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Present state of corrosion inhibitors in Japan

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Abstract

In this report, the utilization, research and development of corrosion inhibitors in Japan and the action mechanism of corrosion inhibitors are explained, and their effects and future utilization are also described. In Japan, corrosion inhibitor was commercialized in the 1970s, and the use of these showed the rapid elongation as a countermeasure of the use of sea sand as an aggregate for the period 1975–1977 and the use of corrosion inhibitors decreased after 1979 because of the regulation for the total amounts of chloride in concrete in the standards. Then, amounts of concretes with corrosion inhibitors decreased in 1990s. However, in the civil engineering and construction industry fields, they seem to have to deal with the problem of increase of chloride content in concrete by the deregulation and the utilization of various industrial waste materials. We should consider the utilization of corrosion inhibitor from the new viewpoint.

Keywords: Corrosion inhibitor; Sea sand; Chloride ion; Eco-cement

1. Introduction

Corrosion inhibitor is the generic name of organic and inorganic admixture ingredients with the effect that delays corrosion rate of the reinforcement by adding them into concrete mixtures. In Japan, it is used for mainly preventing the corrosion of the reinforcement by the salinity from seawater. Various researches and developments on corrosion inhibitors have been done and it was standardized as JIS A 6205, "corrosion inhibitor for reinforcing steel in concrete" in 1982 [1]. In this report, the utilization, research and development of corrosion inhibitors in Japan and the action mechanism of corrosion inhibitors are explained, and their effect and future utilization are also described.

2. Background of the development of corrosion inhibitors in Japan

The transition of the chloride quantity regulation in fine aggregate and concrete is shown in Table 1 [2]. In Japan, sea sand has been used since the latter half in 1940s. Sea sand mainly contains much salinity as sodium chloride. It has been known that the rusting of reinforcement due to sea sand remarkably lowers the durability of concrete. However, the salinity in the concrete was not clearly controlled in those days. Then, the research on the use of sea sand as an aggregate in reinforced concrete structures was carried out only since 1956; and, in 1957, Architectural Institute of Japan issued the regulation that the chloride tolerance in a fine aggregate is 0.01% or less in converting into sodium chloride. In 1960s, the mass usage of marine aggregates for concretes until now as a concrete aggregate arose as the result of depletion of aggregates from river and the environmental damages by extracting the aggregate from the mountain. The use of sea sand increased rapidly as the countermeasure for the problems. Especially, such situations are remarkable in Western Japan. Therefore, it was not possible to deal with the increase in amounts of chloride in concretes under existing regulations. Then, since 1970s the investigation on sea sand has been carried out again. They mitigated the tolerance of chloride in a fine aggregate to 0.1% or less at the case that some countermeasures for the chloride are taken. As one of the countermeasures for the change in

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Table 1
History of standard for chloride in concrete and corrosion inhibitor in Japan [2]

Year	Contents	The tolerance of chloride without countermeasure	The maximum tolerance of chloride with countermeasure
1956	The report on sea sand was carried out in Architectural Institute of Japan		
1957	The tolerance of chloride in sand aggregate has been decided by Architectural Institute of Japan (JASS 5)	0.01% by NaCl/fine aggregate	
1972–74	JCI started the research council on influence of chloride from sea sand		
1974	Corrosion inhibitor has commercialized		
	Japan Society of Civil Engineers specified the tolerance in RC standard specifications	0.1 wt% NaCl/fine aggregate	
1975	Revision of JASS 5 • Change of the tolerance • The specification of the corrosion inhibitor	0.02 wt% NaCl/fine aggregate	0.1 wt% NaCl/fine aggregate
	• The relaxation of the tolerance of chloride in concrete • The regulation on the use of the corrosion inhibitor	0.04 wt% NaCl/fine aggregate	0.2 wt% NaCl/fine aggregate
1979	Revision of JASS 5	0.04 wt% NaCl/fine aggregate	0.1 wt% NaCl/fine aggregate
1982	JIS A 6205 “corrosion inhibitor for reinforcing steel in concrete” has been instituted		
1986	The correspondence of chloride to regulation of total emission and countermeasure for alkali aggregate reaction	0.3 kg Cl^-/1 m^3 of concrete	0.6 kg Cl^-/1 m^3 of concrete
	Revision of JASS 5 and RC standard specifications	0.3 kg Cl^-/1 m^3 of concrete	0.6 kg Cl^-/1 m^3 of concrete
1987	Revision of JIS A 6205		

regulation for chloride content in fine aggregate, the development of corrosion inhibitors has been conducted. Afterwards, increasing in the use of organic chemical admixture such as water reducing agent has brought about the possibility that chloride was involved from as well. For this reason, the object of the regulation of chloride content was changed from the amount of sodium chloride in a fine aggregate to the amount of chloride ions in concrete mixtures. At present, the amount of chloride ions are regulated with 0.30 kg or less per 1 m^3 of concrete, and 0.60 kg or less when the corrosion inhibitor was used [3].

3. Corrosion of the reinforcement and action mechanism of corrosion inhibitors

3.1. Corrosion of the reinforcement

The corrosion reaction mechanism of reinforcement is shown in Fig. 1 [4], and the rusting model of the reinforcement is in Fig. 2 [5]. The corrosion reaction is an electrochemical reaction. This reaction caused the oxide film on the surface of steel bars, and the defect of film may form a local cell in water. In this case, a part of the film works as a negative electrode, and the defect of film works as a positive electrode. Each reaction is as follows [4]:

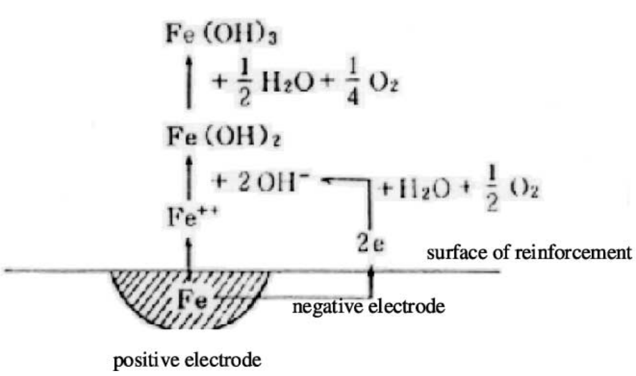

Fig. 1. Reaction mechanism of the corrosion of reinforcement [4].

(1) The anodic reaction

$$Fe \rightarrow Fe^{2+} + 2e$$
$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$
$$Fe(OH)_2 + 1/2H_2O + 1/4O_2 \rightarrow Fe(OH)_3$$

(2) The cathodic reaction

$$2OH^- + 2e + H_2O + 1/2O_2 \uparrow$$
$$2e + 2H^+ + 1/2O_2 \rightarrow H_2O$$
$$2e + 2H^+ \rightarrow H_2 \uparrow$$

When $Fe(OH)_3$ generated by the corrosion of the reinforcement expands by about 2.5 times of the origin volume, crack and peeling of the concrete occur. The

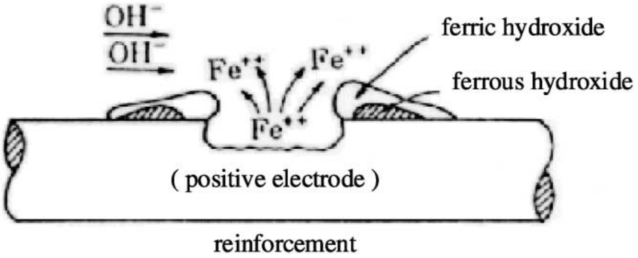

Fig. 2. Rusting of the reinforcement [5].

inside of a good quality concrete is a strong alkali (pH 12.5–13) in the presence of calcium hydroxide and alkali hydroxides. In such an environment, a film of ferric hydroxide (γ-$Fe_2O_3 \cdot nH_2O$) with about 20–60 Å thickness is formed. This film becomes the passive film, which is very stable under the condition of strong alkali, and it protects the reinforcement from corrosion. It is known that it reacts with the calcium aluminate in the cement, when chloride ions exist in concretes, and forms Freidel salt ($3CaO$–Al_2O_3–$CaCl_2$–$10H_2O$) and it fixes chloride ions. Therefore, the existence of reactive small amounts of chloride ions does not contribute to the corrosion of the reinforcement. The passive film of the reinforcement surface is destroyed when large amounts of chloride ions exist, and the corrosion is generated. This phenomenon is caused by the following reasons such as peptizing films of chloride ions, the promotion of dissolution of ferrous ion by the adsorption, progressing of the reaction by the generation of the complex, the catalyst effect for the anodic reaction, the generation of intermediate product by the direct reaction with iron, lowering of pH around the reinforcement, increasing in the electric conductivity. However, chloride ions seem to work catalytically because chloride ions are not included in components formed by corrosion reaction. When sodium chloride is introduced from seawater, chloride ions are fixed as Freidel salt. Then, sodium ion increases in the liquid phase of concrete and it intends to take a charge balance and hydroxyl ion is supplied from calcium hydroxide. Further the alkalinity in the concrete is raised, and it becomes a cause of the alkali–aggregate reaction. Attention is also necessary on this point, because large effect is given to the concrete structure as well as the corrosion of reinforcement. Alkali content in the concrete is regulated with 2.5 kg or less per m^3 in the case of using chemical admixture in JIS A 6204 [6]. Such shortage of the thickness of reinforcement cover, cracks and cold joints, etc. as structural defects lose the density of concretes as a whole, and the neutralization reaction by the intrusion of carbon dioxide and water is promoted, and then the passive film of reinforcement is destroyed. The similar phenomenon happens when the voids are produced by the bleeding under the reinforcement. Therefore, it is necessary to make the concrete dense as well as decreasing amounts of chloride ions intruded, in order to prevent the corrosion of the reinforcement.

3.2. Type of corrosion inhibitors and their action mechanism

The corrosion of reinforcement is electrochemical reactions, and anodic reaction and cathodic reaction progress simultaneously. So, it is possible to suppress the corrosion of the reinforcement, if one side or both of the reaction are stopped. The type of the corrosion inhibitor can be classified into 3 [4,7]. The polarization of the reinforcement in the use of using various corrosion inhibitors is shown in Fig. 3 [5].

3.2.1. Anode type corrosion inhibitor

The anodic reaction is suppressed by passivating the metal by forming dense film in the surface oxidizing the metal. Therefore, it is general to use oxidizing agents such as chromates and nitrites as a component.

3.2.2. Cathode type corrosion inhibitor

The cathodic reaction is suppressed by reacting with the ion of liquid phase, forming a film of salts with poor solubility in water, on the negative electrode. Such chemical compounds as carbonate, phosphates, silicate, polyphosphates, etc. are included in the cathode type of corrosion inhibitor. The dosage of them tends to increase because the depression effect is inferior to the anode type corrosion inhibitor.

3.2.3. Mixed (type) corrosion inhibitor

In this agent, the corrosion by adsorbing on metal surfaces, and inhibiting the reaction with the corrosive substance. The material with the hydrophobic group that have polar groups such as N, S, OH is effective. Organic polymer compounds such as amine and surface activity action are used.

As a corrosion inhibitor for the concrete used in Japan, the anode type is general. The nitrites are mainly used as a component. Reactions of the nitrites are as follows [4]:

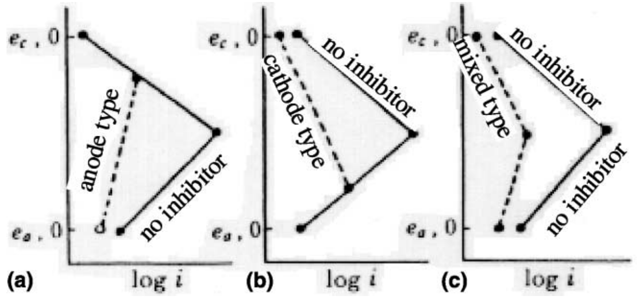

Fig. 3. Action of the corrosion inhibitor [5].

$$2Fe^{2+} + 2OH^- + 2NO_2^- \rightarrow 2NO\uparrow + Fe_2O_3 + H_2O$$

This reaction progresses faster than the corrosion reaction. Fe_2O_3 forms the passive film on the surface of reinforcement, and the corrosion can be suppressed; and, it is said that the combined use of several corrosion inhibitors is more effective than the use of a single corrosion inhibitor. In Japan, most commercial corrosion inhibitors are of organic polymer chemical compounds combined with a nitrite.

4. Recent market trend of corrosion inhibitors

The production of concretes with a corrosion inhibitor has changed as shown in Fig. 4 [5]. Corrosion inhibitor was commercialized in the 1970s, and the use of it lasted as a countermeasure of the sea sand problem as concrete aggregate for 1975–1977. However, it is the most effective to remove salinity itself in order to suppress corrosion of steel in concrete. Therefore, the regulation put the priority on decreasing the total amount of the chloride in the concrete. Therefore, the use of corrosion inhibitors decreased after 1979. Then, the amount of concrete with a corrosion inhibitor decreased to 300,000 m^3 in the 1990s. The use of corrosion inhibitors was about 1000 tons a year. After that, the application of corrosion inhibitor was investigated as a countermeasure of neutralization of salinity from the outside. But, the use of them for such a purpose has not increased.

5. Research on recent corrosion inhibitors

As mentioned above, the long-term effect of corrosion inhibitor cannot be expected for chloride ions intruding from the outside. However, it seems to be effective, if suitable amounts of a corrosion inhibitor are used in concretes. The new methods by the use of corrosion inhibitors are examined. Some researches on them are as follows.

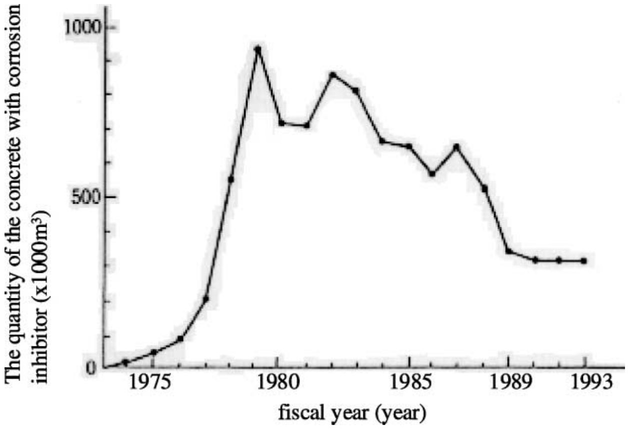

Fig. 4. Present condition of corrosion inhibitor by the fiscal year independence [5].

5.1. Combined use of an accelerator with chloride ions and a corrosion inhibitor

Hama et al. [8] tried to produce admixture ingredient that mixed calcium nitrite with calcium chloride. The outline of it: the concentration of nitrite ion, chloride ion and hydroxide ion were measured with time and accelerated corrosion test in concretes. The results of them are shown in Figs. 5 and 6. Then, it was shown that there was sufficient suppressing effect for corrosion when nitrite ions existed even if concentrations of chloride ions surpass the value of the regulation. Though calcium chloride shows large effect as an accelerator, it is rarely utilized at present, because chloride ions are contained. However, the manufacturing of admixture seems to be possible, if it is used within the limitation of chloride ion in concrete.

5.2. Corrosion inhibitor for "Eco-cement"

In Japan, the discharge of non-industrial wastes has reached at the about 50,000,000 ton in 1990, and most of them are disposed in ground as an incinerated ash. Securing the landfill disposal field becomes difficult recently, and the new technology regarding the utilization of industrial waste is studied. One of them is "eco-cement" which made of ash from incinerated wastes [9]. There are two types of eco-cement: normal type eco-cement and rapid hardening type eco-cement. Espe-

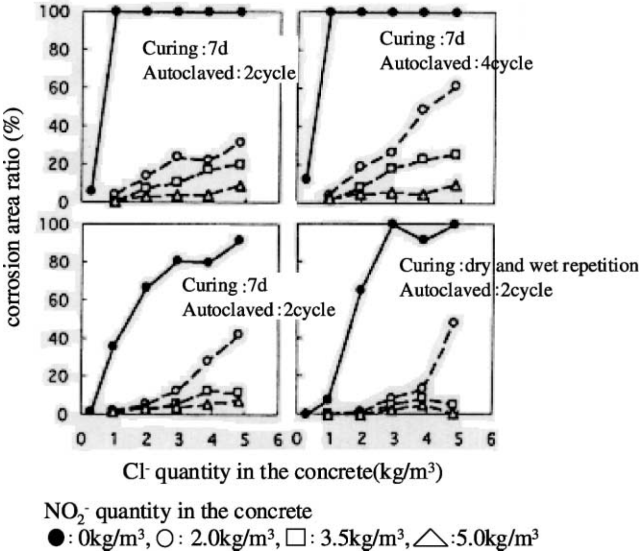

Fig. 5. Relationship between Cl^- quantity and corrosion area ratio in concrete with different NO_2^- quantity [8].

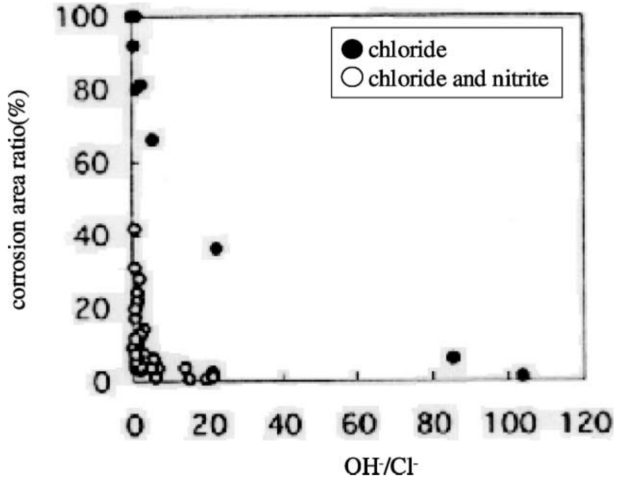

Fig. 6. Relationship between OH^-/Cl^- and corrosion area ratio (result after 2 cycle autoclaving) [8].

cially, the rapid hardening type eco-cement contains chloro calcium aluminate as a main mineral composition, and the chloride content in the incinerated ash is rather high. Therefore, amounts of chloride ions are higher than the regulation value for usual cements. At present, the final adjustment for instituting a new Japanese Industrial Standard for the eco-cement is studied. Then, a technical report (TR), which is the previous step of the standardization, has been issued [11]. The tolerance of chloride ions of normal type common eco-cement is regulated with less than 0.1% by the mass of cement. A rapid hardening type eco-cement is regulated with 0.5–1.5%. Arai and Ono [10] examined the effect of various polycarboxylic acids on the corrosion inhibition of reinforcement in concretes with eco-cement. It was shown in Figs. 7 and 8 that the inhibiting effect of phthalic acid was higher than calcium nitrite type corrosion inhibitors. In addition, it was shown that the combined use of phthalic acid and slag heightened inhibiting effect. In future, the regulation for amounts of chloride ions in JIS may be changed to ISO.

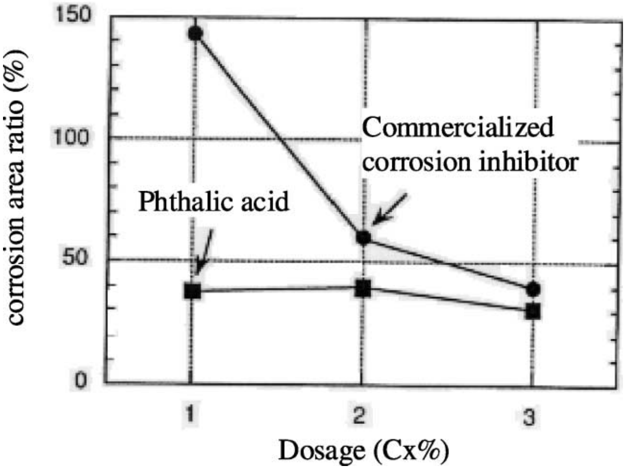

Fig. 7. Corrosion inhibition effect of phthalic acid and a commercialized corrosion inhibitor [10].

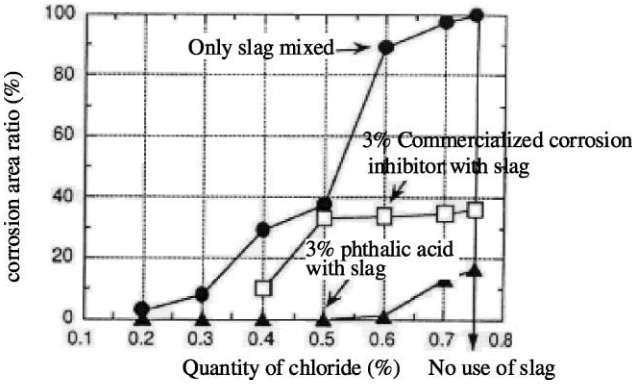

Fig. 8. Corrosion inhibition effect using phthalic acid with slag [10].

5.3. Application to the repair method

Recently, as a countermeasure for the increase in salinity intermittently, for example, exposure into the sea where the tide is repeated or dispersion of chloride in the use of snow melting agent in cold regions, some methods are used practically to cover the reinforcement by the resin such as epoxy or other organic polymers, to coat the surfaces of concrete structures after the installation, or to install the electrode in concrete and prevent corrosion electrically, etc. Corrosion inhibitors are effective for existing concretes including Cl^- ions, but the long-term anticorrosive effect of these cannot be expected [12]. Therefore, there seem to be many cases in which they are used as a supplementary inhibitor in the repair method.

6. Summary

This report is summarized as follows. The corrosion inhibitor has been developed in order to suppress the damage of chloride ions when using marine aggregate is compulsory. However, the use of present corrosion inhibitor tends to decrease as the limitation of total chloride quantity in concrete. But, further improvement will be required as a special cement with chloride are developing regarding to environmental preservation and recycling promotion of industrial waste in future.

In the civil engineering and construction industry fields, it seems to be desired to deal with the increase in the amount of chloride ions to be allowed in the concrete by deregulation and utilization of the industrial waste. Based on such trend, new utilization of corrosion inhibitor is desired from the new viewpoint of the durability of concretes with the aforesaid materials.

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