

Magnetic Field Effect on Electrode Reactions. II. Effects on the Potential of an Iron Electrode in an Iron(III) Chloride Solution under Galvanostatic Conditions

Magne Waskaas

Telemark University College, Institute of Technology, Kjølnes Ring 56, N3914 Porsgrunn, Norway

Waskaas, M., 1996. Magnetic Field Effect on Electrode Reactions. II. Effects on the Potential of an Iron Electrode in an Iron(III) Chloride Solution under Galvanostatic Conditions. – Acta Chem. Scand. 50: 521–525. © Acta Chemica Scandinavica 1996.

Under galvanostatic conditions, both the anodic and cathodic electrode potentials of a working electrode of iron in a stirred iron(III) chloride solution increase when exposed to static magnetic fields. The increase was found to depend on the magnetic flux density and the electrolyte concentration. Also, the increase in the anodic electrode potential was observed within the pre-passive potential region of the iron electrode, and the increase in the cathodic electrode potential was associated with an increase in the cathodic limiting current density. Results from experiments using stainless steel as working electrode in 1 M iron(III) chloride, and experiments using iron in 1 M iron(II) chloride, showed no effect of the magnetic field. The observed results were found to be explainable in terms of neither external electromagnetic interference nor electromagnetic induction, i.e. magnetohydrodynamics.

The purpose of this study is to examine experimentally what effects static magnetic fields have on the anodic and cathodic potentials of an iron electrode in contact with a stirred electrolyte. In addition, possible electromagnetic interferences are studied.

The study is based upon a previous experimental study, in which the results showed that under open-circuit conditions, a ferromagnetic iron electrode in the paramagnetic iron(III) chloride solution becomes more positive when exposed to static magnetic fields.¹

Results from other studies indicate that magnetic fields exert a perceptible influence on the metal/electrolyte interfacial potential difference. The observed effect is linked to charge-transfer- and mass-transport-controlled processes, and has been explained in terms of magnetohydrodynamics.^{2–12}

Preconsiderations

In this section, some considerations concerning electrochemical reactions in an electrochemical cell consisting of an iron electrode in an iron(III) chloride solution are given, together with possible interactions due to electromagnetic induction.

In an electrochemical cell, both anodic and cathodic reactions will occur between the iron electrode and the

solution. The main anodic reaction will be:¹³



The most common cathodic reactions in acid solutions are:¹³



In the further consideration, the following assumptions are made: (1) Experimentally it is observed that the rate of hydrogen evolution [eqn. (2)] is decreased markedly by addition of an oxidizer such as ferric ions to acid solutions.¹³ Therefore, in this consideration hydrogen evolution [eqn. (2)] is ignored. (2) The exposure chamber which will be used in this study is the same as that used in the previous experimental study.¹ Since the exposure chamber was designed to reduce the contact between the solution and air to a minimum, oxygen reduction [eqn. (3)] is eliminated. (3) Since iron corrodes rapidly in acid solutions, metal deposition [eqn. (5)] is negligible.¹³

Based upon these assumptions, only metal dissolution [eqn. (1)] and ferric ion reduction [eqn. (4)] are taken into consideration.

The net electrode current density (I) is the sum of the positive current density corresponding to metal dissolution (I_m) and the negative current density (I_r) corresponding to ferric reduction, and is given by:¹³⁻¹⁵

$$I = I_m + I_r \quad (6)$$

Upon open-circuit conditions ($I=0$), the corrosion current density (I_{corr}) is defined as:¹⁴

$$I_{\text{corr}} = I_m = -I_r \quad \text{at } E = E_{\text{corr}} \quad (7)$$

The corresponding electrode potential is called the mixed potential or the corrosion potential (E_{corr}).

At steady state, metal dissolution [eqn. (1)] is described by the polarization (η), which is the deviation of the electrode potential from the corrosion potential:¹⁶

$$I_m = I_{\text{corr}} \exp\left(\frac{F}{2RT} \eta\right) \quad (8)$$

where F is the Faraday constant, R is the universal gas constant, and T is the temperature in K.

Polarization occurs when anodic and cathodic reactions are limited by various physical and chemical factors, and can be divided into two different types, charge-transfer polarization and concentration polarization. Charge-transfer polarization refers to an electrochemical process which is controlled by the reaction at the metal-electrolyte surface. Concentration polarization refers to electrochemical reactions which are controlled by diffusion in the electrolyte.¹³

To maintain the reaction in eqn. (4), Fe^{3+} ions from the bulk have to move up to the iron electrode to receive electrons from the electrode, i.e. there is a passage of an electrode current. Consequently, there exists a stagnant layer of thickness (δ), the Nernst diffusion layer, near the electrode surface where the Fe^{3+} concentration ($C_{x=0}^{\text{Fe}^{3+}}$) is less than the bulk concentration ($C_b^{\text{Fe}^{3+}}$). In unstirred solutions $\delta \approx 0.0004$ m. In stirred solutions δ becomes lower and the electrode current increases with increasing stirring rate.^{14,17}

Suppose the electron transfer occurs only due to the limiting current density; the corrosion current density, I_{corr} then is equal to $-I_L$, and is given by¹⁸

$$I_{\text{corr}} = -I_L = -I_r = \frac{FD}{\delta} C_b^{\text{Fe}^{3+}} \quad (9)$$

where D is the diffusion coefficient of Fe^{3+} ions.

At large anodic and cathodic polarizations ($|\eta| \gg RT/nF$),¹⁹ the relationship between the applied electrode potentials and the electrode currents is described by eqns. (8) and (9).

Concerning possible electromagnetic interference, two cases are considered.

In stirred electrolytic solutions, an applied magnetic field will cause an effect upon the flow of the ions due to the Lorentz force, i.e. induction.²⁰ Consider a circular ion flow with radius r , within a magnetic field B at a stirring rate ω , and the electrical conductivity σ ; the induced current density (I_s) is²⁰⁻²²

$$I_s = \frac{\omega}{4\pi} Br\sigma \quad (10)$$

Concerning possible transient effects due to turning the magnetic field on or off, the induced current density (I_t) in a closed circuit is given by²⁰⁻²²

$$I_t = \frac{dB}{dt} \sigma l \quad (11)$$

where l is the length of the current path.

Experimental

Apparatus. The experimental setup is shown in Fig. 1. The exposure chamber was filled with an electrolytic solution, and placed between the poles of an electromagnet. The solution was stirred by a rotating cylinder. The electromagnet (Newport) produced a static magnetic field with magnetic flux densities up to 800 mT. The magnetic poles were circular with a diameter of 10 cm and an area of 78.5 cm². The gap between the poles was 3.0 cm.

The exposure chamber which consisted of two parts was made of Teflon plastics and is shown in Fig. 2. The two parts of the chamber were held together with screws of a non-magnetic material (brass). The dimensions of

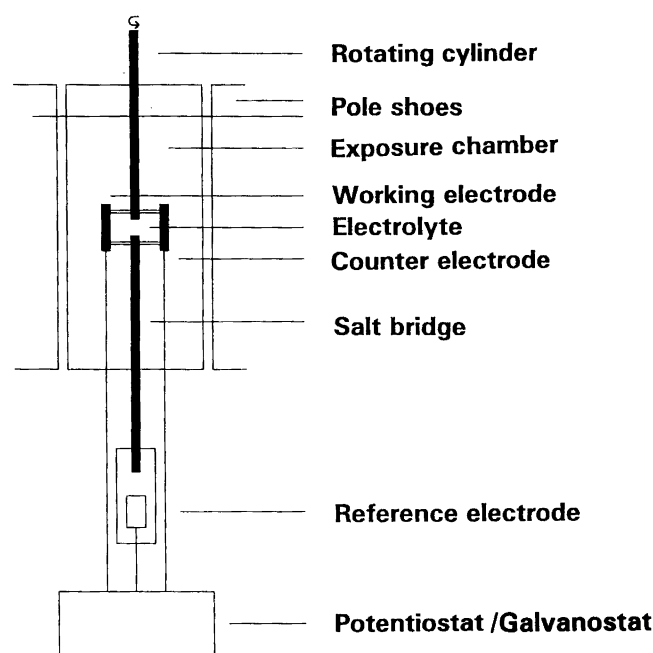


Fig. 1. The experimental setup.

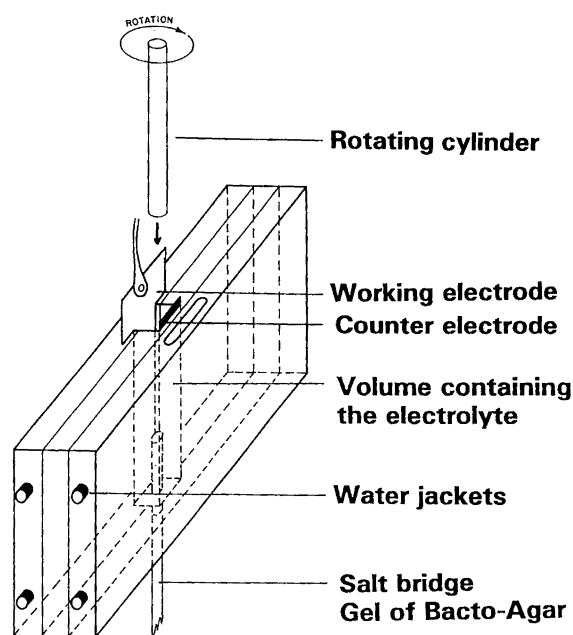


Fig. 2. The exposure chamber.

the exposure volume containing the electrolytic solution were $1 \times 1 \times 4 \text{ cm}^3$.

The working electrodes used in the exposure chamber were made of iron (St 12-03 DIN 1623) which is ferromagnetic, and stainless steel, which is paramagnetic.²³ The electrodes were rectangular and with an area of $1 \times 4 \text{ cm}^2$ and a thickness of 0.7 mm. The counter electrode was made of stainless steel with an area of $1 \times 4 \text{ cm}^2$. Both the electrodes were put vertically in the exposure chamber and placed perpendicular to the field in the middle of the magnetic gap. The magnetic flux density was measured to be homogeneous all over the electrode within an accuracy of 1 mT. To tighten, a gascheck ring of rubber was put around the electrode.

The reference electrode (a standard calomel electrode) was placed into a solution in a chamber outside the magnetic field, as indicated in Fig. 1. The solution was the same and with the same concentration that was used in the exposure chamber. Between the exposure chamber and the reference chamber, there was a saltbridge which consisted of a tube containing a gel of agar and potassium nitrate. The distance between the two chambers was 30 cm.

The working electrode, the counter electrode and the reference electrode were connected to the potentiostat/galvanostat (Wenking MP87) in conjunction with two digital multimeters (Fluke 87). The application of the current between the counter electrode and the working electrode leads to an electric potential difference between the working electrode and the reference electrode and the occurrences of electrode reactions. The currents were introduced by the potentiostat/galvanostat which was switched into the galvanostatic mode. The currents and the corresponding electrode potentials were measured by multimeters.

The electrolytes used were iron(III) chloride, iron(II) chloride and distilled water. The paramagnetic iron(II) chloride and iron(III) chloride solutions were prepared from the respective crystals with freshly distilled water. The 1 M iron(III) chloride solution was measured to have pH 0.3. Both the electrolytes have paramagnetic properties.²³

To reduce concentration variations, the electrolytic solution was stirred by a rotating cylinder. The cylinder was mounted vertically into the solution in the exposure chamber, and was parallel to both the working electrode and the counter electrode, as indicated in Fig. 2. The solution covered 3.5 cm of the cylinder. The rotating cylinder, which was made of glass with a diameter of 0.6 cm, was driven by a drill (Ika-Werk, RW 20). A rotating cylinder of the non-magnetic and non-conducting material glass was used to avoid additional induced currents.

The temperature of the electrolytic solution was measured by a thermocouple thermometer (Fluke 52).

Procedure. For each experiment the following preparation procedure was carried out. New working electrodes and the counter electrode were washed in a solution made of hydrochloric acid and containing ions of antimony and tin before using them in the experiments. The exposure chamber was taken apart, the electrodes were removed and the chamber was cleaned by distilled water and then dried. A new working electrode and the counter electrode were put in place and the exposure chamber was put together. The exposure chamber was placed in the magnetic gap. A fresh solution of electrolyte (3 ml) was then filled into the exposure chamber. The measurements started 3 min after the exposure chamber was filled with electrolyte. After the end of each experiment the whole preparing procedure was done over again.

To obtain the relationship between the polarization (η) and the electrode current, the following procedure was carried out. Initially, the galvanostat was adjusted in such a way that the electrode current was equal 0.5 mA. The applied current was then stepped by certain intervals in anodic and cathodic directions, and the corresponding electrode potentials were measured. The results were plotted in $\log I/E$ diagrams.

The current was measured as a function of the applied potential, at a fixed rotation speed (120 r.p.m.) and magnetic flux density (0, 400 or 800 mT). The exposure schedule for each applied potential difference was 0, 800, 0 mT. The time elapsed at each magnetic flux density was 1 min. The current without exposure to magnetic field was found by linear interpolation, i.e. the measured currents before and after exposure to magnetic field were summarized and divided by two. Experiments with distilled water were used to examine whether the measured effects of the magnetic field were due to possible induced currents in the electrode and the conductors, i.e. electromagnetic interference (EMI).

For all the experiments the temperature was $25 \pm 1.5^\circ\text{C}$.

Results and discussion

Figure 3 shows the anodic and cathodic polarization curves with and without a 800 mT magnetic field for two different working electrodes. The electrolyte was 1 M iron(III) chloride.

Figure 4 shows the anodic and cathodic polarization curves with and without a 400 mT magnetic field for two different working electrodes. The electrolyte was 1 M iron(III) chloride.

Figure 5 shows the anodic and cathodic polarization curves with and without a 800 mT magnetic field for two different working electrodes. The electrolyte was 0.5 M iron(III) chloride.

The results obtained from all experiments show an increase in the electrode potential due to the magnetic field. This holds for applied current densities up to 20 mA cm^{-2} . Also, it was observed that the effect depends on both the magnetic flux density and the concentration of the solution. According to the anodic polarization, the effect was observed within the pre-passive region of the iron electrode.^{13,24,25} According to the cathodic polarization, also, the results indicate that the magnetic field causes an increase in the limiting current density, or corrosion current density. According to this, the experimental results indicate that the magnetic field causes an increase in the reaction rates in both the

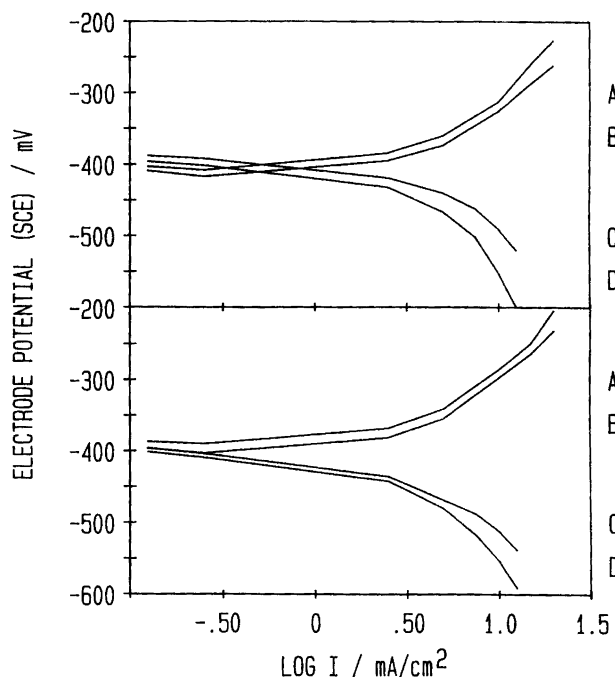


Fig. 3. The measured anodic and cathodic polarization curves for two different working electrodes with (A and C) and without (B and D) exposure to a 800 mT magnetic field. The working electrodes were made of iron, the electrolyte was 1 M iron(III) chloride, and the stirring rate was 120 r.p.m.

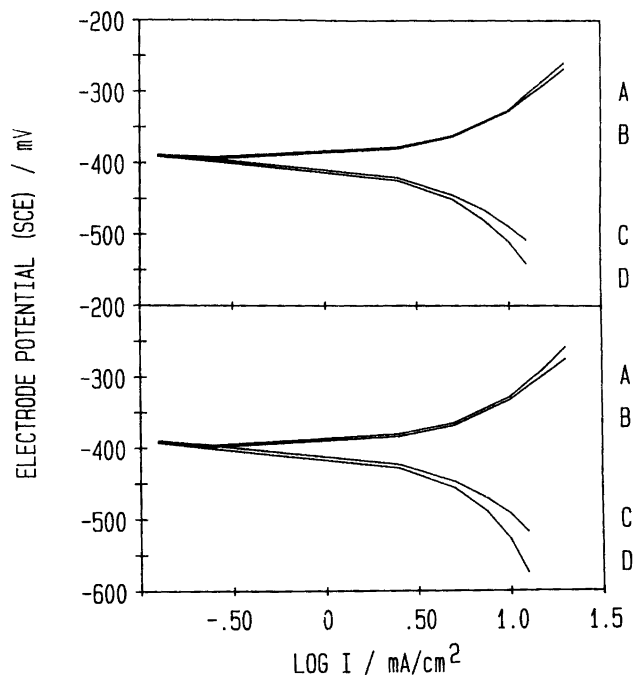


Fig. 4. The measured anodic and cathodic polarization curves for two different working electrodes with (A and C) and without (B and D) exposure to a 400 mT magnetic field. The working electrodes were made of iron, the electrolyte was 1 M iron(III) chloride, and the stirring rate was 120 r.p.m.

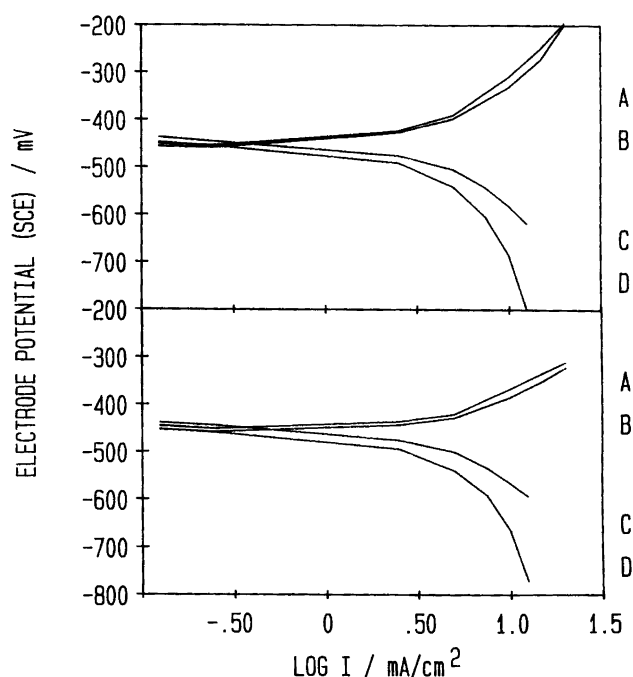


Fig. 5. The measured anodic and cathodic polarization curves for two different working electrodes with (A and C) and without (B and D) exposure to a 800 mT magnetic field. The working electrodes were made of iron, the electrolyte was 0.5 M iron(III) chloride, and the stirring rate was 120 r.p.m.

metal dissolution [eqn. (1)] and the ferric ion reduction [eqn. (4)].

Results from experiments using stainless steel as working electrode and 1 M iron(III) chloride, and from experiments using iron as working electrode and 1 M iron(II) chloride, showed no significant effect of the magnetic field on the electrode current.

Concerning possible induction effects, three phenomena were studied. In worst case, it is supposed that the induced currents flow through the working electrode. The induced current density (I_s) due to stirring rate is calculated by eqn. (11). Suppose $\omega = 2$ rps (120 r.p.m.), $B = 0.8$ T, $\sigma = 4.7$ S m⁻¹ (measured) and $r = 0.0113$ m (radius in an equivalent electrode area), $I_s \approx 0.6$ μ A cm⁻². The induced current density (I_t) due to turning the magnetic field on or off, is calculated from eqn. (12). The magnetic flux density increased from 0 to 0.8 T during 5 s. In the worst case, $dB/dt = 0.16$ T s⁻¹, $\sigma = 4.7$ S m⁻¹ (measured), $l = 0.1$ m (the circumference of the electrode), $I_t \approx 7.5$ μ A cm⁻². Comparing these calculations with the experimental obtained results, it is shown that the calculated results are much lower than the experimental results. Results from experiments using distilled water as an electrolyte showed no effect of the magnetic field.

According to this, the obtained effects of the magnetic fields are not a result of external electromagnetic interference, and cannot be explained in terms of electromagnetic induction, i.e. magnetohydrodynamics.

Acknowledgement. I thank Prof. Tor Hurlen at the University of Oslo, Norway, and Assoc. Prof. Per Heggelund at Telemark Institute of Technology, Porsgrunn, Norway for helpful discussions and advice. Also, I thank Inger C. Friestad, Torstein Ingvaldsen, Thomas L. Jensen, Monia Rønningen, Kai N. Sjølyst and Linda Syversen, all students at Telemark Institute of Technology, for help with the experiments.

References

1. Waskaas, M. *Acta Chem. Scand.* 50 (1995) In press.
2. Mohanta, S. and Fahidy, T. Z. *Can. J. Chem. Eng.* 50 (1972) 248.
3. Fahidy, T. Z. *Electrochim. Acta* 18 (1973) 607.
4. Fahidy, T. Z. *Chem. Eng. J.* 7 (1974) 21.
5. Fahidy, T. Z. *J. Appl. Electrochem.* 13 (1983) 553.
6. Aogaki, R., Fueki, K. and Mukaibo, T. *Denki Kag.* 9 (1975) 504.
7. Aogaki, R., Fueki, K. and Mukaibo, T. *Denki Kag.* 9 (1975) 509.
8. Takahashi, F., Sakai, Y. and Tamura, T. *Electrochim. Acta* 28 (1983) 1147.
9. Mori, S., Satoh, K. and Tanimoto, A. *Electrochimica Acta* 39 (1994) 2789.
10. Kelly, E. J. *J. Electrochem. Soc.* 124 (1977) 987.
11. Iwakura, C., Kitayama, M., Edamoto, T. and Tamura, H. *Chem. Lett.* (1984) 809.
12. Yamanaka, S., Aogaki, R., Yamato, M., Ito, E. and Mogi, I. *Sci. Rep. Res. Inst., Tohoku Univ., Sendai, Ser. A* 38 (1993) 399.
13. Fontana, M. G. and Greene, N. D. *Corrosion Engineering*, McGraw-Hill, New York, 1978, pp. 7–27 and 313–319.
14. Vetter, K. J. *Electrochemical Kinetics*, Academic Press, New York 1967, pp. 10–230 and 732–734.
15. Koryta, J., Dvorák, J. and Kavan, L. *Principles of Electrochemistry*, Wiley, Chichester 1993, pp. 381–384.
16. Wranglén, G. *Metallens Korrosion och Ytskydd* (Corrosion and Surface Protection of Metals), Almqvist & Wiksell, Stockholm 1967, pp. 84–87. *In Swedish.*
17. Bard, A. J. and Faulkner, L. R. *Electrochemical Methods*, Wiley, New York 1980, pp. 1–53.
18. Delahay, P. *New Instrumental Methods in Electrochemistry*, Interscience Publishers, New York 1954, pp. 219–229.
19. Bockris, J. O. M., Bonciocat, N. and Gutmann, F. *An Introduction to Electrochemical Science*, Wykeham Publications, London 1974, pp. 53–74.
20. Shercliff, J. A. *A Textbook of Magnetohydrodynamics*, Pergamon Press, Oxford 1965, pp. 31–59.
21. Reitz, J. R. and Milford, F. J. *Foundations of Electromagnetic Theory*, Addison-Wesley, Reading, MA 1962, pp. 182–243.
22. Sheppard, A.R. and Eisenbud, M. *Biological Effects of Electric and Magnetic Fields of Extremely Low Frequency*, New York University Press, New York 1977, pp. 4–20.
23. Weast, R. C., Ed., *CRC Handbook of Chemistry and Physics*, 68th edn., CRC Press, Boca Raton, FL, 1988.
24. Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, Oxford 1966, pp. 307–321.
25. Hurlen, T. *Kjemi* 9 (1980) 28. (*In Norwegian.*)

Received September 18, 1995.