Analytical Study of the Formation Process of Hemimorphite—Part II —Analysis of the Formation Process from Corrosion Products of Zinc by the Anodic Oxidation Method—

Hideki Nagata*, Morio Matsunaga** and Kunisuke Hosokawa**

* *Department of Biotechnology & Water Treatment, TOTO LTD.*

** *Department of Applied Chemistry, Faculty of Engineering,
Kyushu Institute of Technology*

In order to verify the mechanism of the formation process of hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$) in galvanized steel pipe for water service, the formation of hemimorphite in the corrosion process of zinc was confirmed through a procedure by which anodic oxidation was united with aging, which was named the anodic oxidation method. Zinc coupons were anodically oxidized in sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) solution using a galvanostat and then were aged in aqueous solution. The corrosion products on the surface of the zinc coupons aged for the prescribed periods were analyzed using Fourier-transform infrared micro spectroscopy and energy dispersive X-ray analysis. The surface morphologies of the aged coupons were observed using a scanning electron microscope and an optical microscope. Samples of the corrosion products and the solution in which the coupons were aged were analyzed using inductively coupled plasma emission spectroscopy. In combining the results of the co-precipitation method with the results of the present study, it was proved that hemimorphite formation in the zinc-silicate-water corrosion system proceeded in the following sequence:

- 1) precipitation of $\text{Zn}(\text{OH})_2$ as a corrosion product of zinc
- 2) adsorption of dissolved silicate onto the precipitate of $\text{Zn}(\text{OH})_2$
- 3) breaking of the structure of $\text{Zn}(\text{OH})_2$ by the adsorbed silicate
- 4) formation of an amorphous compound as a precursor of hemimorphite
- 5) rearrangement of atoms into the framework of the hemimorphite crystal

In addition, two types of morphology of the hemimorphite crystal were found.

Key words: galvanized steel pipe, water supply system, corrosion product, hemimorphite, dissolved silicate, adsorption, zinc hydroxide, crystallization, anodic oxidation, micro FT-IR

1. Introduction

We reported in a previous paper¹⁾ that a hemimorphite layer was observed on the interior surface of galvanized steel pipe for water service and that the formation of the hemimorphite layer on the zinc coating prevented galvanic protection by zinc. Then we proposed a mechanism of the formation process of hemimorphite in practical corrosion in water pipes. As part of the investigation to verify the mechanism, a co-precipitation method was performed and then the crystallization process of hemimorphite from amorphous compound of a precursor was elucidated²⁾. In the co-precipitation

method, however, the precursor was obtained from a precipitate in homogeneous solution, not from corrosion products on metallic zinc. Therefore, in the present study, zinc coupons were anodically oxidized in silicate solution and aged in aqueous solution in order to simulate practical corrosion. The procedure of the corrosion process was divided into an anodic oxidation process and an aging process for convenience, although these processes cannot be separated in practical corrosion. The formation process of a precursor at the initial stage and the crystallization process of the precursor were elucidated using Fourier-transform infrared micro spectroscopy (micro FT-IR), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and inductively coupled

* 2-1-1 Nakashima, Kokurakita-ku, Kitakyushu, 802 Japan

** 1-1, Sensuicho, Tobata-ku, Kitakyushu, 804 Japan

pled plasma emission spectroscopy (ICP).

2. Experimental

A zinc coupon with dimensions of 20 by 10 by 1 mm was polished using a 320 grit alumina polishing belt and a 3 mm ϕ hole was punched out on one side of the plate. Then the coupon was washed and degreased ultrasonically in trichloroethane and acetone. A zinc wire (one mm ϕ of diameter) was twisted through the punched hole and pressed strongly onto the coupon which was employed as the working electrode. The counter electrode was a stainless steel sheet (type 430, 60 by 40 by 0.4 mm).

An electrolyte was provided as follows: a sodium metasilicate solution (1.67×10^{-2} mol dm $^{-3}$, 1000 ppm as SiO $_2$) was decarbonated with N $_2$ gas bubbling, and the pH was adjusted to 11.5 with hydrochloric acid.

After 150 cm 3 of electrolyte was held at 85°C in N $_2$ atmosphere, the working electrode and the counter electrodes were immersed in the electrolyte. The counter electrodes were placed equidistant from both sides of the working electrode. The working electrode was then anodically oxidized using a galvanostat. Anodic current was passed for 2 hrs at a current density of 0.1 mA cm $^{-2}$. After anodic oxidation, the working electrode was removed from the electrolyte, immersed in 8 cm 3 of distilled water and aged at 85°C in a water bath for a prescribed period. All chemicals used in the experiments were reagent grade and were dissolved in distilled water.

After aging or anodic oxidation for a prescribed period, the corrosion products on the surface of the working electrode were observed using an optical microscope (OM) and SEM and were analyzed using micro FT-IR and EDX. The corrosion products of the aged specimens and samples of the solutions in which the specimens were aged were analyzed using ICP. The SEM and EDX were operated at an accelerated voltage of 5 kV. The FT-IR measurement was made microscopically. The corrosion products were picked up and placed on the KBr crystal under OM observation and were then analyzed using an IR microscope at a wavenumber resolution of 4 cm $^{-1}$ between 430 cm $^{-1}$ and 4000 cm $^{-1}$. The samples for ICP measurement were prepared by dissolving the corrosion products in 20 cm 3 of 1 normal KOH solution. The solution samples were measured after filtration and dilution.

Fig. 1 Surface morphologies of a specimen before and after 15 days.

(A) before aging, (B) after aging.

3. Results

Zinc coupons oxidized anodically in silicate solution were aged for the prescribed periods between 0 and 30 days. Before and after aging, the surface morphologies of the specimens were photographed. Fig. 1 shows the surface morphologies of one of the specimens before and after aging for 15 days. The corrosion products around the representative points were picked up or scraped up and analyzed. Point A represents the metallic surface before and after aging. Point B represents the corrosion products scattered on the surface before and after aging. Point C represents the thick, wide area of corrosion products near the punched hole before and after aging. Point D represents the metallic surface before aging but the corroded part after aging.

Fig. 2 shows the STD spectrum and the IR spectra of the corrosion products picked up at each point. As shown in Fig. 2, the corrosion products at point C showed the closest spectrum to that of the standard among the spectra at the 4 sampling points. All of the spectra, however, showed a configuration similar to that of the STD spectrum, although the degree of similarity varied with the sampling point, especially in the range from 800 cm $^{-1}$ to 1200 cm $^{-1}$.

Fig. 3 shows the scanning electron micrographs

Fig. 2 IR spectra of corrosion products at typical points on the surface of a specimen aged for 15 days.

of the surfaces nearby the sampling points for the FT-IR measurement. Fig. 3 (A), (B) shows that swordlike crystals grew from the crowded field of the laminated discs of the small crystals at point A. It can also be seen in Fig. 3 (C) that the swordlike or laminated discs of crystals grew among the amorphous products at point D.

Fig. 4 shows the representative IR spectra of the corrosion products at point C on the surfaces of the aged specimens for the prescribed periods

between 0 and 30 days. The IR spectra of the corrosion products before aging showed three major broad bands which had peak tops at 3360 cm^{-1} , 945 cm^{-1} , and 570 cm^{-1} , respectively, and two weak, broad bands at 1630 cm^{-1} and 695 cm^{-1} . The corrosion products of the specimens aged up to 6 days exhibited spectra similar to that of the corrosion products before aging. The configurations of these spectra were analogous to that of the 18-hr aged co-precipitated (ACP) sample obtained from the mixed solution of the Zn/Si molar ratio of hemimorphite in a parallel paper²³. After 9 days, the three major broad bands began to deform in shape and other absorption bands began to appear. The specific bands of hemimorphite appeared after 12 days, and those specific bands became sharp and strong as the aging time increased. After 30 days, the spectrum showed almost the same configuration as that of the STD spectrum.

Fig. 5 shows the scanning electron micrographs at point C on the surface of the specimens aged for 15 and 30 days. It can be seen in Fig. 5 that the swordlike crystals were growing in every direction among the amorphous products after 15 days, and bunches of crystals grew up like chrysanthemum flowers after 30 days.

Table 1 shows the concentrations of Zn and Si in the KOH solutions in which the corrosion products were dissolved and the molar ratios of Zn/Si calculated from those concentrations. The concentrations of Zn and Si were measured at the same time using ICP. As shown in Table 1, the molar ratios of Zn/Si for all of the specimens

Fig. 3 Scanning electron micrographs at typical points on the surface of the specimen shown in Fig. 1 (B).

(A) view at point A, (B) enlarged view of the center of micrograph (A), (C) view at point D.

Fig. 4 IR spectra of corrosion products at point C on the surface of aged specimens.

before and after aging indicated slightly lower values than the stoichiometric ratio of hemimorphite ($Zn/Si=2$).

Table 2 shows the concentrations of the dissolved silicate calculated as SiO_2 in the solutions

Table 1 Concentrations of Zn and Si dissolved in KOH solutions and molar ratios of Zn/Si.

Aging time (days)	Concentration (mg/dm ³)		Molar ratio Zn/Si
	Zn	Si	
0	1.19	5.22	1.88
1	0.26	0.94	1.55
6	0.54	2.44	1.94
9	0.15	0.43	1.55
12	0.29	1.16	1.72
15	1.25	4.38	1.50
25	0.51	2.01	1.69
30	0.86	3.71	1.85

Table 2 Concentrations of silicate in solutions after aging.

Aging time (days)	Concentration as SiO_2 (mg/dm ³)	
1	14.0	14.2
25	432	346
30	493	395

in which the specimens were aged. The ICP measurements were made for two different samples for each aging time. It turned out that the concentration of the dissolved silicate increased after

Fig. 5 Scanning electron micrographs at point C on the surface of aged specimens.
(A) aging time: 15 days, (B) aging time: 30 days.

Fig. 6 Scanning electron micrographs of the surface of a specimen after anodic oxidation.

(A) circular precipitates, (B) corrosion products covering partly the precipitate, (C) corrosion products scattered on the surface, (D) metallic surface.

long periods of aging.

Fig. 6 shows scanning electron micrographs of the surface of a specimen after anodic oxidation at 0.1 mA cm^{-2} for 2 hrs in the metasilicate solution. Micrographs (A), (B), (C) in Fig. 6 represent the three types of typical surface morphologies at the localized corrosion areas scattered on the surface such as point B before aging in Fig. 1. The first type was a circular precipitate (bright SEM image) around a corrosion pit as shown in micrograph (A). The second one was a circular precipitate partly covered with corrosion products (dark SEM image) as in micrograph (B). The third one was the corrosion products clinging on the surface as in micrograph (C). Micrograph (D) shows a typical metallic surface.

Fig. 7 shows the EDX spectra taken from the surface products of the same specimens as in Fig. 6. Spectra (A), (B), (C) in Fig. 7 were taken from the rectangular surface area surrounded by a white frame in micrographs (A), (B), (C), respectively, in Fig. 6. Spectrum (D) in Fig. 7 was taken from the metallic surface area of micrograph (D). The characteristic X-ray peaks of Zn, Si, and O were observed in all these spectra. Spec-

Fig. 7 EDX spectra of the corrosion products on the surface shown in Fig. 6.

(A) circular precipitate in micrograph (A), (B) corrosion products on circular precipitate in micrograph (B), (C) corrosion products in micrograph (C), (D) metallic surface in micrograph (D).

trum (D) exhibited a strong X-ray peak of the Zn-L line and some of X-ray peaks of the Si-K and O-K lines. Spectrum (A) exhibited a strong Zn-L line and very weak but slightly stronger Si-K and O-K lines than those in spectrum (D). Spectrum (B) exhibited a strong Zn-L line and moderately strong Si-K and O-K lines. Spectrum (C) showed the same features as spectrum (B). The thick, wide area of corrosion products such as point C in Fig. 1 (A) also showed spectra similar to spectrum (B) or (C).

4. Discussion

4.1 Corrosion Products of Zinc and Their Crystallization Process

As shown in Fig. 1, the corrosion products were localized on the surface of the specimen after anodic oxidation, especially around the punched hole as shown around point C. This is because the anodic current flows easily out from the pe-

rimeter of the punched hole owing to flaws in the punch.

Since a considerable volume of the corrosion products existed around the punched hole on all the aged specimens from the initial stage of aging, we could see the crystallization process of corrosion products at point C. As shown in Fig. 4, the IR spectra of the corrosion products showed a transition quite similar to that of the IR spectra of the ACP samples obtained from the mixed solution of the Zn/Si molar ratio of hemimorphite in a parallel paper²³. This fact indicates that the corrosion products at point C crystallize through the same process as that on the ACP samples. It is well-known that zinc hydroxide forms as the corrosion product when zinc is anodically oxidized in neutral or weak alkaline solution^{33,42}. Accordingly, in the anodic oxidation method, it can be said that zinc hydroxide formed in the weak alkaline silicate solution during the anodic oxidation. It is reasonably estimated from such a situation and the results of the co-precipitation method²³ that the corrosion products crystallize into hemimorphite.

As shown in Fig. 4, the 605 cm^{-1} band did not split at the stage of the crystallization, and neither did the 605 cm^{-1} band in the IR spectra of hemimorphite (Zn/Si=2) and the ACP samples obtained from excess Si solution (Zn/Si=2/5)²³. On the other hand, the 605 cm^{-1} band of the IR spectra of the ACP samples obtained from the mixed solution having a Zn/Si molar ratio of 2 had been split from 60 hrs of aging to 90 days²³. It is evident from the molar Zn/Si ratio in Table 1 that the corrosion products contained excess Si compared with the stoichiometry of hemimorphite. The excess Si condition in the compounds might cause a delicate change in the structure of the pyrosilicate group, which would be reflected in the splitting of the 605 cm^{-1} band.

4.2 Growth Process and Morphology of Hemimorphite Crystals

It is apparent from the IR spectra in Fig. 2 that hemimorphite was forming at other representative points as well as point C. It is likely that some difference can be seen in the morphology of hemimorphite crystals at each point, and that such a difference was caused by the difference in the growth process of the crystals. Palomar and Hoyos²⁵ investigated the morphology of the hemimorphite crystals precisely. According to their paper, a flake of hemimorphite is a swordlike, plate-shaped crystal which has a well-developed

plane parallel to the (010) plane and is pointed to [001], the *c*-axis of a cell. A flake of hemimorphite forms a twin crystal which has the twinning plane (001) and forms a mass like a flower. As shown in Fig. 3 and Fig. 5, we also observed such swordlike crystals and masses like flowers. It is evident that all of these are hemimorphite crystals.

It can be seen at point C that the twinning crystals of hemimorphite were growing in every direction among the amorphous products in Fig. 5 (A) and that each of them grew to form the flowers of crystals in Fig. 5 (B). On the other hand, it appears in Fig. 3 (A) like that the swordlike or laminated disks of crystals were growing directly from the specimen's surface at point A. The reason for this can be considered that at point C, the crystals could grow in every direction because the precursor existed from the initial stage of crystallization. However, at point A, the crystals could not help growing upward because the dissolved silicate was provided from the bulk of solution as the corrosion of zinc proceeded at point A. The situation at point D would be intermediate between that at point A and point C. The morphology at point B was similar to that at point C. It is noteworthy that the morphology of the hemimorphite crystals showed the laminated disks as well as the swordlike plates as in Fig. 3 (B). It appears from the morphology in Fig. 3 (A) that the laminated disks grew first, and the swordlike plates grew later at some site of the laminated disks of crystals. It is not yet clear whether or not the structure of the laminated disks of the crystals is as complete as that of the swordlike crystals.

Here a question arises from the interpretation of the morphology in Fig. 3 (A): where did the dissolved silicate come from? There is no dissolved silicate in the solution at the beginning of aging because the specimen which was oxidized anodically was immersed in distilled water. It can be estimated from the results shown in Table 2 that the solid (probably gelatinous) silicate which was adsorbed and deposited onto the surface of the specimens redissolved into the solution after immersion. As shown in Table 2, since the concentrations of silicate in the solutions after 25 or 30 days of aging were comparable with that in the solution during the anodic oxidation (1000 mg dm^{-3}), it would be sufficient to provide the silicate to form the hemimorphite crystal. This redissolution of silicate caused a consequent crystallization of hemimorphite. Consequently, it was

unexpectedly verified that the corrosion of zinc in silicate solution was accompanied by the formation of hemimorphite under appropriate conditions.

4.3 Initial Formation Process of Corrosion Products

It is considered that zinc hydroxide forms when zinc corrodes in neutral or weak alkaline solution, and dissolved silicate is adsorbed and deposited onto the surface of the precipitate of zinc hydroxide, if dissolved silicates exist in the solution. We can see conspicuous examples which exhibited such a process in Fig. 6. Two areas of circular precipitates which look bright in Fig. 6 (A) must be mainly composed of zinc hydroxide, although small amounts of adsorbed silicate, judging from spectrum (A) in Fig. 7, exists on the surface. It can be presumed that divalent zinc cations dissolved out of a pit located near the center of a circle and deposited circularly as hydroxide around the pit. Judging from spectrum (B), the compounds which look dark in Fig. 6 (B) must be composed of a mixture of silicate and zinc hydroxide. Fig. 6 (B) shows a conspicuous example in which the silicate was adsorbed onto the surface of the precipitate and the consequent corrosion products partly covered the surface of the precipitate. Fig. 6 (C) shows an example in which the corrosion products entirely covered the surface of the precipitate. These localized corrosion areas correspond to point B in Fig. 1 (A), and these corrosion products looked white under OM observation. Since the corrosion products near the punched hole, corresponding to point C, exhibited an EDX spectrum similar to that in Fig. 7 (B) or (C), the corrosion products at point C would be formed through the same process as that in Fig. 6. From these observations, the same inference as that in a parallel paper²⁾ can be drawn: at the first stage of hemimorphite formation, the dissolved silicate is adsorbed onto the surface of the zinc hydroxide precipitate, and at the next stage, the dissolved silicate breaks down the structure of the zinc hydroxide and forms the new bonds resulting in amorphous compound as a precursor of hemimorphite.

5. Conclusions

We confirmed that hemimorphite was formed from the corrosion products of zinc in silicate solution and analyzed the formation process of hemimorphite morphologically as well as spec-

troscopically. We may reasonably conclude from the results of the present study, in addition to the results of the co-precipitation method, that the formation process of hemimorphite during the corrosion process of zinc in aqueous silicate solution is the following:

1) When zinc corrodes in neutral or weak alkaline solution, zinc hydroxide is formed as the corrosion product and deposits around the corrosion pit, and dissolved silicate is adsorbed onto the zinc hydroxide precipitate.

2) In the corrosion products formed through the above process, the adsorbed silicate breaks the structure of zinc hydroxide and forms the new bonds of the amorphous compound as a precursor of hemimorphite.

3) In the amorphous compound, a rearrangement of atoms occurs over a long period to form the framework of hemimorphite.

4) Hemimorphite crystals show two types of morphologies, swordlike plates and laminar disks, and these shapes of crystals grow into a variety of masses according to the corrosion condition.

In a series of studies, the formation process of hemimorphite in the zinc-silicate-water corrosion system was elucidated. Although the experimental conditions were accelerated and simplified compared with the practical corrosion system in water pipes, it appears that the results of the studies verify the proposed mechanism of the formation process of hemimorphite in practical water pipes.

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