

Effect of trace amount of ferrous and ferric ions on the dissolution of iron plate in magnetically treated 3% sodium chloride solution

† Atsushi Chiba*, Tomohiro Ohki, and Wen-Chang Wu**

*Department of Materials Chemistry, Faculty of Engineering, Yokohama National University
79-5, Tokiwadai, Hodogaya-Ku, Yokohama 240-8501, Japan

**Department of Chemical Engineering, Southern Taiwan University of Technology
1 Nan-Tai Street, Yung-Kang City, Tainan Hsien, Taiwan, 710 R.O.China

A 3% NaCl solution of 1 dm³ circulated with 1.5 dm³/min by a pump for 24 h in the presence of magnetic field. An iron plate immersed in a 100 cm³ of test solution for 24 h. The rest potential and pH on surface fixed after 3 h. Containing 0~120 ppm of Fe(II) ion, the dissolution in the magnetically treated solution rose comparing with that in the non-magnetically treated solution. The dissolution amount reached to maximum at 50 ppm, then fixed in the non-magnetically treated solution. When Fe(II) ion existed in the magnetically treated solution, dissolution accelerated a little. In the non-magnetic treated solution containing 10~125 ppm of Fe(III) ion existed, the dissolution accelerated. The dissolution amounts reached to maximum at 50 ppm, then decreased from maximum value. In the magnetically treated solution, the dissolution amounts reached to minimum until 50 ppm, then increased from minimum value. The dissolution amounts affected larger with increasing of magnetic flux density. Fe(II), Fe(III) ions and magnetic treatment affected to formation of Fe(OH)₂ and/or Fe₃O₄ films. The magnetically treated effects memorized about one month.

Keywords : corrosion, iron, 3% NaCl solution, magnetic treatment, ferrous ion, ferric ion

1. Introduction

Many technologies are available to protect an iron against corrosion media. One of the common techniques is to use magnetic field effects. The magnetic field effects on the dissolution and corrosion of metals were differed in the corrosive environments. The dissolution was accelerated and/or inhibited. Any mechanisms of magnetic field effects were unknown. If the inhibition effects are expected, the magnetic field effects have been larger economically than the anticorrosion engineering by the chemicals and other techniques.

The magnetic field effects on the dissolution and corrosion were some reports. Anodic dissolution was studied specially. Anodic dissolution became uniform.¹⁾ A mass transfer was affected.^{2),3)} The anodic dissolution rate was differed when the direction of a magnetic force line to dissolution face was differed.⁴⁾ The formation rate of passive film was faster and corrosion inhibited.⁵⁾ The inhibition of dissolution was depended on the change of surface conditions.⁶⁾ The corrosion was affected the formation of oxide film on the surface.⁷⁾ Generally, the

corrosion and dissolution were inhibited as the changing rate was faster from red rust to black rust. Effect of magnetic fields on electrochemical process had been published.⁸⁾

In this study, the authors were estimated that dissolved iron ion prepared to dissolution and corrosion, effect of concentration of iron ions in magnetically treated 3 % NaCl solution determined.

2. Experimental procedure

The magnetic field was prepared with samarium-cobalt permanent magnet, and the magnetic flux density used 0.2, 0.4 and 0.6 T. A 3 % NaCl solution of 1000 cm³ circulated with 1500 cm³/min by the pump for 24 h in the magnetic field under close system. A FeCl₂ or FeCl₃ was added in this solution. A test solution of 100 cm³ which contained Fe(II or III) ion in the rang of 0 to 125 ppm was taken in a Erlenmeyer flask with stopper. The test specimen was prepared from an iron plate (99.99 %, 0.1 cm) by cutting specimen into a small plate with dimension 1 cm x 5 cm. The surface polished with 2000 emery paper, immersed for 1 min in 6 mol /dm³ HCl solution and washed distilled water before each experiment. An iron plate hung with

† Corresponding author: a-chiba@ynu.ac.jp

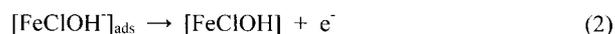
silk thread, and immersed for 24 h. The temperature was kept at 298 ± 0.5 K during the measurement. The effects of chloride ion in FeCl_2 or FeCl_3 on the dissolution were neglected.

The dissolution amounts were measured by the o-phenanthroline absorptiometry. The test solution was filtered. The adhesion materials on the surface of the iron plate were dropped on the cake with the spatula. A cake was dissolved with 2 cm^3 of 6 mol/dm^3 HCl, and was mixed to the test solution. Thereafter, distilled water was added, and made up 250 cm^3 . After a $1\sim 10 \text{ cm}^3$ of this solution was sampled, 2 cm^3 of acetate buffer solution (pH 5.25), 2 cm^3 of 0.25 % o-phenanthroline ethanol solution and 1 cm^3 of 1 % hydroxylamine hydrochloride were added. Distilled water added and made up 25 cm^3 . The concentration measured at 508 nm.

3. Result and discussion

3.1 pH

The pH changes of test solution on the surface are shown in Fig. 1 and 2 as a function of immersion time. The initial pH, 4.7, of test solution increased to 6.1~6.4 after 6 h, thereafter pH was stabilized with a immersion time elapsed in the magnetically treated solution. The value of pH was differed with the taken of Fe(II) and Fe(III) ions and those concentration. In the non-magnetically treated solution, the pH of solution without iron ion was higher comparing with that solution containing of Fe(II) and Fe(III) ions and mixture. In the magnetically treated solution, the pH of solution without iron ion was higher than that containing of 50 ppm of Fe(II) ion and mixture of Fe(II) and Fe(III) ions, and was lower than that containing a 50 ppm of Fe(III) ion. The magnetic treatment effects had a little as the difference of pH was about 0.1 at each immersion time. In the early stage of corrosion, the pH of each test solution on the surface was about 4.8~5.0. Next chemical and electrochemical reactions were considered. Eqs. (1)~(3) were proposed in weak acidic chloride solution⁹⁾ as follows.



And HCO_3^- ion existed as CO_2 gas in air dissolved in the test solution.

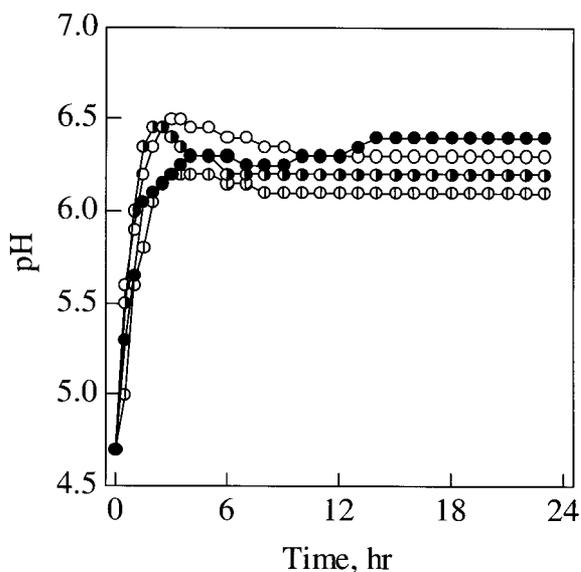


Fig. 1. pH on surface in non-magnetically treated solution
Concentration: ○; Non-addition, ●; Fe(II) 50ppm, ⊙; Fe(III) 50ppm, ●; Fe(II) 25ppm and Fe(III) 25ppm

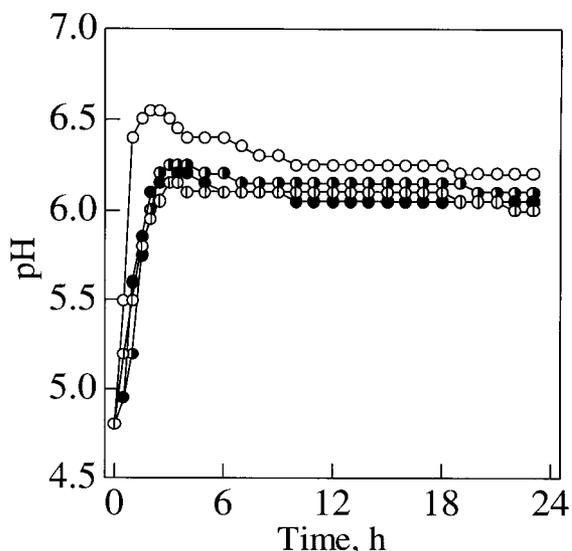


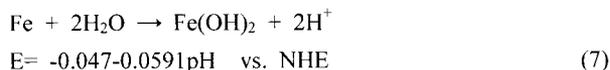
Fig. 2. pH on surface in 0.6T magnetically treated solution
Concentration: ○; Non-addition, ●; Fe(II) 50ppm, ⊙; Fe(III) 50ppm, ●; Fe(II) 25ppm and Fe(III) 25ppm

This equilibrium was depended on the pH and did not depended on the electrode potential. The reaction (5) was estimated.

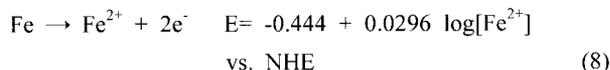


Further, next reactions were consisted,





However, the main reaction was given by equation (8),



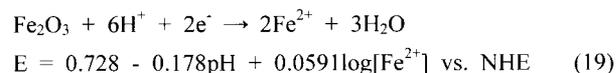
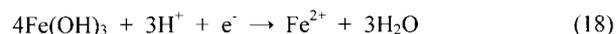
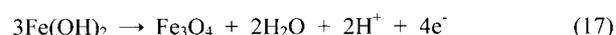
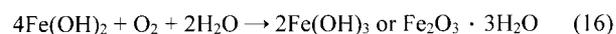
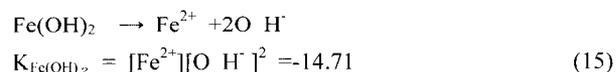
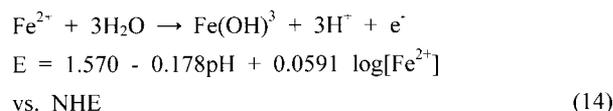
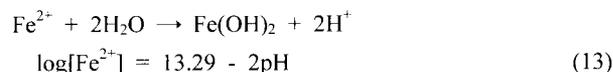
Cathodic reactions were given by equations (9)~(11).



The rise of pH could be explained with the reaction (10). The potential is -0.62 V vs. NHE under about 6 to 7. Fe(II) ion was many change to black magnetic iron oxide, or black magnetite Fe_3O_4 or into white $\text{Fe}(\text{OH})_2$. To fit the general scheme of emphasizing the dependence of pH and potential, it is useful to write the equilibrium of ferrous hydroxide as follows.



But, next equations were considered, as follows,



The pH was fixed at about 6.0~6.5 after 6 h of immersion. The hydroxide of main product was observed. Some time, Fe_2O_3 and Fe_3O_4 films were observed on a part of surface. So, we can conclude that the surface of iron plate is covered by productive insoluble hydroxide, and this

hydroxide was changed to oxide after 6 h of immersion.

3.2 Rest potential

The rest potentials are shown in Fig. 3 and 4. The rest potentials shifted in the based direction with time elapsed, and stabilized at approximate -650 mV vs. Ag/AgCl after 6 h of immersion. We can conclude that the dissolution

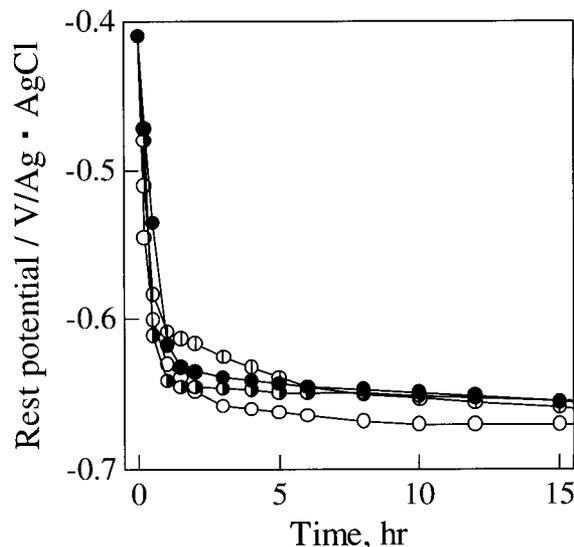


Fig. 3. Effect of iron ions on the rest potential in non-magnetically treated solution

Concentration: \circ ; Non-addition, \bullet ; Fe(II) 50ppm, \odot ; Fe(III) 50ppm, \bullet ; Fe(II) 25ppm and Fe(III) 25ppm

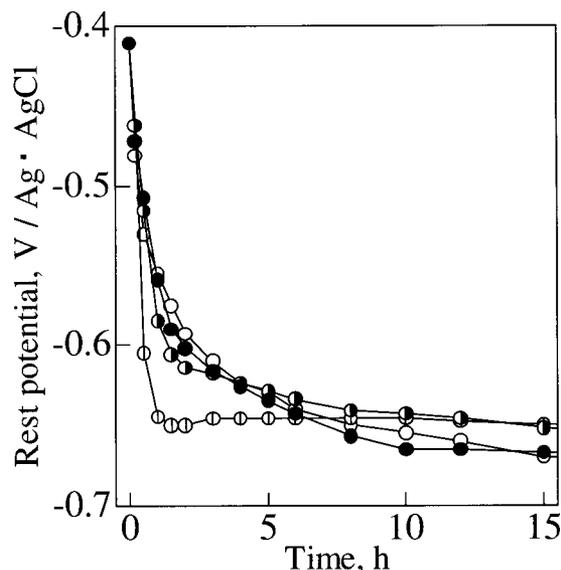


Fig. 4. Effect of iron ion on the rest potential in 0.6T magnetically treated solution

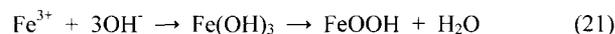
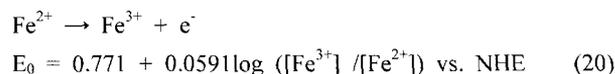
Concentration: \circ ; Non-addition, \bullet ; Fe(II) 50ppm, \odot ; Fe(III) 50ppm, \bullet ; Fe(II) 25ppm and Fe(III) 25ppm

of iron plate was prior generated, thereafter the corrosion products were covered on surface gradually. The precipitation of $\text{Fe}(\text{OH})_2$ and Fe_3O_4 film were observed on surface after 24 h of immersion. The rest potentials were differed with a trace amount of iron ions.

In the non-magnetically treated solution, the rest potentials in the absence of iron ions were noble comparing with that in the presence of iron ions. We can conclude that the trace amount of $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ ions in the solution was affected to corrosion and dissolution of iron plate. The actual dissolution amount was measured, as the details of the effect on the magnetic treatment were the indistinctness.

3.3 Dissolution amount

Effect of immersion time on the dissolution amount is shown in Fig. 5. $\text{Fe}(\text{III})$ ion was not detected in the test solution at 24 h of immersion testing. We can estimate that $\text{Fe}(\text{II})$ ion was not oxidized to $\text{Fe}(\text{III})$ ion with O_2 gas in the test solution during the magnetic treatment of 24 h. But, $\text{Fe}(\text{III})$ ion was examined as $\text{Fe}(\text{II})$ ion was oxidized to $\text{Fe}(\text{III})$ ion in the long times under an atmosphere of air. $\text{Fe}(\text{III})$ ion changed to hydroxide as follows.



In the test solution containing of 50 ppm $\text{Fe}(\text{II})$ ion, the dissolution amount increased with magnetic treatment

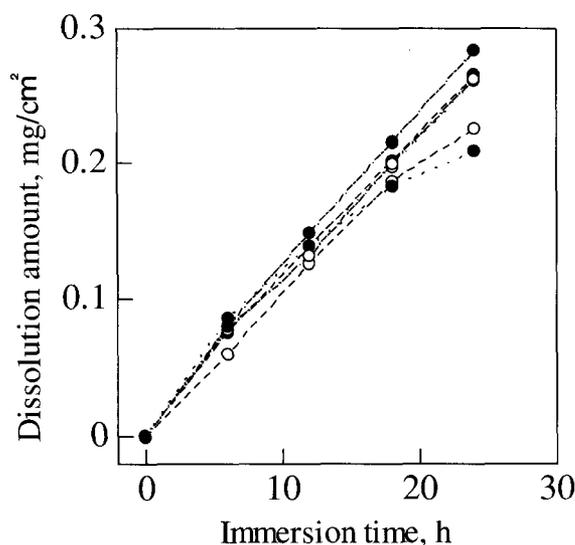


Fig. 5. Effect of immersion time on the dissolution amount. ○; Non-magnetic treatment, ●; Magnetic treatment, ---; Non-addition, -.-.-; $\text{Fe}(\text{II})$ 50ppm, ···; $\text{Fe}(\text{III})$ 50ppm

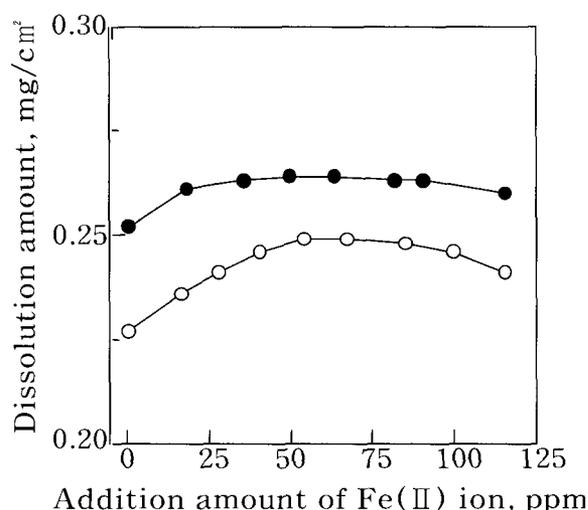


Fig. 6. Effect of ferrous ion on the dissolution amount ○: Non-magnetic treatment, ●: Magnetic treatment

comparing with that without magnetic treatment. In the test solution containing of 50 ppm $\text{Fe}(\text{III})$ ion, the dissolution amount reduced with magnetic treatment comparing with that without magnetic treatment over 12 h of immersion. In the mixed solution of 25 ppm $\text{Fe}(\text{II})$ and 25 ppm $\text{Fe}(\text{III})$ ions, the dissolution amount increased with magnetic treatment.

Effect of $\text{Fe}(\text{II})$ ion concentration in the test solution on the dissolution amount after 24 h of immersion is shown in Fig. 6. The dissolution amounts in the magnetically and non-magnetically treated solutions were accelerated with increasing $\text{Fe}(\text{II})$ ion in solution. The dissolution amounts in the magnetically treated solution were larger than that in the non-magnetically treated solution. We can conclude that the magnetic treatment inhibited the reactions of equations (7), (13), (14) and (16), or accelerated the reaction of (15).

Effect of $\text{Fe}(\text{III})$ ion concentration in solution on the dissolution amount is shown in Fig. 7. A 10~125 ppm of $\text{Fe}(\text{III})$ ion was contained in a solution. The dissolution amounts increased until 50 ppm of $\text{Fe}(\text{III})$ ion, thereafter decreased with increasing of $\text{Fe}(\text{III})$ ion in the non-magnetically treated solution. The dissolution amounts decreased until 50 ppm, thereafter increased with increasing of $\text{Fe}(\text{III})$ ion in the magnetically treated solution. The dissolution amount accelerated in the magnetically treated solution comparison with that in the magnetically treated solution under 10 ppm of $\text{Fe}(\text{III})$ ion. The dissolution amounts inhibited in the range to 10~125 ppm in the magnetically treated solution. The following experiments were examined about 50 ppm, as the concentration range of 40~80 ppm was more prepared to dissolution.

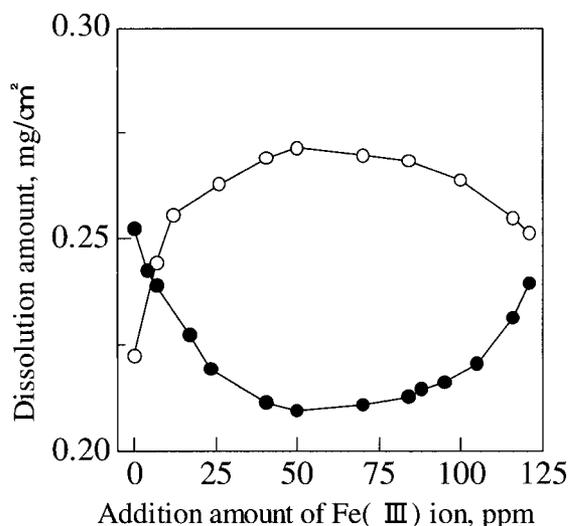


Fig. 7. Effect of ferric ion on the dissolution amount
 ○: Non-magnetic treatment, ●: Magnetic treatment

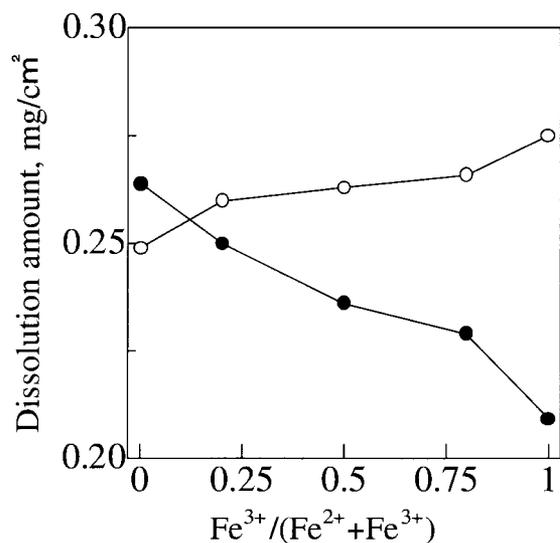


Fig. 8. Effect of mixture of ferrous and ferric ion on the dissolution
 Fe(II) + Fe(III) = 50ppm, ○: Non-magnetic treatment, ●: Magnetic treatment

We conclude that the magnetic treatment of solution accelerated the reactions of equations (20) and (21).

Effect of the mixed portions of Fe(II) and Fe(III) ions on the dissolution is shown in Fig. 8. The dissolution amount increased in the non-magnetically treated solution, and decreased in the magnetically treated solution with increasing Fe(III) ion.

It was estimated that the corrosion products had been formed on the surface as the measurement potential did not agreed with the value of equation, even if the disso-

lution amount and pH are substituted for the reactions of equations (7), (8), (13), (14), (15), (19) and (20).

3.4 Magnetic flux density

Effect of magnetic flux density on the dissolution amount is shown in Fig. 9. In the non-containing and containing of 50 ppm of Fe(II) ion, the dissolution amount increased with increasing of magnetic flux density. However, the dissolution amounts were reduced with increasing of magnetic flux density in the solution containing of 50 ppm of Fe(III) ion. It was concluded that magnetic treatment was accelerated to dissolution during early period of immersion.

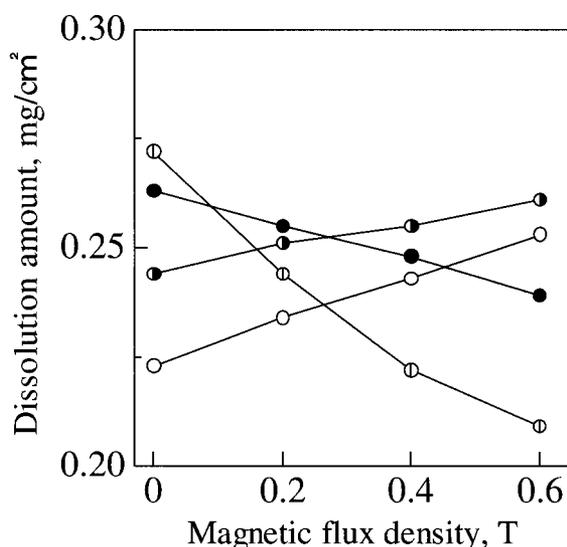


Fig. 9. Effect of magnetic flux density on the dissolution
 Concentration: ○; Non-addition, ●; Fe(II) 50ppm, ⊙; Fe(III) 50ppm, ●; Fe(II) 25ppm and Fe(III) 25ppm

3.5 Memorization of magnetic treatment effect

Effect of memorization after magnetic treatment on the rest potential is shown in Fig. 10. The test solutions were left at 298 K after the magnetic treatment. The magnetic treatment effects disappeared as the locus of rest potential approached to that of non-magnetically treatment solution.

Effect of memorization after the magnetic treatment on the dissolution amount is shown in Fig. 11. The dissolution amount in magnetically treated solution which was not contained Fe(II) ion was reduced with increasing of leaving days. The dissolution amount in magnetically treated solution containing of 50 ppm of Fe(II) ion was increased with increasing of leaving days. It was estimated that magnetic effects disappeared after about one month.

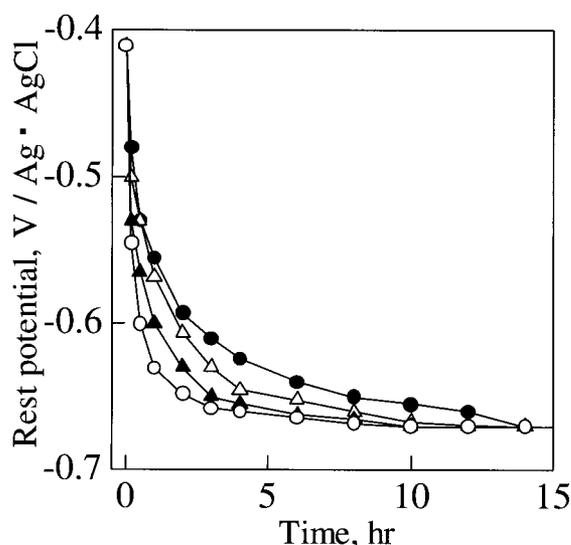


Fig. 10. Effect of memorization after treatment on the rest potential

○: Non-magnetic treatment, ●, △, ▲: Magnetic treatment, Left day: ○, ●: 0 day, △; 10 day, ▲; 20 day

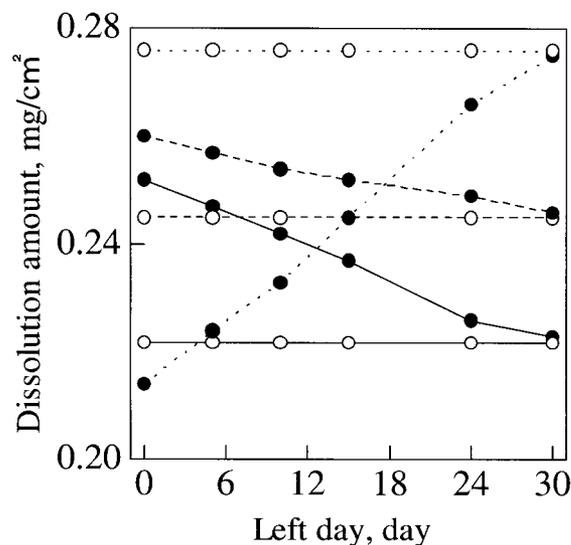


Fig. 11. Memorization of magnetic treatment. Non-magnetic treatment, ●: Magnetic treatment, Concentration: —; Non-addition, ----; Fe(II) 50ppm, ···; Fe(III) 50ppm

The dissolution amount in magnetically treated solution which was not contained Fe(III) ion was reduced with increasing of leaving days. The dissolution amount in magnetically treated solution containing of 50 ppm of Fe(III) ion was increased with increasing of leaving days. It was estimated that magnetic effects disappeared after about one month.

4. Conclusions

1) The dissolution was accelerated in the magnetically treated 3% NaCl solution containing 10~125 ppm of Fe(II) ion.

2) The dissolution was inhibited in the magnetically treated 3% NaCl solution containing 10~125 ppm of Fe(III) ion. The inhibition effects were most largest in containing 40~80 ppm of Fe(III) ion.

3) It was concluded that magnetically treated solution containing of Fe(II) ion was inhibited to formation of Fe(OH)₂ and/or Fe₃O₄ film and magnetically treated solution containing of Fe(III) ion was accelerated to formation of Fe(OH)₂ and or Fe₃O₄ film.

4) The magnetically treated effects were disappeared after about one month

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