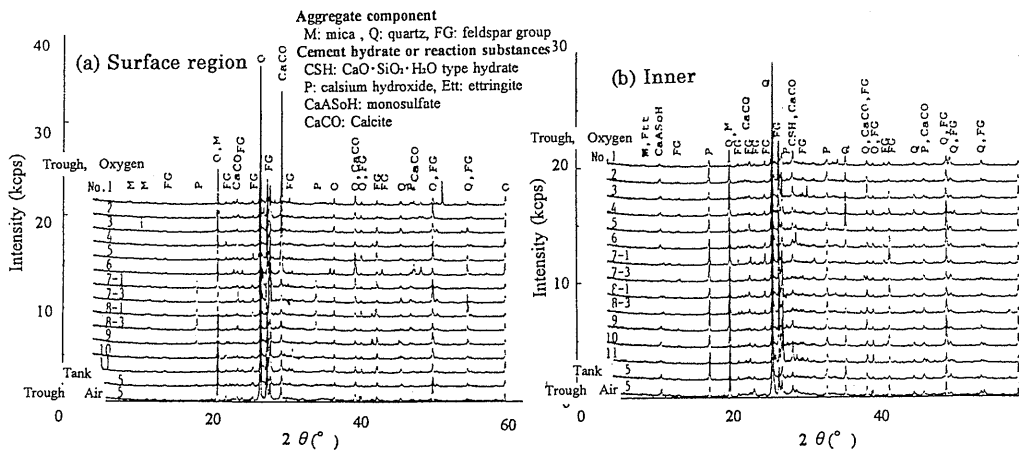


Fig.17 Results of powder X-ray diffraction

5. EXPLAINING THE CORROSION MECHANISM AND PREDICTING DETERIORATION

5.1 Explaining the Corrosion Mechanism

The main factor causing corrosion from the outside toward the inside of the test specimen is, according to the results of this study, erosive carbon. The erosive carbon present in sewage process water includes free carbonic acid which is released on reaction with the calcium ions in concrete. Quantitative analysis of the interaction between this carbonic acid and cement compounds or hydration products is difficult due to the effects of changing water quality, water flow, and the other factors related sewage process water. However, in general, the erosion mechanism due to free carbonic acid is thought to be as follows. Sewage process water quickly penetrates into the concrete, with the degree of penetration and the resulting corrosion depending on

the composition of the concrete. The erosive free carbonic acid links with calcium ions at the surface or penetrates into the concrete through the interfacial zone between aggregate particles and cement. As it penetrates, it reacts with hydration products, such as calcium hydroxide, deposited at the and forms calcium carbonate. By penetrating into capillary pores, it reacts with hydration products or unhydrated cement compounds. In this process, carbonation occurs and causes corrosion of the concrete, which is then affected by water flow and other conditions. The degree of corrosion differs with water-cement ratio and unit cement weight, because the reaction rate of the penetrating process water is influenced by pore volume and reaction area and is controlled by the pore structure, including interface area. For instance, even if the total pore volume is equal, differences can occur in the area of the wall that the pore forms due to the pore diameter. The total pore surface area becomes large if there are many micropores. Therefore, with a constant process water quality, the reaction is greater for concrete with small water-cement ratio. The reaction rate decreases rapidly toward the inside of the sample. This decrease also becomes more significant as the total reaction area increases.

When there is much free erosive carbonic acid in the sewage process water, calcium carbonate is the main product at the reaction site. Although the pores become temporarily less porous, calcium carbonate dissolves on attack by free erosive carbonic acid. The calcium ionized in the process water again becomes linked with free erosive carbonic acid. As a result, the calcium dissolves and is consumed. In such a reaction process, there is a boundary phase of alkali type compounds such as calcium or magnesium compounds between the corroded portion and the non-corroded portion, and this can be observed from the discoloration described in section 4.1 b). This type of reaction is repeated near the surface of the eroding concrete. The concentration gradient of calcium ions between the surface and the inside was confirmed even by surface analysis in section 4.2 d). This mechanism shows that calcium ions move to the surface due to the concentration gradient and may cause gradual changes in the structure of the intact portion. Thus, the following may occur : secondary corrosion →erosion→deterioration of structure further inside.

5.2 Predicting Deterioration

Deterioration of the system under consideration is mainly controlled by the corrosion rate of concrete. However, a decline in the performance of reinforced concrete may occur if corrosion occurs in the concrete cover and the reinforcing rods. Therefore, corrosion may invade more deeply than the index indicates. Thus, the progress of carbonation and decrease of cover concrete become the most important indices of deterioration. We have reported that the existence of free erosive carbonic acid differs over the years with fluctuations in alkalinity and other factors of the process water [7],[15]. As described in Section 2, the free carbonic acid in the process water can be divided into subordinative and erosive carbon dioxide, with both considered related to alkalinity [16].

Calculating the free carbon dioxide using a previously reported method [17] from the pH and alkalinity values, which have been regular test items in water quality tests over the past 20 years, the change in free carbon dioxide over time at the facility is

shown in Fig.18. For the calculation, the mean value for one year was adopted, with means found for each month. Also, the relation between the free carbon dioxide and erosive free carbon dioxide was calculated and is shown in Fig.19, which presents the correlation between erosive free carbon dioxide and free carbon dioxide. The increase in free carbon dioxide suggests the possibility of an increase in the amounts of erosive free carbon dioxide.

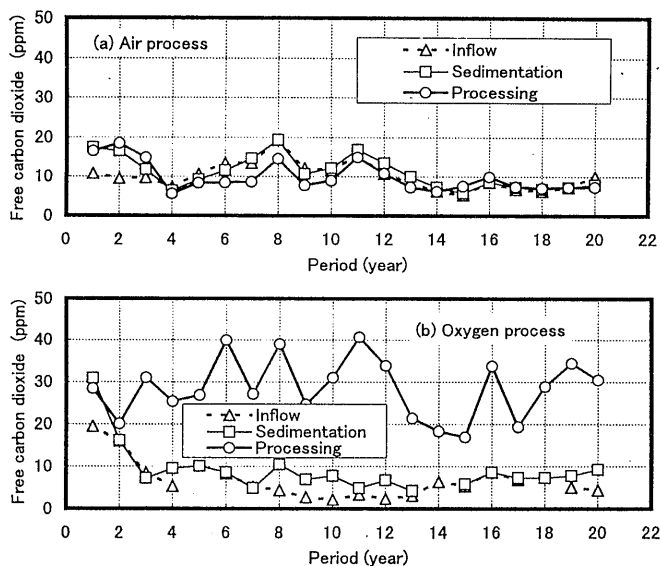


Fig.18 Changes in free CO₂ in each system

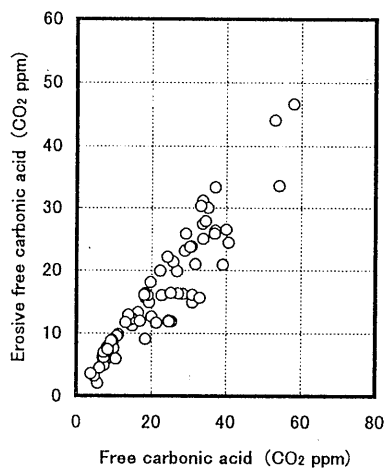


Fig.19 Relationship between free CO₂ and erosive free CO₂

Comparison of the free carbon dioxide in each system shown in Fig.18 indicates little fluctuation among locations, such as the inflow, processing, and sedimentation processes, in the air process. However, with the oxygen treatment process, with some exceptions, there was a large amount of free carbon dioxide in the process water. This shows that a large amount of carbon dioxide is discharged when organic substances are decomposed by bacterial activity with aeration. Also, the mean values for the first 10 years slightly exceed those for the latter 10 years. In water supply facility design, there is a general possibility of a large amount of erosive free carbon dioxide being present when the free carbon dioxide level exceeds 20 mg/l. Although aeration processing or alkali processing has been recommended previously [11], the calculated free carbon dioxide value exceeds 20 mg/l. According to previous work, severe erosion may occur when the level of erosive free carbon dioxide reaches 60 mg/l or more [18]. This value does not exceed the calculated value of the erosive free carbon dioxide. However, even if each value is below 60 mg/l, the degree of the erosion may be high if the hardness of the water is low. Fig.20 shows the relation between the calculated free carbonic acid in the process water and the mean value of the mass loss of conventional concrete in the trough of the oxygen process. The value of free carbon dioxide was calculated from values accumulated until the year prior to mass measurement. The mass loss shows close correlation to the accumulated value of free carbon dioxide. Therefore, the mass loss of conventional concrete is considered to be influenced by the free carbon dioxide. The relation between the mass loss of the test specimen in the trough environment and the accumulated value of free carbonic acid over one year, shows the state on the same regression curve in all values of the air and

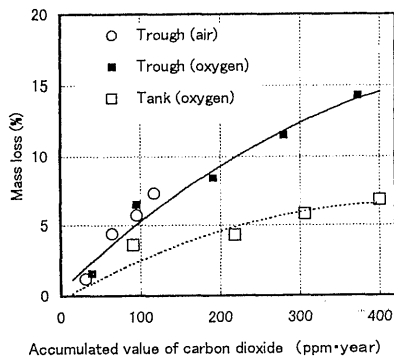


Fig.20 Relationship between free CO₂ and erosive CO₂

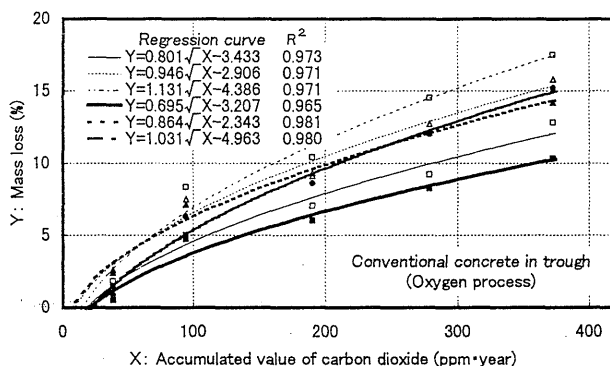


Fig.21 Prediction (regression curve accumulated CO₂ against mass loss)

oxygen process. In the test specimen in the sedimentation tank of the oxygen process, a different tendency was observed in the regression curve than for the result in the trough of the oxygen process in the same free carbon dioxide environment. These results show that the erosion rate is affected not only by the water flow but also by the water quality in the processing system environment, and that the action of the flow in the trough promotes physical erosion in addition to chemical erosion. Fig.21 shows the regression curve applied to the relation between the accumulated value of free carbon dioxide and the mass loss of conventional concrete in the trough of the oxygen process. Mass loss is related to the square root of the accumulated value of free carbon dioxide as follows:

$$Y = \alpha \sqrt{X} + \beta \quad (1)$$

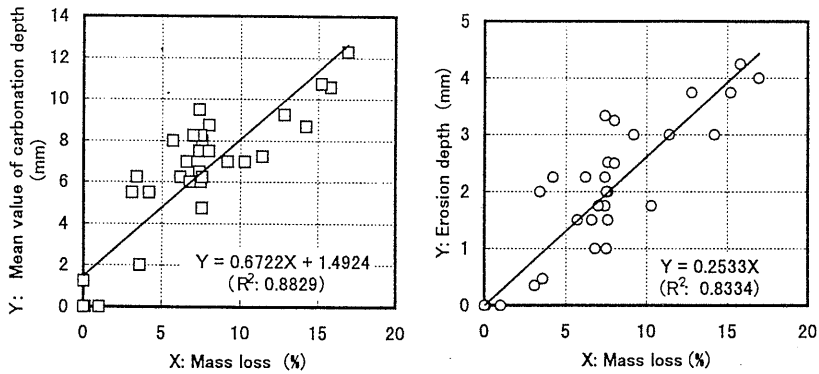
where, Y: mass loss (%); X: mean value of accumulated free carbon dioxide until the year prior to mass measurement (ppm·year); α , β : regression coefficient and constant of regression curve.

Each regression curve based on expression (1) showed extremely good correlation. As described above in predicting deterioration, the most important factors are mass loss, which is an estimate of the decrease in the amount of cover concrete, and the progression of the carbonation depth, or erosion depth, which are closely related to mass loss. The relations between mass loss, carbonation depth, and erosion depth in the trough are shown in Fig.22. Variations were observed in the linear regression results but the mass loss correlated with the depth of carbonation and erosion. Thus, carbonation depth and erosion depth can be expressed in terms of the annual accumulated value of free carbon dioxide in a similar way to expression (1).

$$Y' = \alpha' \sqrt{X} + \beta' \quad (2)$$

where, Y': carbonation depth or erosion depth (mm); X: annual accumulated free carbon dioxide (ppm·year); α' , β' : coefficient and constant.

The annual variation was predicted from the variation in free carbon dioxide over the past 20 years in Fig.18. Little fluctuation in the level of free carbon dioxide is expected over the long term. About 30 ppm deterioration can be expected annually as the mean value from the movement average over time. For example, the largest mass



(a) Relationship between mass loss and carbonation depth

(b) Relationship between mass loss and erosion depth

Fig.22 Relationship between mass loss due to carbonation depth or erosion

loss of 20-25 % over 20 years is predicted for concrete in the trough of the oxygen process, which is the severest environment. Calculating the test specimen area based on a mass decrease of 20% gives an erosion depth of about 3 mm. On the other hand, an erosion depth of about 5 mm is obtained from the relation with mass loss based on expression (2). The difference in erosion depth is nearly twofold. Changes in erosion depth or carbonation depth might be estimated from measured mass loss data and calculated free carbon dioxide. This method can be used to predict deterioration and suitable repair times. However, some structures may require repair earlier than predicted due to invasion by corrosion greater than the deterioration index and for other reasons. Further detailed studies are needed, because the corrosion and deterioration of concrete is influenced by the water quality, flow, and other changes in the environment. Continuous control of water quality is necessary based on consideration of bacterial and protozoa activity, the water flow, and other factors.

6. CONCLUSION

The following conclusions were reached from the results of exposure tests conducted over 10 years in the end processing system of a sewage treatment facility.

(1) Changes in appearance, decreases in mass, and changes in relative dynamic modulus of elasticity were observed with exposure time for various test specimens. Differences in environment led to variations in the degree of corrosion, with the most severe suffered by specimens in the trough of the oxygen system. Looking at mix proportion factors in the case of non-lining concrete, the mass loss at a water-cement ratio of 55 % and 60 % was larger than that at 50 %. Therefore, a low water-cement ratio is one effective way to control corrosion. Also effective is to increase the unit cement weight. Still another is treating the concrete surface with a lining. Almost no corrosion was observed for test specimens with epoxy-resin lining even after more than 10 years.

(2) The decrease in maximum bending load was large after exposure for more than 10

years, with particularly serious decreases in specimens with high water-cement ratios and without lining in the trough of the oxygen treatment process. Therefore, even the bending strength decreased in the case of high water-cement ratio or without lining. In contrast, corrosion can be prevented by adapting a high unit cement weight and low water-cement ratio, and also by lining the concrete.

(3) The decline of the physical properties of the concrete as seen in the pore structure was obvious in the surface region. Therefore, sewage process water was judged to have a great influence on the pore structure. Change in the pore structure clearly differed with or without lining. Therefore, the use of a lining gives effective protection against long-term attack by process water, as in this facility.

(4) In this processing system, corrosion is considered to have been mainly caused by erosive free carbonic acid. The carbonates decompose cement hydration products of concrete and finally reduce them to ions. The structure is gradually destroyed through the mechanism of ion dissolution.

(5) The mass loss, carbonation depth, and erosion depth were judged to be related to changes in the amount of free carbon dioxide, based on calculations of free and erosive free carbon dioxide and various experimental results. Applying a regression curve to the above relation showed a good correlation, especially between the free carbon dioxide and mass loss. This allows the deterioration to be estimated and the repair time predicted. Control of the water quality can reduce the progress of deterioration, which is influenced by changes in bacterial and protozoa activity or water flow and other factors.

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