Influence of a Magnetic Field on the Electrochemical Rest Potential

F. M. F. Rhen, a,* Dámaris Fernandez, a,b G. Hinds, a and J. M. D. Coey a

aDepartment of Physics, Trinity College, Dublin 2, Ireland
bFacultad de Química y Biología, USACH, Santiago, Chile

The influence of an external magnetic field on the rest potential $E_0$ of ferromagnetic and nonferromagnetic electrodes is studied. The shift $\Delta E_0$ is measured as a function of magnetic field magnitude and direction, pH, electrolyte composition, solution agitation, and electrode roughness. Anodic shifts can be observed not only for ferromagnetic electrodes (iron, cobalt, nickel), but also for nonmagnetic electrodes (zinc, manganese). The essential condition to observe the shift is that the electrode should be actively corroding. An anodic shift is observed when the cathodic corrosion current is mass-transport limited. The primary mechanism for the effect is agitation of the electrolyte near the electrode surface due to Lorentz force acting on the corrosion currents directly, or via the electrokinetic effect. A smaller influence of magnetic field gradient produced by ferromagnetic electrodes is identified.

© 2005 The Electrochemical Society. [DOI: 10.1149/1.2135207] All rights reserved.

It has been known for well over 100 years that the electrochemical rest potential $E_0$ of an iron electrode appears to be modified by a magnetic field $B$.1 Only lately has the phenomenon been re-examined with a view to explaining how the shift in rest potential $\Delta E_0(B)$ can come about.2–8 The direct effect of a magnetic field on the chemical potential of ferromagnetic iron is expected to be small, amounting to only about 0.1 mV per tesla, whereas the observed shifts can be as high as 50 mV per tesla. Different investigators have proposed quite different origins of the effect.

All are agreed that the shift in rest potential for iron is anodic; the potential moves toward more positive values when the field is applied. Waskaas and Kharkats2-4 reported anodic shifts for iron in a variety of different electrolytes. The largest shift in 0.8 T was 45 mV.

Dass et al. also favored an explanation in terms of magnetic-field-driven mass transport.10 In view of these disagreements regarding the origin of the effect, we have undertaken a systematic investigation, varying the electrolyte, the pH, the ionic strength, the dissolved oxygen concentration, the electrode roughness and rotation speed, and the direction and magnitude of the applied field from 0 to 5.5 T. We also include some results on electrodes other than iron, which are crucial for a proper understanding of the nature of the shift.

The paper is in five parts. After this introduction there follows a brief discussion of experimental methods. Then the main experimental results for iron are set out. These results beg a series of questions:

1. Does the electrode have to be ferromagnetic?
2. Does it have to be corroding, and, if so, must the corrosion be under mass-transport control?
3. What magnetic force (s) influence (s) the mass transport, and how do they act?

These questions are answered in the light of further experimental results presented in the discussion section, and finally the conclusions are drawn. A preliminary account of some of the results on a zinc electrode was published recently.11

Experimental

Most of the measurements were carried out in a standard three-electrode electrochemical cell using a Solartron SI 1280B potentiostat, but in some cases the potential difference between the working and reference electrodes was measured with a Keithley 195 digital voltmeter. The working electrode was normally iron, the reference electrode was Ag/AgCl or Hg/HgSO4, and the counter electrode when one was required for polarization experiments was Pt. The cylindrical cell of volume 50 mL was 4-cm-diam for 6-cm length; it could be placed between the poles of a 300-mm electromagnet with a 60-mm gap which produced a uniform field (<1 part in 103 inhomogeneity over the cell) of up to 1.5 T, or in the 105-mm room-temperature bore of a superconducting magnet which produced a uniform field (<1 part in 103) of up to 5.5 T. The pH of the solution was adjusted when necessary by the addition of an appropriate acid–HNO3 for nitrate solutions and H2SO4 for sulfate-based
solutions without any supporting electrolyte. Deaerated solutions were prepared by flowing Ar gas through the solution for 30 min, and during the experiments a flow of Ar was kept above the solution in such a way as not to interfere with the bulk solution. The leads to the cell were twisted pairs arranged to minimize induced potentials due to time-varying magnetic fields. The field orientation was horizontal in the electromagnet and vertical in the superconducting magnet. The working electrode, typically 5 mm, could be mounted in either orientation. Some experiments used a rotating disk electrode of 6-mm diam, or an electrode of 1-mm diam, which could be retracted by 8 mm within a Teflon shield in order to limit convection. For precise measurements of small shifts in potential, the applied field was modulated at a frequency of 0.2 Hz and the voltage was sensed using lock-in detection. In the following section, all shifts of the rest potential are for a field of 1.5 T, unless stated otherwise.

Table I. Rest potential shift \( \Delta E_0 \) measured for iron in 1.5 T in various solutions. The magnetic field was applied parallel to the electrode surface.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration (M)</th>
<th>pH</th>
<th>( \Delta E_0 ) (mV)</th>
<th>( \Delta E_0 ) (Ar-saturated)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(NO₃)₃</td>
<td>1</td>
<td>1</td>
<td>35</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>FeSO₄</td>
<td>1</td>
<td>1</td>
<td>10</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>FeCl₃</td>
<td>1</td>
<td>0.1</td>
<td>12</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0.1</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>KNO₃</td>
<td>1</td>
<td>1</td>
<td>25</td>
<td>21</td>
<td>Smooth electrodes</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1</td>
<td>32</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0</td>
<td>126</td>
<td>120</td>
<td>Smooth and rough electrodes</td>
</tr>
<tr>
<td></td>
<td>1 and 3</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>Smooth and rough electrodes</td>
</tr>
</tbody>
</table>

Results

Figure 1 shows a typical result for iron where the rest potential is measured as the field is switched on and off. Apart from the anodic shift, \( \Delta E_0 \), it should be noted:

1. There is an underlying cathodic drift of order of 0.02 mV s\(^{-1}\).
2. The magnitude of \( \Delta E_0 \) depends on the orientation of the 1.5-T field relative to the electrode; when this is changed from parallel to perpendicular to the electrode surface for the vertical electrode in the electromagnet, there is a decrease of \( \Delta E_0 \) from 35 to 23 mV (Fig. 1b).
3. While the response on switching the field on is practically instantaneous, a relaxation process with a characteristic time of order 20 s is evident when the field is switched off, especially in the parallel configuration. The time required to bring the field up to 1.5 T or to reduce it to zero is 10 s.

Table 1 summarizes the shifts measured in different conditions with the field applied parallel to the surface of the iron electrode (B₁ configuration). \( \Delta E_0 \) ranges from zero up to 120 mV. In view of the uncertainties in the on/off measurement, values are quoted to the nearest millivolt. All shifts are anodic. The shifts in aerated and deaerated electrolytes are compared.

Figure 2 illustrates the effect of changing the pH of a deoxygenated KNO₃ electrolyte. The data show that large effects occur only when pH is low. They suggest that paramagnetic ions in the electrolyte may not be necessary for the observation of the effect. The iron electrode is strongly corroding when the pH is less than 3, in accordance with the following reactions

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \tag{2a}
\]
\[2\text{NO}_3^- + 4\text{H}^+ + 2\text{e}^- \rightarrow 2\text{NO}_2 + 2\text{H}_2\text{O} \quad [2b]\]

Comparison of \(\Delta E_0\) for aerated and deaerated electrolytes shows a systematically lower shift when the electrolyte is deaerated by saturation with argon. For example, no shift at all is observed in deaerated 0.1 M H₂SO₄ (pH 1), whereas the shift in the aerated acid is 2 mV.

In some cases, the rest potential shift was found to decay with time with the buildup of corrosion products on the electrode surface. In the example shown in Fig. 3, the effect of the field has almost disappeared after 1000 s.

An anodic shift \(\Delta E_0\) comparable in magnitude to that obtained in the magnetic field can be obtained by rotating the electrode or stirring the electrolyte. Figure 4 shows \(\Delta E_0\) as a function of rotation rate for a 6-mm-diam iron rotating disk electrode in the absence of any applied magnetic field. In 1 M KNO₃ at pH 1, the shift approaches saturation of 90 mV above 1000 rpm. It is noteworthy that the field and rotation effects are not additive. For example, applying a field of 1.5 T when the electrode is rotating at 1000 rpm contributes an additional shift of less than a millivolt. The shift in 1.5 T is equal to that produced by rotation at 52 rpm. The rotation establishes conditions of forced convection, which enhance mass transport to the electrode surface. Experiments to distinguish radial and axial convection were also carried out where the electrode is shielded from large-scale convection using an insulating polymer sheath [poly(tetrafluoroethylene) (PTFE)]. In one case, the surface of a 1-mm-diam iron wire was flush with the polymer surface, thereby allowing radial convection to take place. To impose an axial convection the wire was retracted 8 mm below the surface of the polymer, creating a channel of 1-mm diam. Observed anodic shifts in 1 M KNO₃ at pH 0.5 were about the same for both experiments (95 mV), suggesting the nature of the large-scale convective flow is unimportant.

Figure 5 illustrates the field dependence of the rest potential shift for KNO₃ solution in fields of up to 5.5 T, applied parallel to the electrode surface. The effect approaches saturation at high field in a way that is quite different to the magnetization itself. Finally, Fig. 6 shows the effect of the magnetic field on polarization curves for the electrode in KNO₃ (pH 1). There is a clear difference between the effect of the field in the active regions of the cathodic and anodic curves. While there is no effect on the anodic current in the active region, the cathodic current is enhanced by more than a factor of 2 in the field. In addition, the anodic polarization curve in the absence of magnetic field indicates a sharp drop in the current at 0.7 V which is associated with the formation of a passive layer. This threshold is shifted anodically by 0.8 V in a field of 1.5 T, as shown in Fig. 7.

Further evidence for the equivalence of stirring and applying a magnetic field on rest potential are the Tafel plots from linear sweep voltammetry for stagnant and stirred solutions, shown in Fig. 8. It is noteworthy that under the same electrochemical conditions, stirring provokes similar shifts in corrosion potentials as those produced by a magnetic field.

The field-induced shifts of rest potential have also been studied for a series of electrodes other than iron. These were chromium, manganese, cobalt, nickel, zinc, copper, and stainless steel. The
shifts for cobalt and nickel were anodic in 1 M nitrate solutions 0.8 and 0.7 mV, respectively. A large shift of 10 mV was found for cobalt in CoSO₄ solution. Those for magnetic and nonmagnetic stainless steel alloys, largely composed of iron but with significantly higher corrosion resistance, were less than 1 mV in conditions where pure iron gave a 35-mV shift. Data on cobalt and nickel are summarized in Table II. The results for the nonferromagnetic electrodes are discussed in the next section.

Discussion

Much of the data presented above points to a close link between the rest potential shift and corrosion. Iron is known to be particularly unstable in the concentrated Fe/H₂O₈NO₃/H₂O solution where the largest effects at pH 1 without any acid addition are observed, corroding at rates of the order a micrometer a minute. The sensitivity to pH, electrode roughness, dissolved oxygen concentration, and the absence of an effect for stainless steel, whether ferromagnetic or not, all point in the same direction.

Another feature that emerges from the data is the equivalence between the field effect and enhanced convection (Fig. 4). The dependence on magnetic field (Fig. 5) resembles that found for the enhancement of electrodeposition currents in the mass-transport-limited regime.⁹-¹¹

In order to better establish the link with corrosion, we have determined the corrosion current at the rest potential as a function of pH. This was measured by electroplating a smooth thin layer of iron onto a Cu electrode and then measuring the time taken for it to dissolve completely. Alternatively, the slope $R_p$, the polarization resistance of the $E-j$ curve was measured at $E_0$, and the corrosion current was derived from the Stern–Geary expression

$$j_{corr} = \frac{1}{R_p} \frac{a}{a + c} 2.303$$

where $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel slopes, respectively. The Stern–Geary coefficient $[(\beta_a + \beta_c)/2.303(\beta_a + \beta_c)]$ was estimated by weight loss measurements at low pH.

Figure 9 is a plot of $j_{corr}$ vs $\Delta E_0$. It shows data on iron, measured for a 1.5-T applied field parallel to the surface of the electrode in 1 M KNO₃ solution at different pH values, which are the same as those used in Fig. 2. The highest corrosion rate corresponds to pH 1, and the lowest correspond to pH 7. The trend of the data establishes the primary link between the field shift and the corrosion current.

Active corrosion occurs in electrodes where there is no passive layer. At low pH and in deoxygenated electrolytes, the anodic dissolution of iron

$$Fe \rightarrow Fe^{2+} + 2e^-$$

is balanced by a cathodic reaction such as

$$2H^+ + 2e^- \rightarrow H_2$$

or
be sensitive to field-induced convection, and the corrosion other activation-controlled, the mass-transport-limited current will However, if one of the reactions is mass-transport-limited and the cathodic or anodic reaction is more easily enhanced by the field. If both were equally sensitive there would probably be no shift. However, if one of the reactions is mass-transport-limited and the anodic dissolution reactions are usually kinetically controlled while cathodic reactions may be either kinetically or mass-transport-controlled. In the case of iron, Fig. 6 shows that the cathodic current arising from nitrate reduction (Eq. 5b) is mass-transport-controlled, while the anodic dissolution reaction is activation-controlled. This results in an anodic shift in rest potential in the presence of a magnetic field, as illustrated by the Evans diagram in Fig. 11.

Because the hydrogen-ion reduction (Eq. 5a) is not mass-transport-limited, the applied field cannot increase its rate. This is consistent with the observation that there is no shift at all for a deaerated water with pH 1 adjusted with H2SO4. The small shift in aerated acid solutions is explained by enhancement of the reduction of O2 in acid media (O2 + 4H+ + 4 e− → 2H2O), which is mass-transport-controlled. It is interesting to note that hydrogen or nitrate ions do not by themselves provoke a shift; there is no effect for H2SO4 (pH 1, argon-saturated) or for KNO3 at pH 7, but when the nitrate solution is acidified to pH 1 there is a large field-induced shift (Table I). Here the nitrate ions provide the mass-transport limitation, while the hydrogen ions are required for the nitrate-ion reduction (Eq. 5b).

The proposed mechanism is as follows: When pH is low enough, the measured rest potential corresponds to the free corrosion value, i.e., that potential obtained when an anodic/cathodic couple is established on the electrode. In stagnant conditions, potential and current are determined by the match of both reaction rates at certain value. The anodic dissolution of iron is followed by a buildup of corrosion products in front of the electrode. This, in stagnant conditions, reduces the ion transport from or toward the metal surface. When the magnetic field is applied, the buildup of corrosion products is affected in such way that mass transport is enhanced; hence, the corrosion current j0 increases and E0 is shifted toward more positive values. The decay of the effect over time, shown in Fig. 3, is related to the buildup of corrosion product on the electrode surface. This gradually modifies the mass-transport regime from convective diffusion in a fluid to diffusion through a porous barrier, which becomes increasingly unaffected by the field-induced flow. This is consistent with the slow underlying cathodic drift in rest potential, which reflects the reduced efficiency of the cathodic mass-transport process with time.

The fact that observed anodic shifts in 1 M KNO3 at pH 0.5 were about the same (95 mV) for both 8-mm retracted and nonretracted wire experiments using the PTFE sheath suggests that the magnetic-field-induced convection occurs near the electrode surface.

At this point in the discussion we turn to the first of the questions posed in the introduction; if the origin of the effect is related to corrosion, then the association with iron may be simply coincidental. It so happens that iron corrodes rapidly in Fe(NO3)3 and KNO3, and at low pH, but there may be no requirement for the electrode to be ferromagnetic. To settle the question “Does the electrode have to be ferromagnetic?” we have sought a field-induced shift in the rest potential of a nonferromagnetic corroding electrode. We observed no effect in open-circuit experiments for elements such as copper, which is more noble than iron, despite the fact that Shinohara and Aogaki reported a small anodic shift for Cu in nitrate solutions in the Evans diagram showing the effect of an applied magnetic field on the rest potential. An anodic shift is observed because only the cathodic reaction is sensitive to the applied magnetic field. Here, j0 and E0 stand for limiting current density and rest potential, respectively.

$2NO_3^- + 4H^+ + 2e^- \rightarrow 2NO_2 + 2H_2O$ \[5b\]

We have observed that all measured rest potentials for Fe fall within the range 0 to −0.4 V vs a saturated hydrogen reference electrode (SHE). It can be seen from the Pourbaix diagram of iron in water (Fig. 10) that these potentials are in the corrosion region in acidic solutions. The direction of the shift $\Delta E_0$ seems to depend on whether the cathodic or anodic reaction is more easily enhanced by the field. The proposed mechanism is as follows: When pH is low enough, the measured rest potential corresponds to the free corrosion value, i.e., that potential obtained when an anodic/cathodic couple is established on the electrode. In stagnant conditions, potential and current are determined by the match of both reaction rates at certain value. The anodic dissolution of iron is followed by a buildup of corrosion products in front of the electrode. This, in stagnant conditions, reduces the ion transport from or toward the metal surface. When the magnetic field is applied, the buildup of corrosion products is affected in such way that mass transport is enhanced; hence, the corrosion current $j_0$ increases and $E_0$ is shifted toward more positive values. The decay of the effect over time, shown in Fig. 3, is related to the buildup of corrosion product on the electrode surface. This gradually modifies the mass-transport regime from convective diffusion in a fluid to diffusion through a porous barrier, which becomes increasingly unaffected by the field-induced flow. This is consistent with the slow underlying cathodic drift in rest potential, which reflects the reduced efficiency of the cathodic mass-transport process with time.

Figure 10. Pourbaix diagram for iron in water.

Figure 11. Evans diagram showing the effect of an applied magnetic field on the rest potential. An anodic shift is observed because only the cathodic reaction is sensitive to the applied magnetic field. Here, $j_0$ and $E_0$ stand for limiting current density and rest potential, respectively.

$2NO_3^- + 4H^+ + 2e^- \rightarrow 2NO_2 + 2H_2O$ \[5b\]

We have observed that all measured rest potentials for Fe fall within the range 0 to −0.4 V vs a saturated hydrogen reference electrode (SHE). It can be seen from the Pourbaix diagram of iron in water (Fig. 10) that these potentials are in the corrosion region in acidic solutions. The direction of the shift $\Delta E_0$ seems to depend on whether the cathodic or anodic reaction is more easily enhanced by the field. The proposed mechanism is as follows: When pH is low enough, the measured rest potential corresponds to the free corrosion value, i.e., that potential obtained when an anodic/cathodic couple is established on the electrode. In stagnant conditions, potential and current are determined by the match of both reaction rates at certain value. The anodic dissolution of iron is followed by a buildup of corrosion products in front of the electrode. This, in stagnant conditions, reduces the ion transport from or toward the metal surface. When the magnetic field is applied, the buildup of corrosion products is affected in such way that mass transport is enhanced; hence, the corrosion current $j_0$ increases and $E_0$ is shifted toward more positive values. The decay of the effect over time, shown in Fig. 3, is related to the buildup of corrosion product on the electrode surface. This gradually modifies the mass-transport regime from convective diffusion in a fluid to diffusion through a porous barrier, which becomes increasingly unaffected by the field-induced flow. This is consistent with the slow underlying cathodic drift in rest potential, which reflects the reduced efficiency of the cathodic mass-transport process with time.

The fact that observed anodic shifts in 1 M KNO3 at pH 0.5 were about the same (95 mV) for both 8-mm retracted and nonretracted wire experiments using the PTFE sheath suggests that the magnetic-field-induced convection occurs near the electrode surface.

At this point in the discussion we turn to the first of the questions posed in the introduction; if the origin of the effect is related to corrosion, then the association with iron may be simply coincidental. It so happens that iron corrodes rapidly in Fe(NO3)3 and KNO3, and at low pH, but there may be no requirement for the electrode to be ferromagnetic. To settle the question “Does the electrode have to be ferromagnetic?” we have sought a field-induced shift in the rest potential of a nonferromagnetic corroding electrode. We observed no effect in open-circuit experiments for elements such as copper, which is more noble than iron, despite the fact that Shinohara and Aogaki reported a small anodic shift for Cu in nitrate solutions in Tafel plots with and without field. Hence, we chose zinc and manganese, which are less noble than iron and corrode easily in an acid environment. The standard reduction potential for the reaction $M^{2+} + 2e^−$ is −0.76 V for Zn, −1.03 V for Mn, and −0.43 V for Fe. We find no shift for Zn in ZnSO4 nor in H2SO4, but there is a shift of 4–5 mV for Zn in KNO3 acidified to pH 1. Corrosion of zinc both in ZnSO4 and in H2SO4, which is associated with Reaction 5a is not mass-transport-limited. However, the corrosion in acidified
KNO₃ is mass-transport-limited (5b), hence, the observed field effects for both Zn and Mn (Table III). The field dependence, shown in Fig. 12, can be fitted to $B^{0.8}$ up to the highest fields, as the shift is monotonically increasing in 5 T. Rotating disk electrode measurements indicate that the shift can be as large as 100 mV for a rotation rate of 10,000 rpm.⁶¹ Furthermore, we find a large shift $\Delta E_0 = 42$ mV for Zn in 16 mM CuSO₄ at 1.5 T. In copper sulfate, there is a mass-transport-limited cathodic corrosion current as Cu displaces Zn according to the following reaction: $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$.

These results establish that a ferromagnetic electrode is not essential for the observation of the effect. What is important is that the electrode should be actively corroding and the corrosion should be mass-transport-limited. This conclusion is reinforced by the observations on other nonmagnetic electrodes, summarized in Table III. A shift is observed for manganese and zinc electrodes but not for Al and Cr, which are protected by a passive layer, or for nonmagnetic stainless steel. No shift is observed in the rest potential of copper because the rest potential of copper lies in the region in which the cathodic reaction is not mass-transport-limited.

We now consider how the field acts to increase the cathodic corrosion current. It is convenient to discuss this in terms of the forces acting on the electrolyte in the presence of a magnetic field, mentioned in the introduction. Magnetic field effects on electrodeposition have been discussed by Varma and Selman⁶² and by Fahidy.¹⁷ The concentration gradient force $F_{\text{c}}$ is discounted for the following reasons: diffusion in a concentration gradient is driven by an entropic force $F_{\text{d}} = -RT \nabla c$, which is in the opposite direction to $F_{\text{c}}$, but is over 5 orders of magnitude greater at room temperature; the ratio $F_{\text{d}}/F_{\text{c}} = 2\mu_0RT/\rho B^2$ is $\approx 2.7 \times 10^5$ for a field of 1.5 T and a typical molar susceptibility of $10^{-8}$ m³ mol⁻¹. The concentration gradient force cannot therefore be expected to exercise any appreciable influence on the convection. Furthermore, the results for zinc in KNO₃ demonstrate that it is possible to observe a shift in a system that contains no magnetic cations. The field gradient force is also ruled out as a primary factor by the observations on zinc, which show that a field-induced shift of rest potential can be observed for nonmagnetic electrodes provided they corrode under mass-transport control. The applied field was deliberately arranged to be highly uniform over the cell, so that any field gradients appear only in the vicinity of the edges or rough surfaces of ferromagnetic electrodes.

That leaves the Lorentz force, $F_L$, which is known to induce MHD flow, thereby enhancing the currents during electroplating,¹⁸,¹⁹ or more generally, in a mass-transport-limited regime. Much of the phenomenology at the rest potential is similar to that found for electroplating in a field.¹⁹ Although no net current flows at the rest potential, and hence the net force $F_L = j \times B$ should be zero, the effects on the balancing cathodic and anodic currents are different as shown in Fig. 11. Some sites on the electrode act as cathodes and other anodes allowing flux of current between them. An electronic current goes through the electrode and an ionic current flows from different anodic and cathodic sites on the electrode surface on a microscopic scale; therefore, it is possible to enhance vortex flow on a small scale near the electrode surface. This is the idea behind Aogaki's micro-MHD effect.⁵ We consider that small-scale MHD flow is the principal factor accelerating the mass-transport-limited cathodic reaction, which in turn produces the field-induced rest potential shift. The time for these flows to decay, according to Fig. 1, is of the order of 20 s. The surface potential differences also drive near-surface flow via electrokinetic effects, and the flow associated with these currents will also be modified by the magnetic field.⁶²

This is not to say that the field gradient force cannot play some role in the case of iron and other ferromagnetic electrodes. Roughening the electrode may increase the concentration of paramagnetic species Fe²⁺ and O₂ in its vicinity because of the large field gradients present. There are also field gradients near the edges and corners. In the first case, assuming sinusoidal roughness on a scale of 20 μm, for example, the field gradients $\nabla B$ are of the order $10^7$ T m⁻¹ and the forces $F_{LB}$ are of order $10^2$ N m⁻³. The forces near the edges, where $\nabla B \approx 10$ T m⁻¹ are 3 orders of magnitude smaller. The field gradients due to surface roughness are likely to modify the concentrations of paramagnetic species near the electrode, and hence the electrode potential, but this effect is difficult to disentangle from the straightforward increase in corrosion rate due to electrode roughening.

The increase in potential shift on changing from deaerated to aerated solution raises the possibility of a modest effect of the field gradient on paramagnetic O₂. Unlike NO₃⁻, oxygen is uncharged and therefore unaffected by Lorentz force, which would suggest that the field gradient force could be responsible for the small additional shift as in aerated solution.

### Conclusions

Our primary conclusion is that the field-induced shift of rest potential is associated with corrosion currents in the mass-transport-limited regime and does not depend in any essential way on the electrode being ferromagnetic. It is a coincidence that iron and the other ferromagnetic metals corrode easily. A consequence is that the effect is unlikely to provide a stable electrochemical method of sensing magnetic fields.

The corrosion must be active, and one of the corrosion currents should be mass-transport-limited in order to observe the effect. The field-induced shift can be taken as a signature of mass-transport limitation in corroding systems.

The primary mechanism of the shift is the MHD stirring provided by the Lorentz force. It is not clear on what scale this stirring takes place, but it acts to enhance the mass-transport-limited cathodic current, and the rest potential shifts in an anodic sense, thereby increasing the activation-controlled anodic dissolution current to match.

A modest effect of the field gradient force on paramagnetic O₂ is suggested by the reduction of the rest potential shift upon deaeration. However, it remains a challenge to distinguish field gradient and Lorentz force effects in such complex dynamic systems.
Acknowledgments

One of the authors (D.F.) was supported by CONICYT (Comisión Nacional de Investigación Científica y Tecnológica) Chile during a visit to Dublin. The work forms part of the CINSE project supported by the Science Foundation of Ireland. We are grateful to Alison J. Davenport for some helpful discussions.

Trinity College assisted in meeting the publication costs of this article.

References