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Effect of Oxalic Acid on the Dissolution of Magnetite Coupled with Iron of Various Surface Area

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The effect of galvanic coupling between magnetite and iron on their dissolution was investigated in aqueous solutions containing oxalic acid in the presence and absence of ferrous ion. Four different area ratios between iron to magnetite were studied: 1:1600, 1:400, 1:100 and 1:25 (marked as couple1 through couple 4 hereafter). The objective was to simulate the case of magnetite film partially removed from iron surfaces in the course of chemical cleaning when coupling conditions occur with variable area ratios with time. Measurements of the couple's potential (E_{couple}) and individual currents of magnetite (I_{mag}) and iron (I_{Fe}) (marked as mag1 through mag 4 and Fe1 through Fe4 hereafter) have revealed that as the iron area increases the dissolution of magnetite is accelerated, and the mixed potential for the couple shifts to more positive values; and become nearer to potential of magnetite electrode at same conditions. There was no pronounced effect of the added ferrous ions on the dissolution rate of magnetite. This can be attributed to the dissolution of iron metal in couples in the absence of added Fe^{2+}, which can be provided the solution by the ferrous ions.

Keywords: magnetite dissolution, galvanic couple, iron corrosion, oxalic acid

1. INTRODUCTION

Magnetite is the principle corrosion component of sludge, deposits and thick oxide build up on carbon steel components of boilers, heat exchangers and steam generators and on the primary side of heavy water reactors. [1-3]

The chemical dissolution of iron oxide deposits involves many processes that are designed to enhance the service life of steel industrial equipment. Deposit removal improves heat transfer and reduces pitting corrosion, and reduces the radiation field around nuclear power plants [1,2].

Several processes and formulations are being used to chemically clean the fouled steam generators [4]. Soft cleaning solutions consisting of a weak organic acid, a reducing acid and a complexing agent have been found to be advantageous due to their low corrosivity towards carbon steel and lesser post-cleaning complications compared to mineral acids [5].

Carboxylic acids are usually included in commercial solvents for the chemical cleaning and decontamination of metal surfaces from oxide layers [6].

Oxalic acid is a reagent of choice in many iron oxide solvent formulations [7], e.g. for chemical cleaning of residual sludge heels from high level waste tanks [8]. This is because of its excellent dissolving attack on iron oxides [6,9]. Furthermore, its subsequent removal is relatively easy, either by oxidative or photochemical mineralization to yield carbon dioxide [6].

When the metal surface is exposed to the solution, due to the presence of pores, cracks and other faults in the oxide layer or due to its reduced thickness, the corrosion reaction of the metal start to affect the oxide dissolution. In that case there is a possible galvanic coupling between the oxide and metal [1,3,10].

To simulate some particular situations encountered in the course of actual cleaning, galvanic coupling experiments were performed using spatially separated magnetite and iron coupons with different area. Some studies were suggested that the magnetite dissolve more rapidly when it coupled electrically with iron [5,11] or steel [2,12], because the ferrous ions results from iron acts as effective reducing convert the Fe^{3+} in oxide to Fe^{2+} . Lair et. al were evaluated the galvanic coupling of ferric corrosion products with iron in alkaline solution [13]. The present work is devoted to the study of the galvanic effect between magnetite and iron in solution close to that employed in decontamination process, in presence and absence of ferrous ions, in order to get an insight into its effect into the oxide dissolution. In previous work, we studied the effect of EDTA on the behavior of Fe-magnetite couples [14,15]. This object will focus on the effect of oxalic acid on the dissolution of Fe-magnetite couple .

2. EXPERIMENTAL PART

A magnetite crystal (eSCeTe single Crystal Technology, Enschede, The Netherlands) in the form of a small cylinder with a cross section area of 0.785 cm^2 was mounted in epoxy resin with four iron samples in the form of wires with exposed cross-sectional areas of 0.00049, 0.00196, 0.00785, and 0.0314 cm^2 ,respectively. Figure 1(a) depicts the arrangement of the working electrodes. The spacing between the magnetite and iron surfaces was 0.1 cm. The areas of the tested electrodes were chosen to give the following four area ratios: 1:1600, 1:400, 1:100 and 1:25 , which marked as couple1 through couple 4 hereafter.

The work was conducted at 40^{o}C in an aqueous solution containing 0.1M oxalic acid (HOOCCOOH) with and without ferrous ion. A high concentration of oxalic acid was used to avoid ambiguities caused by oxalic acid adsorption on magnetite at lower concentrations [7]. The solution pH was adjusted to pH 4.0 by adding drops of saturated NaOH solution. At this pH values, a complete ionization of oxalic acid occurred, and the hydro-oxalate species $HC_2O_4^-$ were predominant [7,8]. Ferrous ion were added as ferrous ammonium sulfate ($[NH_4]_2Fe[SO_4]_2$). Test solution was prepared with doubly distilled water and analytical grade reagents. Solution was degassed using high-purity nitrogen gas for 1 h before and during each experiment.

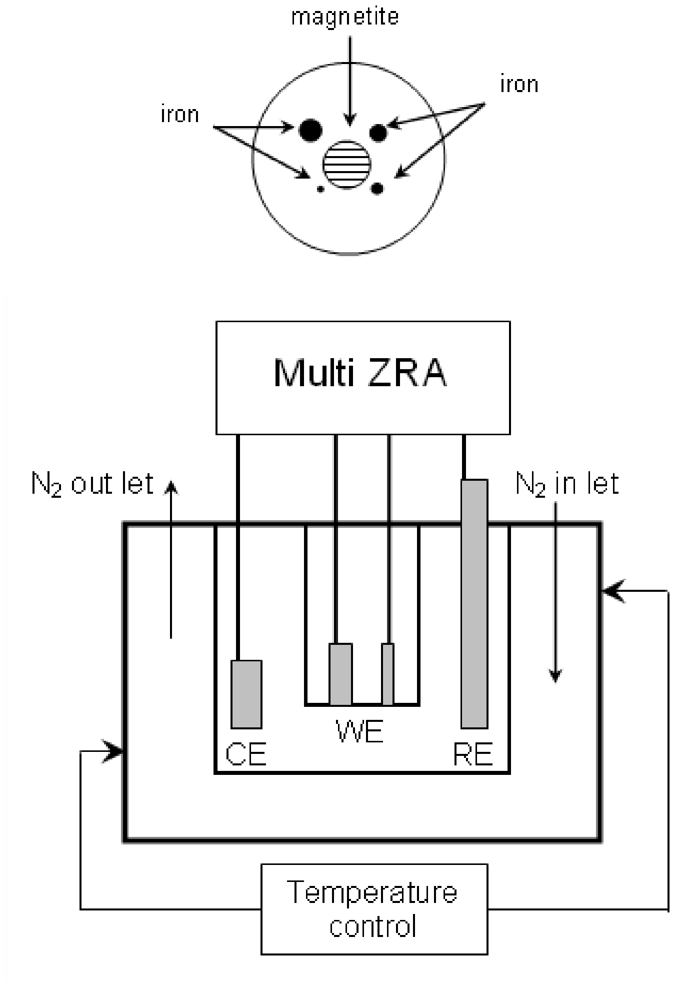

Figure 1. Arrangement of the magnetite and iron electrodes. The exposed cross-sectional area of magnetite was 0.785 cm^2 and 0.00049, 0.00196, 0.00785, 0.0314 cm^2 for the iron electrodes, respectively.

A multi-zero resistance ammeter (ZRA) was used for electrochemical tests (galvanic potential and current measurements, cyclic voltammetry).

The potential was measured against saturated calomel electrode (SCE), and all reported potentials were referred to this reference electrode. A large-area platinum electrode was used as the counter electrode. Before measurements were taken, the working electrode was polished with emery paper, and then washed thoroughly with doubly distilled water. Finally, the electrodes were cleaned ultrasonically for 10 min.

Electrochemical measurement were carried out by measuring the couple's potential (E_{couple}) and the individual currents of magnetite (I_{mag}) and iron (I_{Fe}) (marked as mag1 through mag 4 and Fe1 through Fe4 hereafter) in their respective couples and the potential of uncoupled magnetite and iron for comparison. Then, the cyclic voltammogram was measured by scanning the potential from –1200 mV to 500 mV. The scan rate was 20 mV/s. All tests were repeated twice.

3. RESULTS AND DISCUSSION

Fig. 2 represents the variation of E_{couple} and the individual currents of Fe and magnetite with immersion time in the absence of added ferrous ions. The immersion potential of the four couples had negative values. While the potential of each couples was shifted in the positive direction during the first minutes, the potential of magnetite was drifted to the negative direction, which probably a result of the reduction of surface Fe^{III} ions by the oxalate ions, which can be represented by the following reaction [16]:

$$Fe_3O_4 + 8HC_2O_4^- \rightarrow 2Fe^{III}(C_2O_4)_3^{3-} + Fe^{II}(C_2O_4)_2^{2-} + 4H_2O$$

This agrees with Blesa et al [7] observation, that the dissolution of magnetite is an autocatalytic process, the mechanism involving an interfacial electron transfer between ferrous-oxalate complexes and surface ferric ions; the main reaction does not involve the oxidation of oxalate.

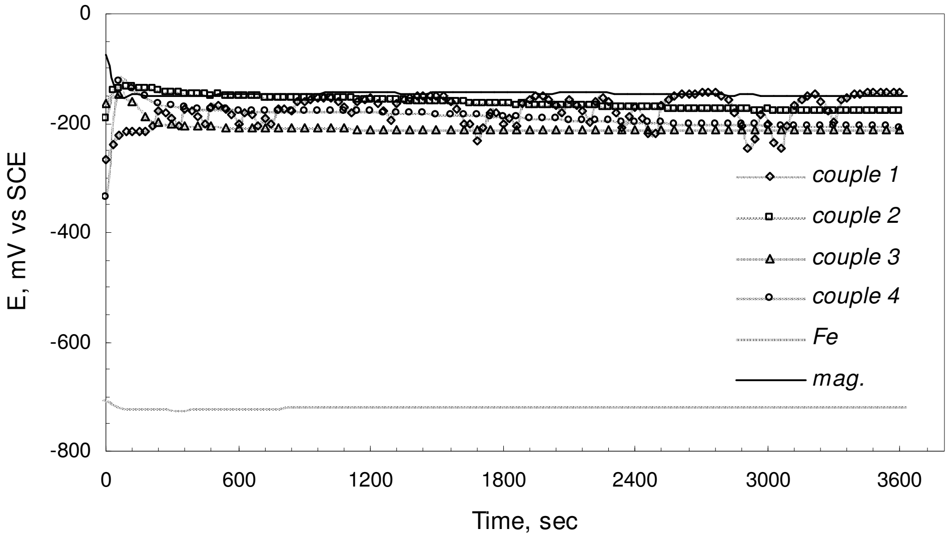

Figure 2. Variation of open circuit potential with time for magnetite and Iron with and without coupling in different area ratios in 0.1 M oxalic acid at pH 4.0 and 40°C

When iron was coupled with magnetite, it was subjected to a high anodic polarization. Several anodic reactions have been proposed, which can be occurred by themselves or simultaneously. Earlier references inferred from the tests results that the anodic reaction was simply corroding to form ferrous ion. However, the more recent tests indicate that the hydro-oxalate species also participates in the corrosion reaction as shown in Equation (3) along with the iron oxidation reaction in Equation (2) [8].

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (2)$$

$$Fe^0 + HC_2O_4^- \rightarrow FeC_2O_4 + H^+ + 2e^- \quad (3)$$

The complex formed is able to passivate the iron surface, as suggested by potential-pH plots for iron on the presence of oxalic acid reported by Saltykov [17]. Thus, the rate of the dissolution of magnetite – expressed as a current - will decrease when it coupled with iron comparison to the state without coupling.

Unless couple 1, the potential reached in a few minutes to a constant value located between those for magnetite and iron under the same conditions.

The constant potential of all couples were nearer to that of magnetite, and shifted slightly in the negative direction as Fe area in the couple increased. This agrees with Plonski results that revealed the couple potential always more negative from magnetite potential [1].

The current of magnetite has negative value on initial immersion, and moved in the positive direction during the first two minutes, as revealed in Fig. 3. Then, it was reached a constant value, which was increased as iron area in couple increased.

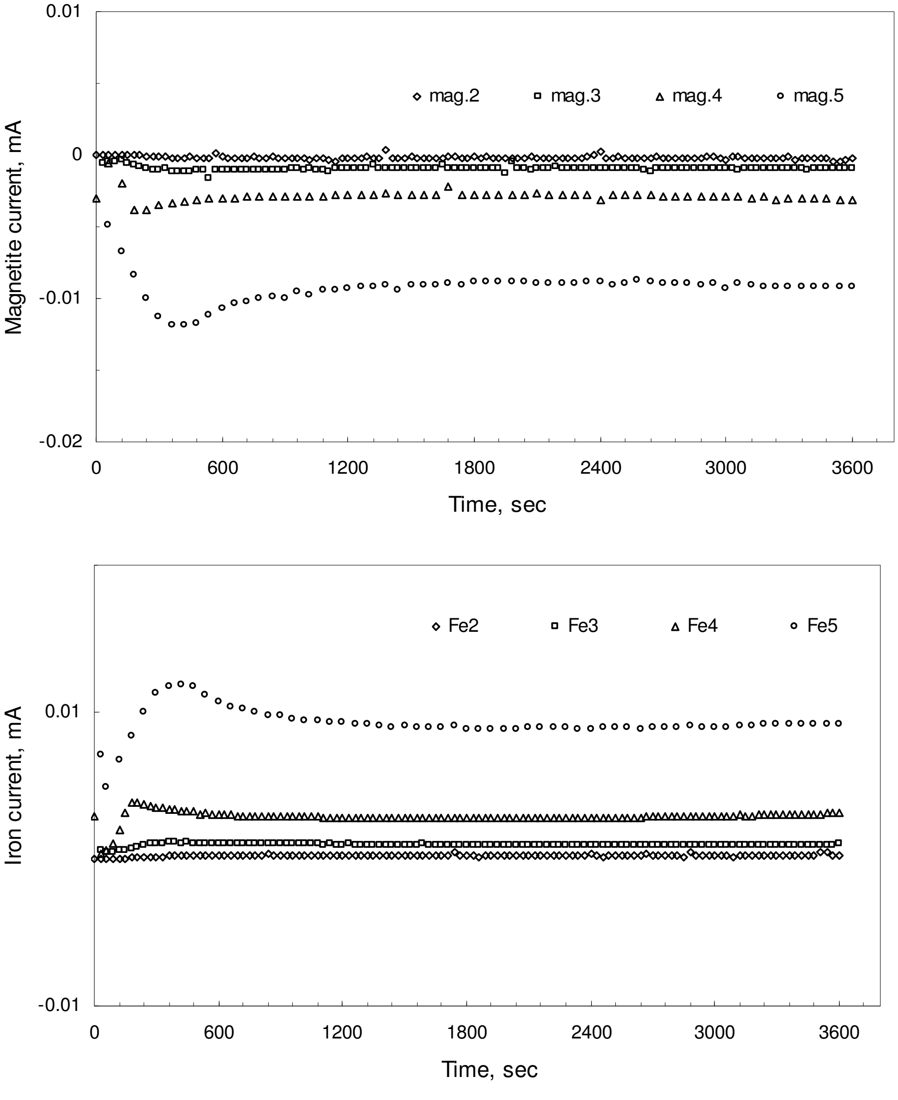

Figure 3. Variation of galvanic currents with time for magnetite and Iron with and without coupling in different area ratios in 0.1 M oxalic acid at pH 4.0 and 40°C

Cyclic voltammetry measurements of magnetite shown in Fig.4, presents a peak during the cathodic scan at potential between –340 ~ -360 mV, which is ascribed to the reductive dissolution of magnetite. The current associated with this peak decreased slightly when magnetite was coupled to iron, but it was affected by the iron area in the couple. A similar peak was observed during magnetite dissolution in other solutions [14,16]. Part of the current density after the peak was due to the hydrogen evolution reaction (HER) [10].

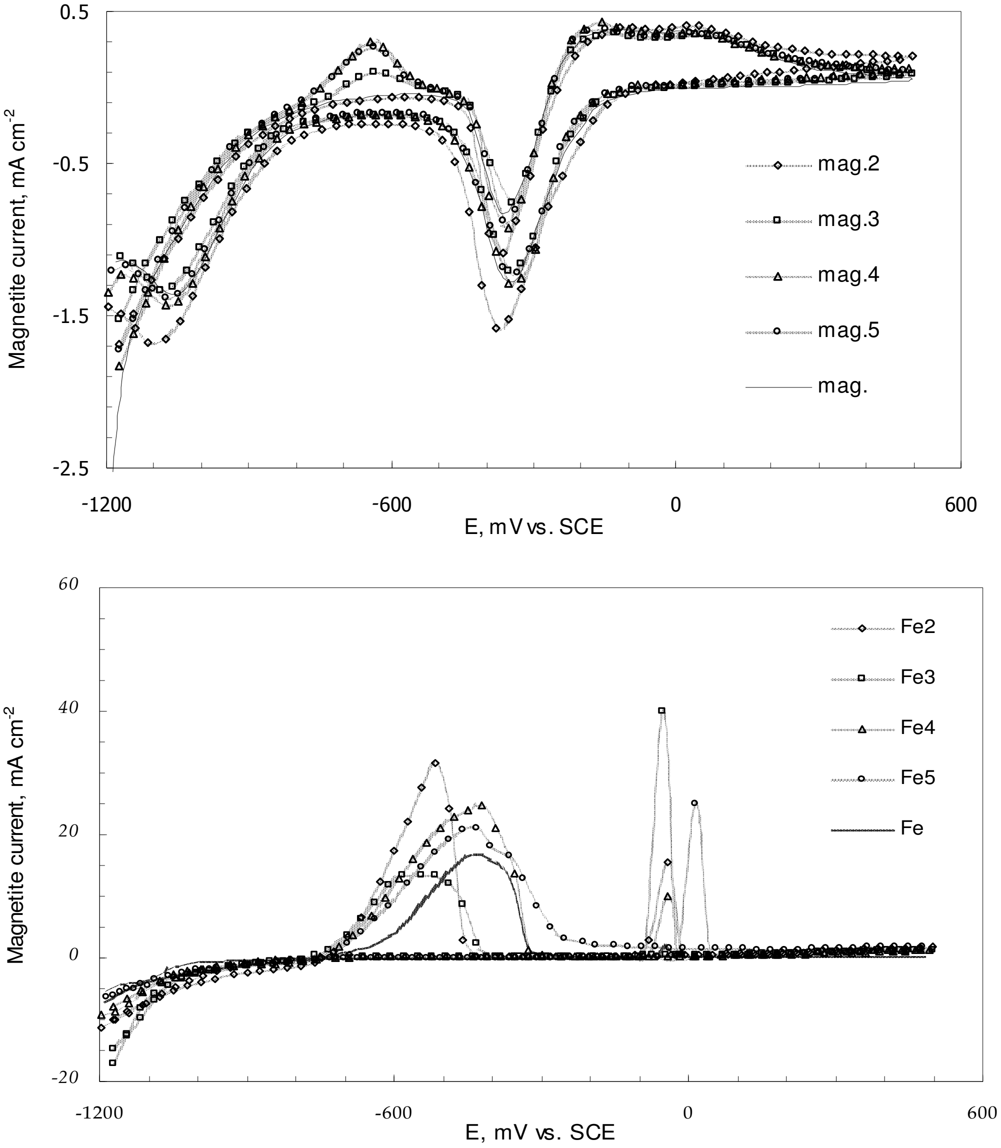

Figure 4. The Cyclic Voltammogram for magnetite and Iron galvanically coupled with different area ratios in 0.1 M oxalic acid solution at pH 4.0 and 40°C : (a) for magnetite (b) for iron

On another hand, a cathodic peak was observed in the anodic scan rather than anodic as would be expected in the reversible electron transfer processes. This behavior was observed by Heaton [18] who studied the magnetite dissolution in acidic media. Unusual for cyclic voltamogramms, this can be explained in terms of the potential dependent reversible passivation suggested by Allen et. al [19], which is also consistent with an explanation of the electron transfer part of the dissolution in terms of a surface process with a limited number of electron acceptors. This dissolution can be written as follow:

$$Fe^{3+}_{surf} + e^{-} \leftrightarrows Fe^{2+}_{surf} \tag{4}$$

No pronounced peak was observed during the cathodic scan on the cyclic voltamogram of iron, but there are two peaks in the anodic scan, which was reported in another work [8]. The first peak which was appeared at approximately -450 mV (SCE) has been interpreted to an indication of a direct oxidation of iron to ferrous ions. This peak shifted to more negative values in the couple 1 and couple 2. The current gradually decreased after this peak, which can be attributed to the passivation by ferrous oxalate precipitate. The second peak has been interpreted as the representing the oxidation of ferrous ion to ferric ion.

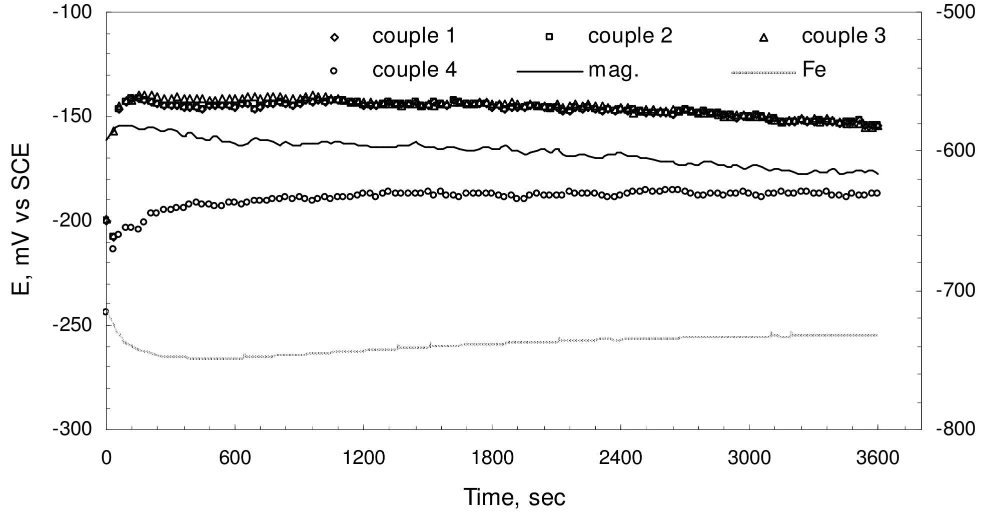

Figure 5. Variation of open circuit potential and galvanic currents with time for magnetite and Iron with and without coupling in different area ratios in 0.1 M oxalic acid + 0.0006 M Fe^{2+} at pH 4.0 and 40°C

The addition of 0.0006 M Fe^{2+} to the test solution resulted in different behavior of the galvanic couples potential with time depending on the iron area in the couple. As can be seen from Fig. 5, couple 1 had a potential that approached that of magnetite while the potential of couples 2 and 3 become more positive than magnetite, and the couple 5 shifted to more negative direction. On the other hand, when the concentrations of added ferrous ions increased to 0.006 M, the behavior of all couples were becomes like that of magnetite, as shown in Fig. 6. Table 1 shows the potential and currents after one hour, it was not revealed a pronounced difference between the values of the couple's potential for the two concentration of added ferrous ion.

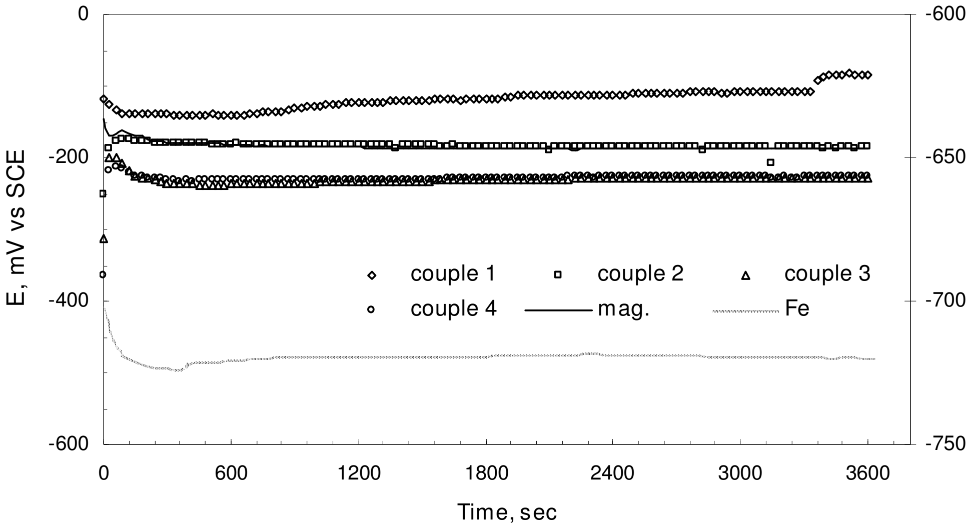

Figure 6. Variation of open circuit potential and galvanic currents with time for magnetite and Iron with and without coupling in different area ratios in 0.1 M oxalic acid + 0.003 M Fe^{2+} at pH 4.0 and 40°C

Table 1. Values of E_{couple} (mV vs. SCE) and I (mA) for magnetite and Iron and their galvanic couples in different area ratios after 1 hour immersion in 0.1 M oxalic acid solution containing different concentration of Fe^{2+} at pH 4.0 and 40°C .

$[Fe^{2+}]$ M	parameter	Galvanic couples				Single electrode	
		couple 1	couple 2	couple 3	couple 4	Fe	Mag.
0.0	E	-146	-178	-212	-206	-719	-150
	$I_{mag.}$	-3 E-4	-9 E-4	-0.003	-0.009	-	-
	I_{Fe}	3 E-4	9 E-4	0.003	0.009	-	-
0.0006	E	-122	-152	-153	-187	-176	-731
	$I_{mag.}$	-1 E-4	-6 E-4	-0.003	-0.008	-	-
	I_{Fe}	1 E-4	6 E-4	0.003	0.008	-	-
0.003	E	-143	-185	-186	-198	-763	-187
	$I_{mag.}$	-6 E-6	-2 E-5	-0.0003	-0.006	-	-
	I_{Fe}	6 E-6	1 E-5	0.0003	0.006	-	-

The cyclic voltammogram of magnetite has the same features in the absence of added ferrous ions, but with a small increase in the peak's current. But the peaks on the anodic scan of the voltamogramm of iron changed in the presence of ferrous ions and disappeared when $[Fe^{2+}]$ increased. Table 2 lists the values of E and I peaks under the same conditions of Fig. 4. This behavior can be explained by the formation of a passive layer on the iron surface from the ferrous ions in the solution.

From these results we can see that the oxalic acid can be dissolved the magnetite coupled with iron, and depending slightly on the iron area in the couple and the concentration of added ferrous ion, but it have a pronounced effect on the iron metal, which observed dissolved in these media.

Table 2. Values of E (mV vs. SCE) and I peak (mA cm^{-2}) in cathodic direction from cyclic voltammetry measurements of magnetite with and without coupling with iron in different area ratios in 0.1 M oxalic acid solution containing different concentration of Fe^{2+} at pH 4.0 and 40°C .

pH	parameter	mag.	couple 1	couple 2	couple 3	couple 4
0	E	-342	-380	-354	-353	-353
	I	-1.27	-1.58	-1.2	-1.29	-1.21
0.0006	E	-354	-380	-364	-352	-355
	I	-1.23	-1.61	-1.28	-1.36	-1.30
0.003	E	-364	-295	-364	-343	-361
	I	-1.36	-0.22	-1.41	-1.19	-1.36

4. CONCLUSIONS

The effect of the galvanic coupling between magnetite and iron with different area ratios between iron and magnetite on their dissolution was investigated in aqueous solutions containing oxalic acid and ferrous ion. In the absence of added ferrous ions, the couples behaves like the magnetite, and the dissolution of magnetite increase with iron area increase, but the iron were subjected to a dissolution process followed by passivation. The dissolution rate of magnetite not affected by adding ferrous ions, whereas the iron were become more passivated when ferrous ions added to the solution.

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