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Nobuyuki Sato*, Hachinohe Institute of Technology, Japan
Syuichi Sugita, Hachinohe Institute of Technology, Japan
Masami Shoya, Hachinohe Institute of Technology, Japan

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Abstract

Experiments were conducted on repression of salt damages, corrosion, and neutralization of concrete by making use of effective microorganisms, their extracts, and effective microorganism-mixed ceramics. We obtained a result that steel plates inserted into chloride ion-added concrete test pieces comprising effective microorganism test materials were found to maintain original luster without corrosion. Furthermore, reduction in the amount of chloride ions contained in concrete was confirmed after surveys by such means as EPMA on behavior of chloride ions in chloride ion-mixed concrete. We have made successful achievements in studies on reaction mechanism governing reaction between synthesized C_3A and chloride ions. We have also confirmed that blending of effective microorganism materials leads to an increase in strength of concrete seen in such effects as brought by AE agents.

Keywords: effective microorganisms, chloride ion, C_3A, rust prevention, neutralization

1. Introduction

There has been a tendency in recent years that salt damages to concrete and reinforcing steel are increasingly highlighted as problems to be solved and reported in mass media including newspapers. Sand used for concrete materials is collected mostly from beach sand in the regions west of Chugoku and Shikoku districts in Japan. The beach sand, generating a large amount of chloride ions, causes internal corrosion as well as neutralization to take place inside reinforcing steel. Thus, it corrodes not only superficial layer of reinforcing steel but also its inner part, thereby leading to a large reduction of strength of reinforcing steel itself. What happens inside concrete triggered by salt is that sodium hydrate ions rise upward, rocks containing silica seep into strong alkalis, and that no function is expected as aggregate, only to cause such phenomena as crumbling of concrete. In regard to the effective microorganism family put now on the market, we have already obtained a material license on rust prevention effect of the material [1], and continued further research on its effect of rust prevention on both concrete and reinforced concrete, to obtain the result of rust containment effect on reinforcing steel. On control test pieces, while on the other hand, substantial development was seen in terms of corrosion. Meantime, issues of neutralization of concrete have close connection with their durability. The containment of neutralization was seen strengthened to a great extent in concrete blended with effective microorganisms. The inhibiting effect on salt damages was found strongly reinforced as well. Studies also were conducted on mechanisms for containing salt damages. We keenly feel it necessary from the viewpoint of preventing environmental destruction to widely use such materials as are safe and commonly found in the natural world in a bid to improve physical properties of concrete.

2. Testing methods

2.1 Test for rust prevention effect by detecting change in steel weight

A steel piece (0.5 mm thick 4NFe) was cut into 5 mm x 5 mm pieces, to be placed horizontally at a depth of 10 mm from liquid surface in a schale with a diameter of 60mm at room temperature (20 C). An electronic scale was used for weight measurement. Sea water and liquid extracted from effective microorganisms served as test specimens for the tests this time. A scanning laser microscope was used for surface observation. And 30 days were chosen as the period of maceration.

2.2 Purification of rust-inhibiting compounds and identification of their chemical structures

A test piece (1 mm thick; SPCCG3141(JIS)) was cut into pieces of 10 mm x 15 mm, to be placed horizontally at a depth of 10mm from liquid surface in a schale with a diameter of 60 mm at room temperature (20 C). 18ml of effective microorganism extract liquid was poured into the schale. Both schales were left untouched for 31 days. A change in steel weight within each of the liquid solutions was observed. The liquid was replenished as appropriate to keep the surface level constant. The weight measurement was conducted after sufficient dehydration, to measure weight transition over the period of 31 days. What appeared on the surface of the steel test pieces, something like white film, was removed as completely as possible by means of a spurter, and put on X-ray diffraction analysis to identify chemical structure of the removed material. Isolation of such chemical compounds as having rust prevention effect was conducted as well on the effective microorganism extract liquid in which a reinforcing steel was dipped, along with chemical structural analyses on the isolated chemicals. 500 ml of the effective microorganism extract liquid was subject to distributive extraction (30 min x 3 times) through the use of 500 ml of n-hexane (special grade), with residual undergoing another distributive extraction by means of 500 ml of methanol (30 min x 3 times). The stratum of methanol extracted was subjected to vacuum concentration, to be concentrated little short of perfect solidification. The resultant residual was put to an open column gas chromatography (20 mmφ x 300 mm) mounted with an ion-exchange resin with phosphate buffer serving as an eluate, to obtain a fraction. Another fractionation was applied to the resultant fraction to isolate crystals, followed by X-ray analysis to perform chemical structural analysis on the relevant compounds. The JCPDS database was used for retrieving chemical compounds with a combined use of an automated search system and manual operations [2].

2.3 Tests for containment of neutralization of concrete and for rust prevention effect

(1) Preparation of test pieces

A test piece was set out to be a rectangular solid with 200 mm in width, 100 mm in depth, and 200 mm in height. The composition and properties of concrete is shown in Table 1.

Table-1 Recipe table for concrete

Table of mixing parameters

Target air volume 5%, slump 8cm

W/C (%)	Gmax mm	Type of product	s/a (%)	Unit volume (kg/m3) W	C	Ceramics	S	G	AE*C (%)	SP*C (%)
		C55				-	834	1077	0.03	-
		Ceramics-5				15.4	827	1068	0.03	0.18
		Ceramics-10				30.7	820	1059	0.35	0.3
		Ceramics-15				46.1	813	1050	0.04	0.35
		EM-No.1-5				-				-
		EM-No.1-10				-				-
55	20	EM-No.1-15	425	169	307	-			0.025	-
		EM-No.3-5				-				-
		EM-No.3-10				-	834	1077		-
		EM-No.3-15				-				-
		EM-X-5				-				-
		EM-X-10				-			0.02	-
		EM-X-15				-				-

* We used EM-No.1, EM-No.3 and EM-X. They are all liquid. We diluted them in 15%, 10% and 5% in water, and used it as water.

* EM ceramics are mixed with cement in 15%, 10%, and 5% of the total quantity after mixing.

* Since effective microorganism extracts all are liquid, they were attenuated into water that served as a diluent solvent, producing solutions with dilution ratios of 5 %, 10 %, and 15 %. Ceramics blended with microorganisms was set out as a mixture with cement at outer percentages of 5%, 10%, and 15%. Effective microorganism materials are basically the same as commercially available EM, allowing for a description here as EM. The recipes described in (3) were taken into consideration.

For a fixed amount of unit water, a water-to-cement ratio was set to 0.55, while the air supply being adjusted targeting at 5 %. Two cases were selected for study: one with no chloride ions added when kneaded, and the other with 5.0 kg/m^3 of chloride ions (mixed in the form of NaCl) as an additive.

The cement chosen was ordinary portland cement, and a fine-aggregate mixture was formed by land sand (density in saturated surface-dry condition of 2.58 g/cm^3; water absorption of 2.19 %), while crushed stones (density in saturated surface-dry condition of 2.66 g/cm^3; water absorption of 0.87 %) were used as a coarse aggregate.

And the mold form housed concrete filled up in two stages. The steel plate used had a size of 15 cm x 15 cm. Dislocated test pieces served as test pieces for neutralization and rust prevention effect tests. The effective microorganism materials used in our experiments were sample culture solution of effective microorganisms and organic metal complex peculiar to outputs from microorganisms, such as effective microorganism extracts, while liquid materials like effective microorganism extracts containing lots of various inorganic or organic compounds were diluted with water into solutions of 5 %, 10 %, and 15 % against water, to be used in place of water. Ceramics was set out as a mixture blended with cement at its outer percentages of 5%, 10%, and 15%. Tests also were conducted on test pieces covering all kinds of effective microorganisms.

(2) Accelerated neutralization test

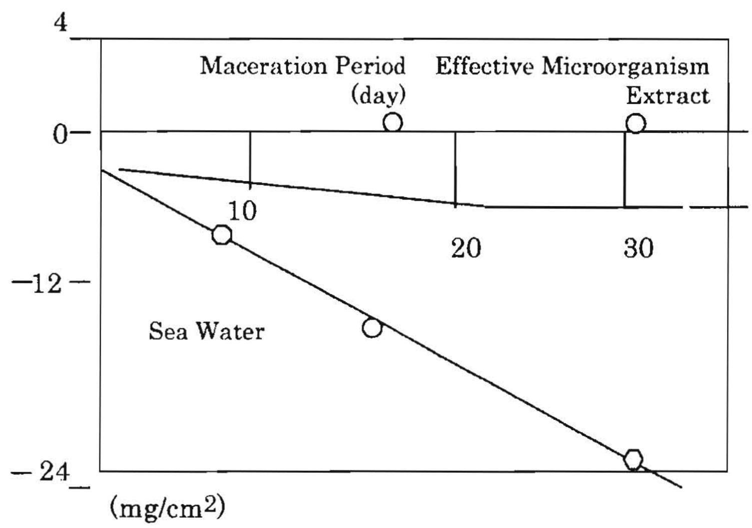
Accelerated neutralization tests were carried out under the environment of carbon dioxide concentration as high as 5 % at temperature 20 C and moisture 60 %, while testing material ages were set out representing four periods as 2, 4, 6, and 8 weeks. The testing conditions are given below:

1) Test pieces having reached a material age (28 days) were dehydrated for 6 days before their upper and under surfaces were sealed by silicon.
2) Four test pieces were picked up from each of the groups with material ages of 2, 4, 6, and 8 weeks.
3) Each test piece was scraped away on its upper surface to make steel plate appear, followed by enough drying of the scraped concrete, before being sprayed by an atomizer complying with JIS K 8001. (Cross sections of concrete served as test pieces.)
4) Depth of the portion showing no color change was measured in millimeters. The measurement was carried out at equally spaced 10 points on about half of the cross section of a concrete test piece to obtain an average neutralization depth for each.

(3) Neutralization and strength tests for effective microorganism materials

1) Test pieces

Test pieces were set out to take a form of a 100 ϕ x 200 mm cylinder with the same compositions of concrete as in Figure-1, to be maintained in water until specified material ages in a circulating water bath with temperature of 20 C $\pm$ 3 C. This is the only experimental item that took up effective microorganisms commonly used in the market; the materials used were EM No.1, EM No.3, EM-X, and EM ceramics.



2) Accelerated neutralization test

This test was conducted in the same manner as described in 3-2-(2). An average neutralization depth was defined as average of neutralization measurements at 10 points, one every 15 mm in the direction of concrete placement starting at 25 mm on the surface on which to pour concrete.

3) Compressed strength test

This test was conducted complying with JIS A1132 and JIS A1108-1999. Material ages were set at 3, 7, and 28 days. Three or more test pieces were used as test pieces for each compressed strength test.

4) Depth of the portion showing no color change was measured in millimeters. The cross section accounts for about half of the concrete test piece. The measurement was carried out at equally spaced 10 points to obtain an average neutralization depth for each.

(4) Corrosion test

1) Emergence of rust was investigated through observation of test pieces having viewable metal surface. After all the steel plates were removed from concrete, weight of steel plates was measured by an electronic scale, one for each of the test pieces of control, effective microorganism extract concrete, and concrete mixed with effective microorganism extract.
2) Behavior of Cl- (chloride ions) ions was studied:
   Test pieces made of concrete blended with effective microorganism testing materials and fragments of a control test piece were cut off by a dry cutter into pieces (200 mm wide, 100 mm long, and 100 mm high). Still another dry cutting was made to get test pieces with height (thickness) of 10 mm. Surface analysis was performed through EPMA applied to these test pieces.

2.4 Study on mechanisms of effective microorganism extracts to reduce the quantity of chlorine ions

(1) Preparation of test pieces

C_3A was synthesized for hydrate test pieces, to which $CaSO_4$-$10H_2O$ was added producing its 20 wt% mixture. Furthermore, effective microorganism extracts were added to the resultant sample creating test pieces with effective microorganism extract concentration of 0, 2, 4, and 8 wt% to C_3A, before being kneaded with water to produce test pieces with a water-solid ratio of 0.65. These pieces were put into rubber formwork, and hardened through hydration at 20 C over 7 days. Test pieces were removed from the formwork after specified time has passed before being crushed into pieces smaller than 150 mesh. Hydrate test pieces to be tested were completed after hydration process was ceased by addition of methanol and acetone solvents with high and middle polar characters. The condition of the hydrate products was checked through XRD for degree of hydration.

(2) Test method

2 grm of hydrate product obtained from the aforementioned (1) was distributed in pseudo-sea water 100 ml adjusted by NaCl and $MgCl_2$-$6H_2O$ with reaction continuing under agitation for 1 minute to 4 weeks before solid-liquid separation was conducted. Hydrate products were identified in the solid phase through XRD, while the quantity of hydrate ions in the liquid phase was determined. The pseudo-seawater was adjusted by addition of calcium chloride anhydride, magnesium chloride anhydride, sodium chloride, and so forth.

3. Test results and discussions

3.1 Tests for iron weight change and rust prevention effect

There are research reports by Hoshimura, Sato, and some others that demonstrated rust prevention effects by effective microorganisms on steel plates. We performed simultaneous tests using 30 test pieces. Figure-1 shows changes in weight of steel plates dipped in seawater (with chlorine ion composition of 1.8 %) in comparison with those in solution blended with effective microorganism extract. Test pieces in seawater were seen showing marked weight change caused by rust. In the case of solution with addition of effective microorganism extract, on the other hand, virtually no emergence of red rust was observed, serving as an evidence for a smaller weight change. This result was presumably brought by elements such as minerals (surmised to be fostered in culture solution) and organic metal complexes contained in effective microorganisms. Figure-2 shows images taken by a laser microscope of the surface of steel plates after being dipped in water solutions for 30 days. Figure (a) displays a steel plate that was dipped in salt solution, implying its surface corroded away with rust. In Figure (b), representing a case where effective microorganism extract solution was tested, no rust was recognized and minerals were confirmed on its surface.

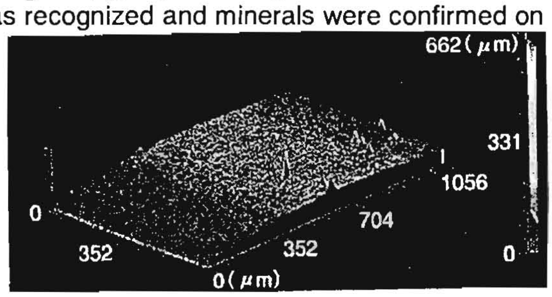


Figure-1 Weight changes in steel plates

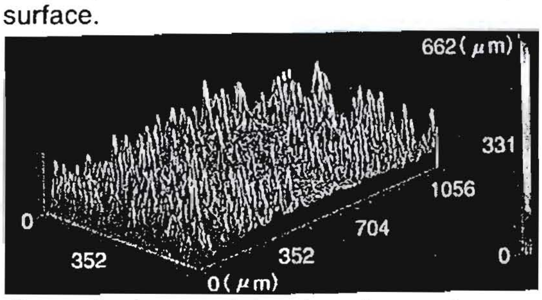


Figure-2 Images taken by a laser microscope

3.2 Isolation of rust inhibiting compounds and identification of their chemical structures

For test pieces in seawater, a decrease of 23 mg/cm^2 in weight was confirmed. On test pieces in effective microorganism extract solution, on the other hand, no red ruster appeared, only to show a slight sign of a trend for weight to decrease. In seawater, ultra-thin film of oxide generated on the metal surface is destroyed, resulting in a decrease in weight due to corrosive reaction of steel. When effective microorganism extract liquid was used for the test, no practical change was observed. This fact drove us to the test described below.

(2) Chemical analysis on rust-inhibiting materials

Purification and isolation processes for chemical compounds obtained in 2.2 are illustrated in Figure-3 as shown below:

EM-X (50lconcentlation) → n−hex suspend in → n-Hex layer or resudas

Resudas +MeOH → MeOH layer or resudas

MeOH layer → Separation (open colume chromatograhy)

↓

HPLC (ODS) → crystal compound

↓

XRD

Figure-3 Purification and isolation processes

The obtained methanol extract was applied to open chromatography to be eluted into phosphoric buffer solution, to obtain a mixture with high compositions of respective compounds. It was further purified by extracting fractions rich in crystal compounds through HPLC (High Performance Liquid Chromatography), thereby isolating the target compound. To get crystal of higher purity, recrystallizing operations followed, resulting in a success in obtaining purified compounds. The obtained crystal was put to infrared spectroscopic analysis, with a sharp peak of absorption obtained in the neighborhood of 3000 cm^{-1}, while other peaks were totally broad meaning no indication of attribution. Then its proton spectral data were sought through NMR without any specific spectra detected, only to have noises sensed. Accordingly, X-ray diffraction analysis was applied with the following measurement conditions: Electrode: Cu; Tube current: 100 mA; Sampling width: 0.02 deg; Wave length: 1.5456 A; and Fluorescent slit: 0.15 WW. As a result, empirical formula and chemical formula of the crystals obtained were identified in the following.

The empirical formula was implied as: $C_{4.4}H_{12.85}Al_2N_{1.15}O_{8.05}P_{1.9}-0.22H_2O$; and the chemical formula as: 0.55$(C_4H_9)_2$-NH-0.3$(NH)_4O$-Al_2O_3-0.95P_2O_5-0.22H_2O. It was confirmed that this chemical compound formed a needle crystal-like film, which coated metal surface, thereby preventing corrosion from developing further. A possibility also was suggested that it might form a film on the surface of concrete with a matrix-type film formed inside.

3.3 Results of accelerated neutralization test and rust prevention test

(1) Results of neutralization inhibition test

Table-2 Depth of neutralization

Week	C55	C5%	C10%	U5%	U10
2	6.1	2.5	1.7	1.8	1.8
4	7.9	2.4	2.2	2.5	2.2
6	8.3	3.1	2.7	3.3	3.7
8	9.5	3.4	3.1	3.4	3.8
(mm)					

C55 = Control test piece (water cementitious material ratio 55 %)
C5 = Test piece of mixed with 5 % Emceramics
C10 = Test piece of mixed with 10 % Emceramics
C15 = Test piece of mixed with 15 % Emceramics
U5 = Test piece of 5 % effective microorganism extract
U10 = Test piece of 10 % effective microorganism extract

Test pieces of C-55 carried depth of neutralization at 6.1 mm in 2 weeks, while those of effective microorganism extract mixed with 10 % ceramics showed that of 2.1 mm for the same period of time. As for data taken after 4 weeks, it stood at 2.2 mm for effective microorganism extract mixture with 10 % ceramics. Regarding changes from after 4 through 8 weeks, test pieces in C-55 column indicated 7.9 mm, while no substantial changes were found in test pieces other than C-55. Namely, it was confirmed that solutions concerned strongly inhibited development of neutralization.

(2) Tests for accelerated neutralization of effective microorganism materials and their strength tests

The tests here used commercially available microorganism materials (EM) having nearly the same composition as the experimental effective microorganisms. The materials are widely used worldwide as agricultural materials. The materials actually used were effective microorganisms (EM No.1), effective microorganism extract (EM-X drinking water), culture fluid for photosynthesis bacteria (EM No.3), and EM ceramics, which is effective microorganism extract mixed with ceramics.

1) Accelerated neutralization test

As shown in Figure-4 through Figure-7, neutralization inhibiting effect was recognized on all the concrete test pieces mixed with EM materials compared with the control test piece.

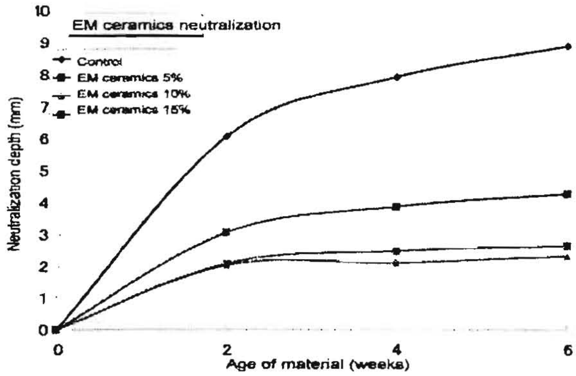


Figure-4 Result of accelerated neutralization test for EM No.1

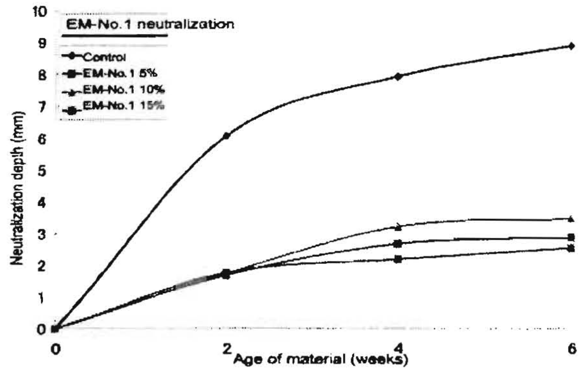


Figure-5 Result of accelerated neutralization test for EM ceramics

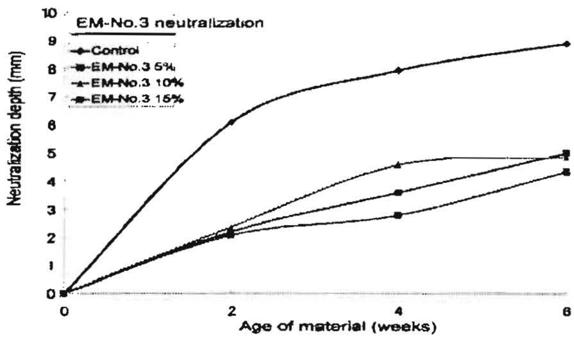


Figure-6 Result of accelerated neutralization test for EM No.3

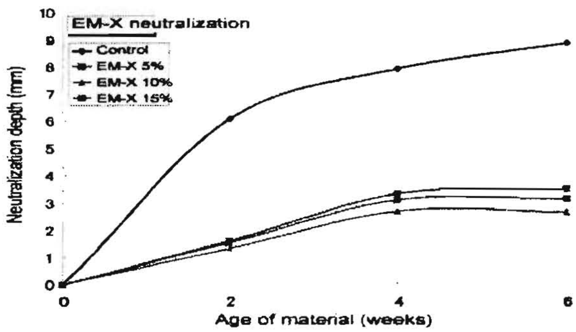


Figure-7 Result of accelerated neutralization test for EM-X

It is learned from these figures that the maximum inhibiting ratio stood at around 70 % compared with the control test piece. No difference is seen, however, in neutralization depth in accordance with changes in their mixing levels. EM No.3 was seen having less inhibiting effect on neutralization than other materials.

2) Test results of compressive strength

Each figure from Figure-8 through Figure-11 shows the result of compressive strength tests. As a result of tests for EM ceramics, EM No.1, EM No.3, and EM-X, all of them were confirmed to have higher compressive strength after compensation than the control, under the condition of water cementitious material ratio of 55 %. Exhibition of initial strength is supposed to be one of characteristic features.

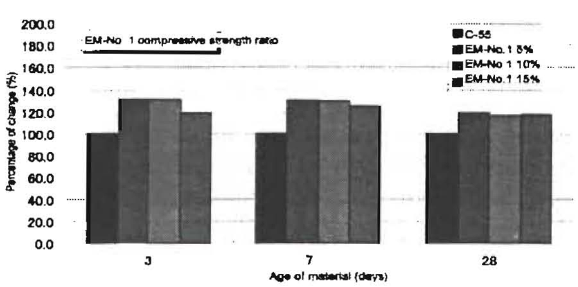


Figure-8 Compressive strength after compensation of EM No.1

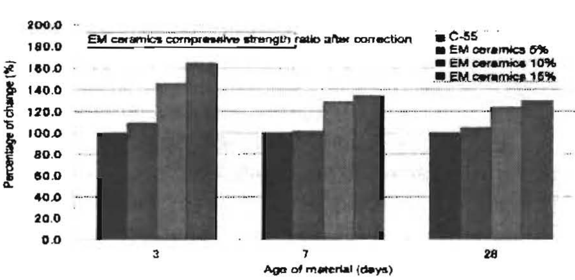


Figure-9 Compressive strength after compensation of EM ceramics

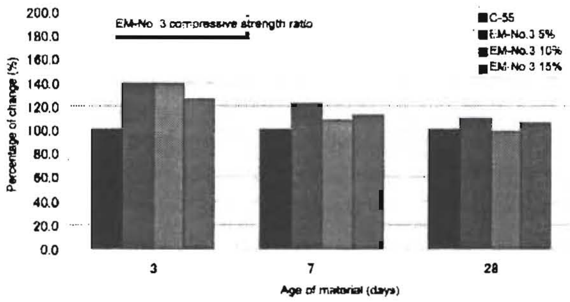


Figure-10 Compressive strength after compensation of EM No.3

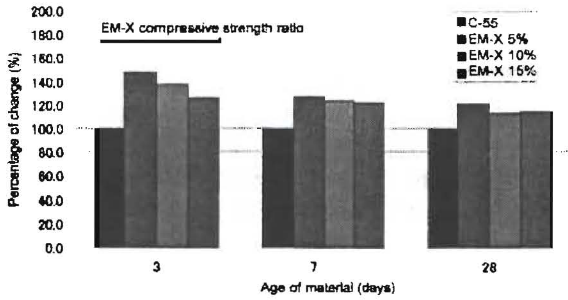


Figure-11 Compressive strength after compensation of EM-X

(3) Results of corrosion tests

1) Results of observation of the metal surface are described. Figure-12 shows a steel plate in the concrete after accelerated neutralization with chloride ions (Cl-: NaCl) contained in effective microorganism extract.

In Figure-13, iron is seen still existing despite considerable degree of corrosion in progress.

2) Behavior of chloride ions monitored through EPMA

Figure-14 shows a cross section of concrete without containing experimental effective microorganism materials. White fine particles represent chloride ions. Figure-15 displays a case with effective microorganisms contained, where no chloride ions are recognized.

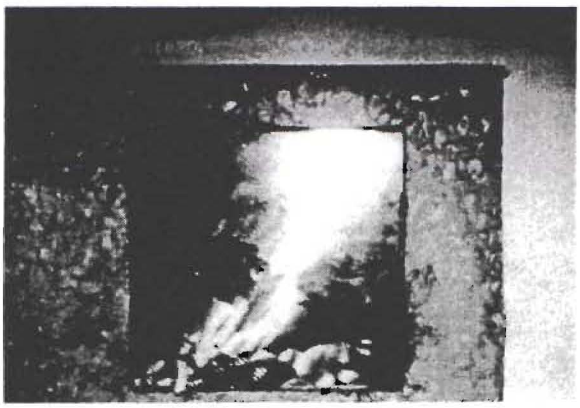


Figure-12 Corrosion inhibiting test for a steel plate (microorganism treatment)

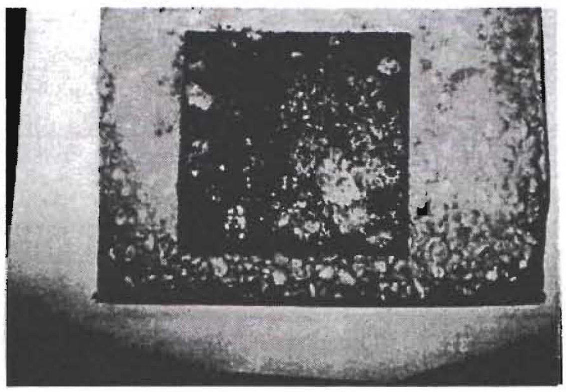


Figure-13 Corrosion inhibiting test for a steel plate (control)

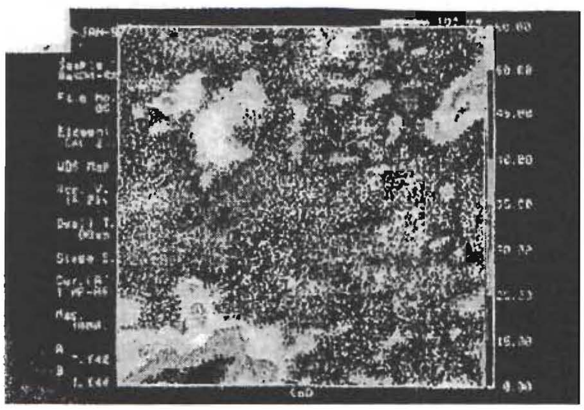


Figure-14 Behavior of chloride ions through EPMA (control)

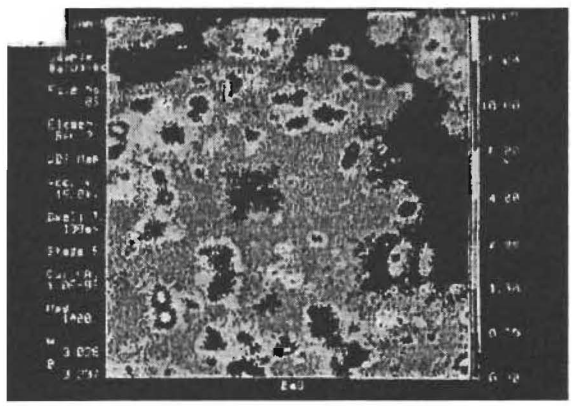


Figure-15 Behavior of chloride ions through EPMA (microorganism treatment)

3.4 Study on mechanisms for reduction of chloride ions

Figure-16 demonstrates a result from XRD analysis on a test piece mixed with effective microorganism extract. This result implies an increase in the amount of Friedel's salt. Measurement of chloride ions led to repeated fluctuation of ups and downs of concentration of chloride ions. It also was learned that time for XRD intensity of Friedel's salt in solid phase to go up accords with time for concentration of chloride ions to decrease. This fact leads to a presumption that chloride ions were taken into hydrate of C_3A and immobilized as Friedel's salt.

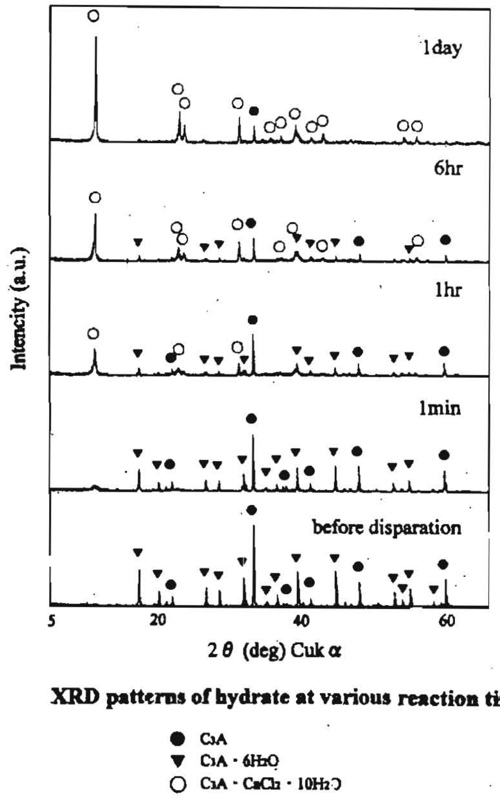


Figure-16 Immobilization of chloride ions (through XRD analysis)

Discussions

There are quite a limited number of reports on improvements of concrete making use of effective microorganism materials. Prior to the research, we performed a through investigation into concrete constructs through combination of nondestructive and destructive inspections. There was a spot where the intensity took maximum at 50 N/mm^2 or more in a large-scale construct. The permeability coefficient stood at 0.0077 KT. A non-destructive testing equipment TORRENT was used in the measurement. In preparing concrete test pieces, improvement of work productivity was taken into account by adding AE conditioner, but even addition of effective microorganism culture failed to enable measurement of air volume. This also led to confirmation of promotion of air-entraining.

Conclusion

. How to implement construction work using concrete is another key factor. Especially, the fact that the more water is contained in concrete, the more fluidity the concrete has, gives rise to easiness to handle, while on the contrary leading to lowering of strength. If too much water is added, rough and large micropores are generated to allow chloride and/or sulfate ions to trespass inside, bringing about reduced strength. It will eventually affect durability of concrete including by way of neutralization.

This study has led us to the conclusions that addition to concrete of useful microorganism materials will surely serve as a safe and economic means that helps inhibit neutralization of concrete and contain its salt damages

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