

Effect of Some Factors on the Behavior of Galvanic Couple of Magnetite and Iron in Aqueous Solutions

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In this study, the effect of some factors on the behavior of the galvanic couples between magnetite and iron, were investigated in aqueous solutions containing EDTA and ferrous ion; in which magnetite dissolved reductively. Different ratios between iron areas to magnetite area were studied. The experiments 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. The effect of ferrous ion concentration, EDTA concentration, solution pH and temperature were studied. The couple potential and individual currents of magnetite and iron were used, which revealed that the reductive dissolution of magnetite increase with either pH decrease or temperature increase. At [EDTA] = 0.02M, and when [Fe²⁺] increase in the solution, the rate of magnetite dissolution increases. On the other hand, at [Fe²⁺] = 0.02, the increase in [EDTA] will cause a larger increase in dissolution rate. The effect of pH on the dissolution rate of magnetite and iron was investigated in the range 2.5 – 4.5. Higher current values recorded at pH 2.5 then decreases with the increases in the pH. This effect can be expected from the reductive dissolution equation, which is related with proton concentration. When temperature increases in the range 40°C to 65°C the dissolution rate also increases.

Keywords: Magnetite; iron; galvanic couple

1. INTRODUCTION

It is now a common practice to chemically clean boilers and heat exchangers to remove deposits, sludge and thick oxide build up of which magnetite is the main constituent [1].

Several processes and formulations are being used to chemically clean the fould steam generators. The minerals acid based processes used earlier are giving way to the new mild organic acid based chemical cleaning processes [2].

The generic iron oxide removal chemical cleaning process using EDTA as a chelate was developed [3,4], and commercially applied at many nuclear power plants. [5]

It is well known that EDTA's a strong complexing agent for various transition metal ions and it has been successfully as a main constituent of the chemical cleaning formulations. Temperature, pH, presence of reducing or oxidizing agents, the complexing power of the pH adjusting agents, presence of corrosion inhibitors and surfactants can all affect the dissolution behavior of the various constituents of the sludge by EDTA. [6]

In a previous study, the effect of Fe area to magnetite area ratio was investigated [7]. In This work we study the effects of some experimental factors that are very common during chemical cleaning of the boilers and heat exchangers on the galvanic couple behavior. These factors are solution pH, temperature, $[Fe^{2+}]$ and $[EDTA]$.

2. EXPERIMENTAL PART

The work has been conducted at 40°C in an aqueous solution containing 0.1M $NaClO_4$ (as supporting electrolyte) and different concentrations of EDTA and Fe^{2+} , at different pH (by adding drops of sulphuric acid). The Fe^{2+} adding as solid salt after N_2 following in solution in test cell for half hour before measurements starts, and to its end, to avoid its oxidation by air. A multi zero resistance ammeter (ZRA) from ACM Instruments was employed for electrochemical tests (galvanic potential).



Figure 1. Scematic diagram of multi electrode

Magnetite single crystal (from eSCeTe single Crystal Technology) and Fe (from goodfellow) were the material tested, in cylinder form. Fig. 1 depicts the arrangement of the working electrode . The areas of the tested electrodes were chosen to make the four following ratios : 1:1600, 1:400, 1:100 and 1:25 and marked as 1, 2, 3 and 4 respectively –table 1-.

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

Electrochemical measurement is carried out by monitoring of OCP and the individual currents of magnetite and iron coupled and uncoupled for one hour. Then recording EIS at OCP in a frequency range of 30 kHz to 10 mHz with an applied sinusoidal potential of 10 mV. Then the cyclic

voltamogramm measure by scanning the potential from -1200 mV to 500 mV by scan rate = 20 mV/sec.

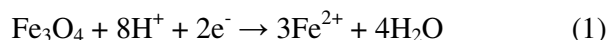
Table 1. The electrodes codes

electrode material	WE no.	Diameter (cm)	Area (cm ²)	Ratio between areas in galvanic couple	galvanic couple code	magnetite code	Fe code
magnetite	1	1.0	0.785	-	-	mag.	-
Fe	1	0.2	0.0314	-	-	-	Fe
	2	0.025	0.00049	1 : 1600	(g.c.1)	mag.1	Fe1
	3	0.05	0.00196	1 : 400	(g.c.2)	mag.2	Fe2
	4	0.1	0.00785	1 : 100	(g.c.3)	mag.3	Fe3
	5	0.2	0.0314	1 : 25	(g.c.4)	mag.4	Fe4

3. RESULTS AND DISCUSSION

3.1. The effect of Fe^{2+} concentration

When EDTA is present in an acidic solution, magnetite dissolve reductively, according to the following reaction [8,9,10,11]:



From which it can be seen that the Fe^{2+} concentration and the hydrogen ion concentration are important factors that can affect the dissolution process.

On another hand, when magnetite galvanically is coupled with iron, the latter will dissolve to provide Fe^{2+} , which forms Fe(II)-EDTA in the solution, that can acts as effective reductant that converts the ferric ions Fe^{3+} in the oxide to Fe^{2+} [12].

To study the effect of ferrous ion, a first test was conducted to explain the behavior of galvanic couples in the absence of Fe^{2+} , in presence of $0.02M$ EDTA and pH 3.5. Its results drown in fig. 2, represent the variation of E_{couple} and the individual currents of Fe and magnetite with immersion time. From this figures it can be seen that the immersion potential of the four couples have negative values. During the first minutes, the potential shifts to more active values, then it changes gradually until it reaches a constant value which is located between those for magnetite and Fe under the same conditions, and shifts to negative direction as Fe area increase. This agrees with Plonski [13] results that revealed that the couple potential always more negative than the magnetite potential. The current of magnetite has high negative value at immersion, and move to positive direction during the first two minutes, then it changes gradually until it reaches a constant value.

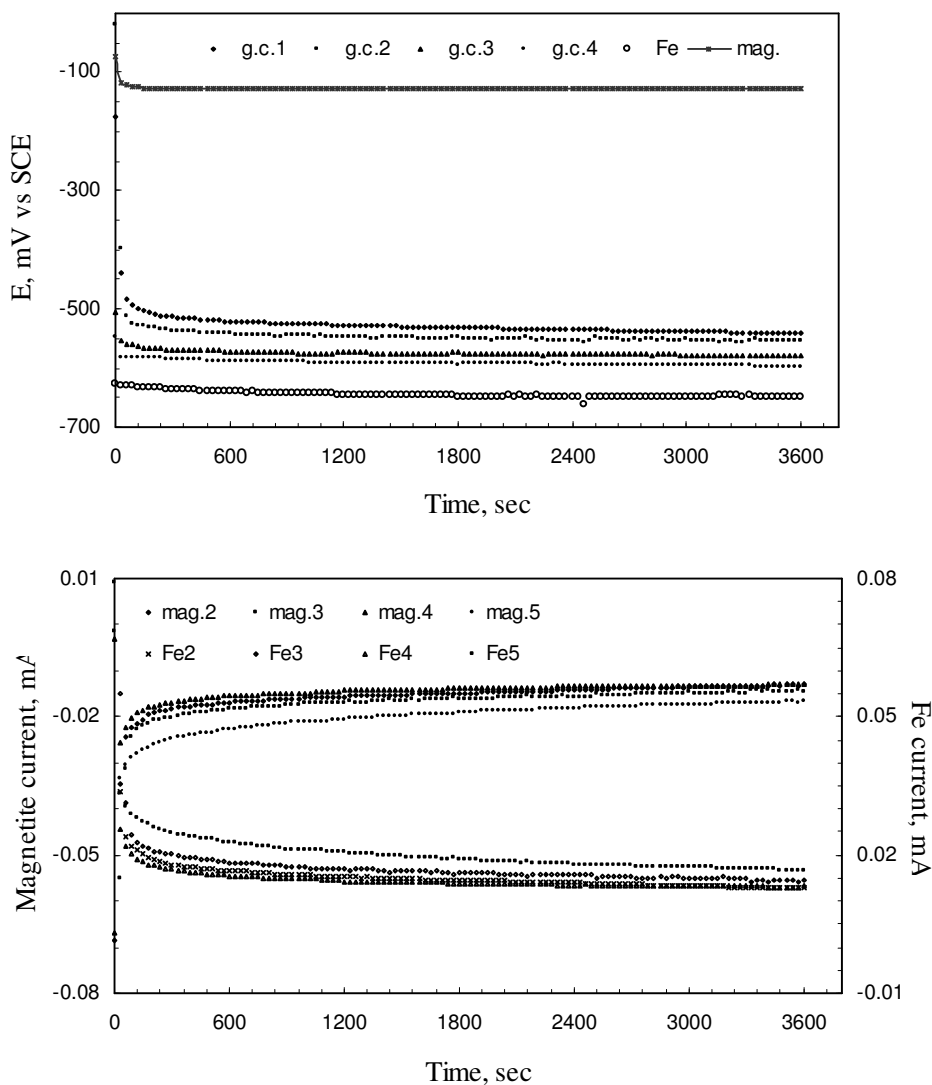


Figure 2. Variation of open circuit potential and galvanic currents with time for magnetite and Iron with and without coupling in different area ratios in 0.1 M NaClO₄ solution containing 0.02 M EDTA at pH 3.5 and 40°C

In other tests, the Fe²⁺ adding to EDTA solution in different concentration : 0.005 , 0.01 and 0.02 M. These additions of Fe²⁺ to the test solution don't change the couples general behavior except the couple 1 in 0.02 M Fe²⁺, which behave as magnetite electrode, as shown in fig. 3. But the couples 2, 3 and 4 behave like iron electrode, the immersion potential of them shifts to more negative values, then it change gradually to reach E_{ss} which have slightly more negative values than that recorded in free Fe²⁺ solution. The difference between E_{ss} values depend on the Fe area in the galvanic couple, as shown in table 2, there is a pronounced increase in the currents of magnetite and iron in the couples 2,3 and 4.

The difference in couple 1 behavior from the other couples can be explained depending on potential as Plonski [13] study, that when initial OCP for couple is more positive than the equilibrium

potential of the hydrogen electrode, the anodic iron oxide formation runs in parallel with iron dissolution in supplying electrons for magnetite reduction. The initial bare metal is recovered by black oxide, which was observed after test end, whereas when OCP of the couple is more negative with respect to the equilibrium potential of HER, the oxide dissolution and the increase in bare metal surface prevail and the potential-time curve decrease monotonically similarly to the case of steel electrodes, and in the present study to iron electrode.

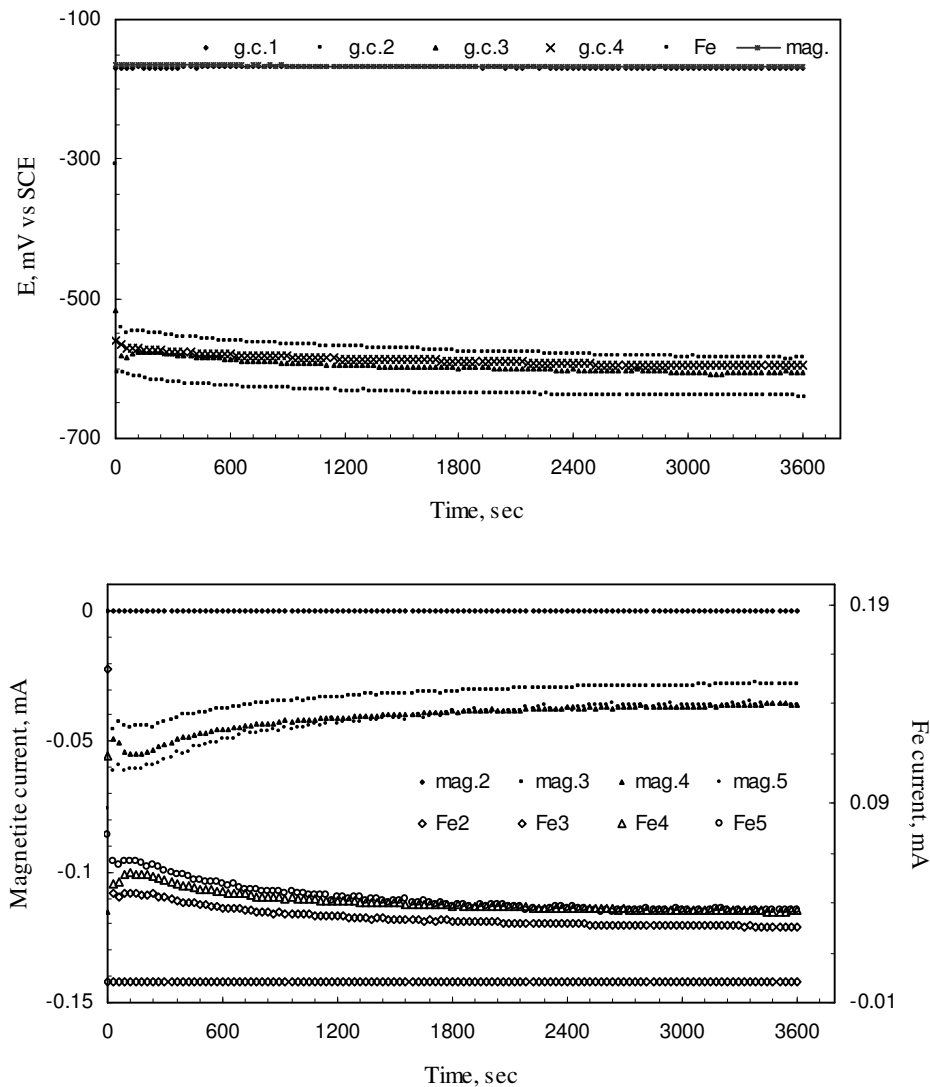


Figure 3. Variation of open circuit potential and galvanic currents with time for magnetite and Iron with and without coupling in different area ratios in 0.1 M NaClO₄ solution containing 0.02 M EDTA + 0.02 M Fe²⁺ at pH 3.5 and 40°C

The difference between the behavior of one couple in presence and absence of ferrous ions can be explained depending on Frenier and Growcock suggestion that the additives shifts the solution potential to negative direction accelerate magnetite dissolution [14].

The above results indicate that the presence of EDTA and Fe^{2+} in solution make a dissolution rate – expressed as passed current – is higher than that in presence of EDTA only. This agree with another studies for systems containing citric acid/ Fe^{2+} [15], oxalate / Fe^{2+} [16].

Table 2. 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 NaClO_4 solution containing 0.02 M EDTA + different concentration of Fe^{2+} at pH 3.5 and 40 °C

[Fe^{2+}]	parameter	Galvanic couples				Single electrode	
		(g.c.1)	(g.c.2)	(g.c.3)	(g.c.4)	Fe	mag.
0.00	E	-540	-553	-578	-597	-648	-128
	$I_{\text{mag.}}$	-0.013	-0.0144	-0.013	-0.0169	-	-
	I_{Fe}	0.013	0.0145	0.0131	0.0168	-	-
0.005	E	-543	-553	-581	-591	-623	-188
	$I_{\text{mag.}}$	-0.0178	-0.0169	-0.0167	-0.0127	-	-
	I_{Fe}	0.0179	0.017	0.0173	0.013	-	-
0.01	E	-551	-577	-591	-604	-665	-174
	$I_{\text{mag.}}$	-0.0205	-0.0225	-0.0238	-0.0223	-	-
	I_{Fe}	0.0204	0.0226	0.0238	0.0222	-	-
0.02	E	-169	-585	-605	-594	-639	-167
	$I_{\text{mag.}}$	-0.026	-0.027	-0.035	-0.035	-	-
	I_{Fe}	0.025	0.028	0.035	0.035	-	-

Table 3. 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 NaClO_4 solution containing 0.02 M Fe^{2+} + different concentration of EDTA at pH 3.5 and 40 °C .

[EDTA]	parameter	Galvanic couples				Single electrode	
		(g.c.1)	(g.c.2)	(g.c.3)	(g.c.4)	Fe	mag.
0.005	E	-577	-570	-637	-588	-625	-90
	$I_{\text{mag.}}$	-0.0219	-0.0273	-0.0261	-0.0264	-	-
	I_{Fe}	0.0214	0.0273	0.0261	0.0264	-	-
0.01	E	-555	-562	-631	-589	-670	-115
	$I_{\text{mag.}}$	-0.028	-0.0314	-0.0331	-0.0395	-	-
	I_{Fe}	0.027	0.0315	0.0331	0.0395	-	-
0.02	E	-169	-585	-605	-594	-639	-167
	$I_{\text{mag.}}$	-0.026	-0.027	-0.035	-0.035	-	-
	I_{Fe}	0.025	0.028	0.035	0.035	-	-

3.2. The effect of EDTA concentration

To study the effect of [EDTA] on the galvanic couples behavior, the three solutions were used, containing 0.005, 0.01 and 0.02 M [EDTA], in presence of 0.02 M Fe^{2+} at pH 3.5. Fig. 4 and 5 shown the OCP results. These curves revealed that the effect of [EDTA] more pronounced than $[\text{Fe}^{2+}]$. There is an increase in the magnetite and iron currents in all galvanic couples as [EDTA] increase, indicating the increase in the dissolution rate. On the other hand, the difference between the effect of 0.01M and 0.02M EDTA is small, they can increase the dissolution more than that of 0.005M, as shown in table 3.

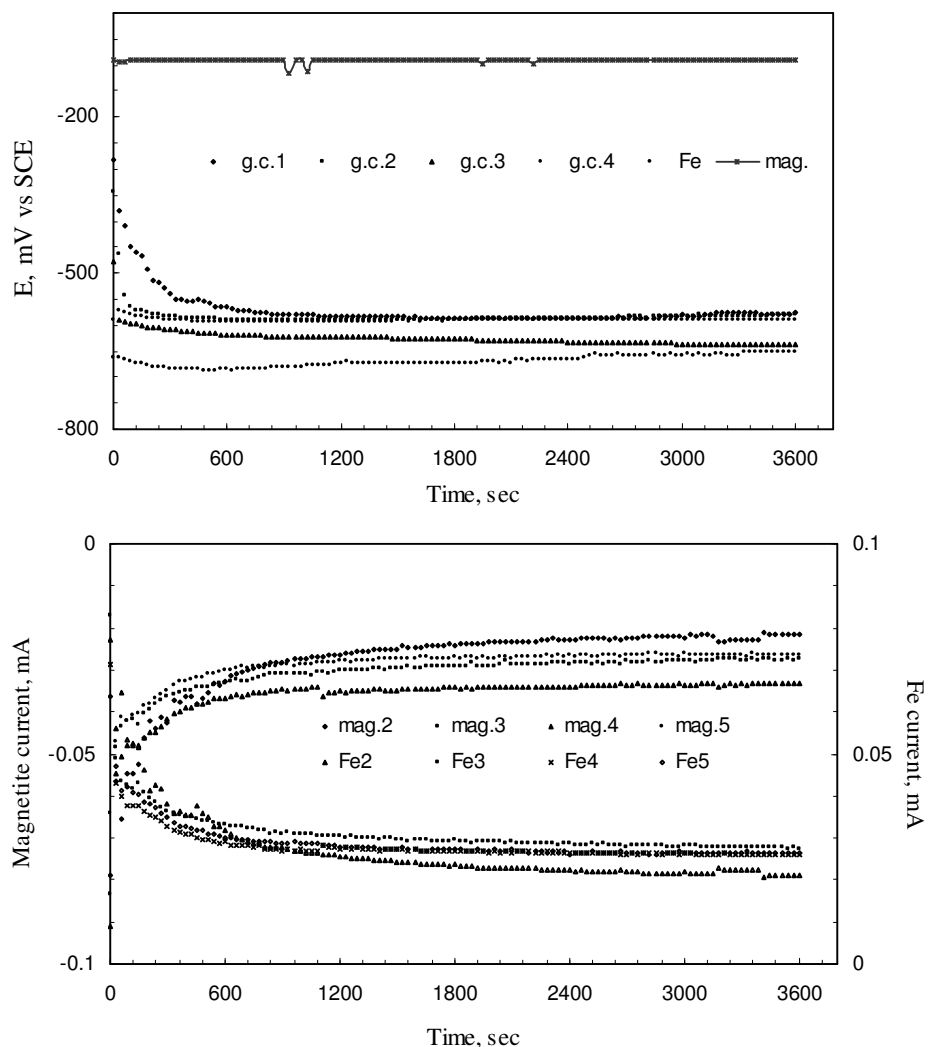


Figure 4. Variation of open circuit potential and galvanic currents with time for magnetite and Iron with and without coupling in different area ratios in 0.1 M NaClO_4 solution containing 0.005 M EDTA + 0.02 M Fe^{2+} (to make ratio 1:4) at pH 3.5 and 40°C

These observations revealed that the EDTA and Fe^{2+} play important role in the magnetite dissolution, but the [EDTA] have a higher effect on the galvanic couples behavior than the $[\text{Fe}^{2+}]$. This can be attributed to the iron in the couple which dissolved directly to make ferrous ions in the solution.

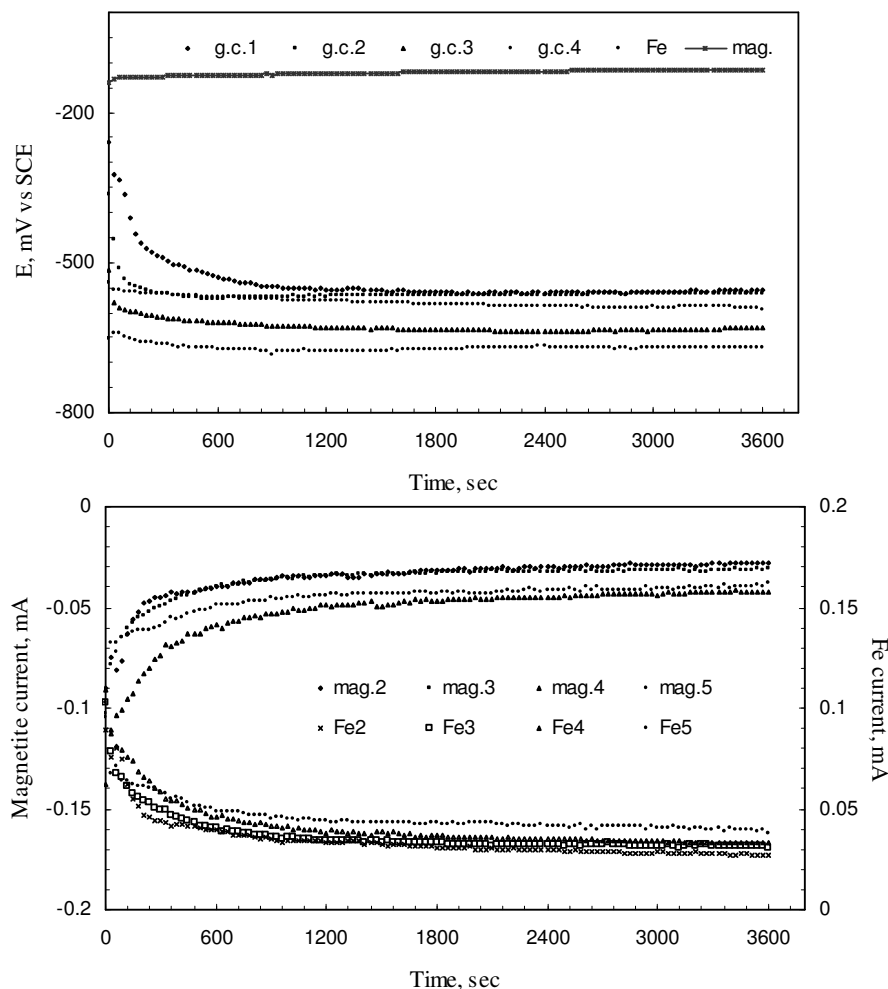
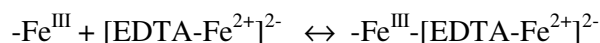


Figure 5. Variation of open circuit potential and galvanic currents with time for magnetite and Iron with and without coupling in different area ratios in 0.1 M NaClO₄ solution containing 0.01 M EDTA + 0.02 M Fe²⁺ (to make ratio 1:2) at pH 3.5 and 40°C

The suggested mechanism for magnetite dissolution involves three steps. The first one represents an adsorption of reductive ion on the oxide surface, which depends on the ratio between [EDTA] and [Fe²⁺] presented initially in the solution [15]. This step can be presented as follow:



The second one is non-reductive dissolution which followed by a reductive dissolution by EDTA/Fe²⁺ complex.

3.3. The effect of solution pH

The effect of solution pH on the behavior of galvanic couples were studied in the range of 2.5 – 4.5 . In fig. 6, the values of E_{ss} and magnetite current plots at different pH, from which it can be seen that when pH increase from 2.5 to 4.5:

1. The general shape of E variation with time does not change for the couples unless the first couple which has a behavior near to that of magnetite alone at the same conditions. The dependence of E on the areas ratios does not change with pH change.
2. For a galvanic couple the E shifts to more positive value, this shift is more clearly at 2.5 .
3. The current of magnet decrease in its negativity.

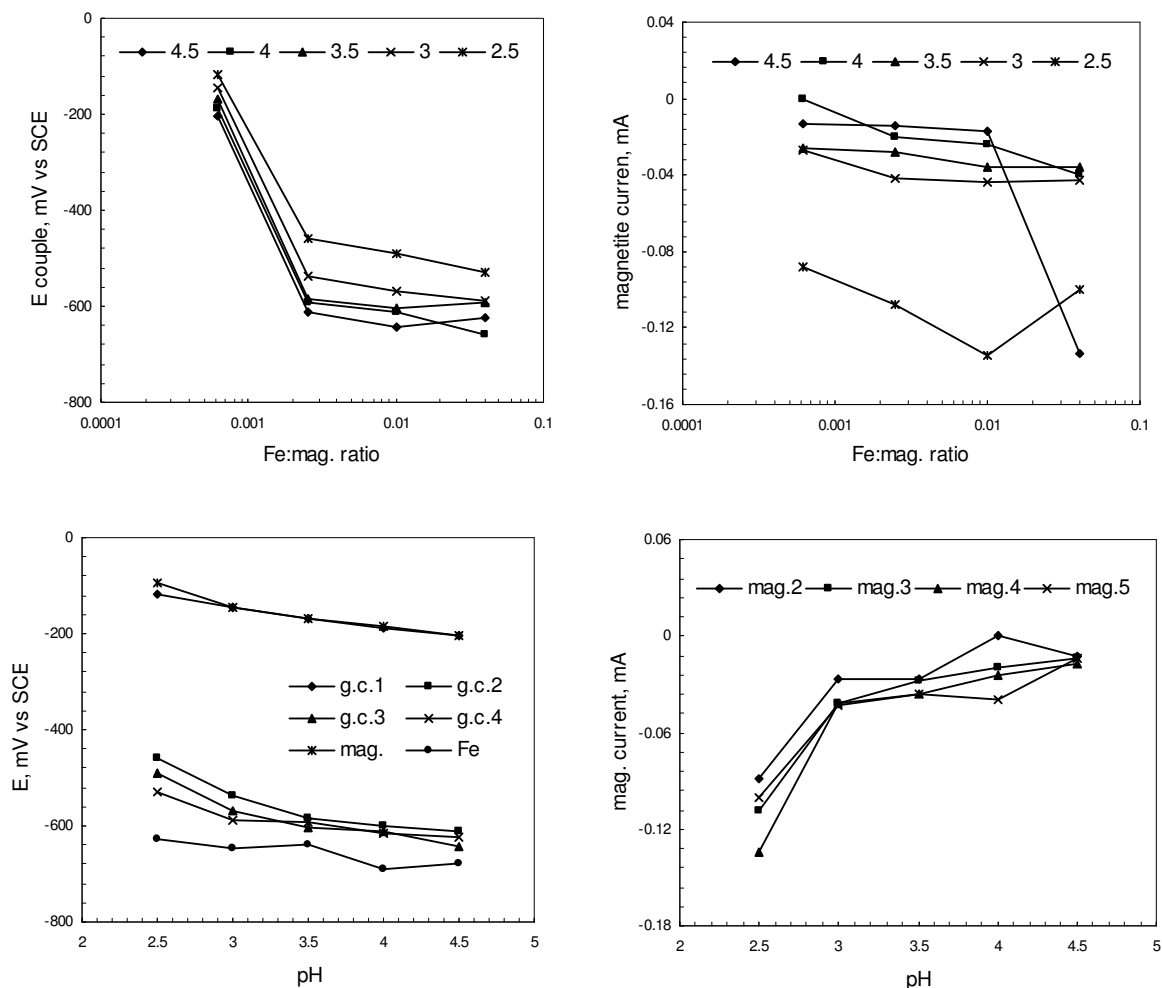


Figure 6. Relations between open circuit potential and galvanic currents for magnetite and Iron with and without coupling in different area ratios in 0. 1 M NaClO₄ solution containing 0.02 M EDTA + 0.02 M Fe²⁺ at different pH and 40°C

The dependence of passed current (I) solution pH was observed elsewhere [17]. Taking I_c values as indication of dissolution rate, it is clear that the reaction rate decrease logarithmically with increasing pH. The rate law is of the following form:

$$\log I_c = \log k - m \text{ pH}$$

While the rate determining step was first order accordance to H^+ , the reaction order can give different values between 0.5-2.0 depending on the hydration, complexation and oxidation/reduction reactions and another factors [18]. From fig. 6, $m = 0.446$. This value agree with that recorded by [19] for magnetite dissolution in $EDTA_{Na_2}$, which equal to 0.5.

This effect is in accordance with the dependence of the reductive dissolution of magnetite on hydrogen ion activity, which can be expressed as the equation (1).

This accelerated effect of acidic solution on the reductive dissolution can be attributed to the potential changes across Helmholtz layer [9]. But this may arrest the activity of complexing agent, thus decreasing the dissolved ferrous ion in the solution [20], which in the present study causing participation of EDTA when pH decrease to 2.0.

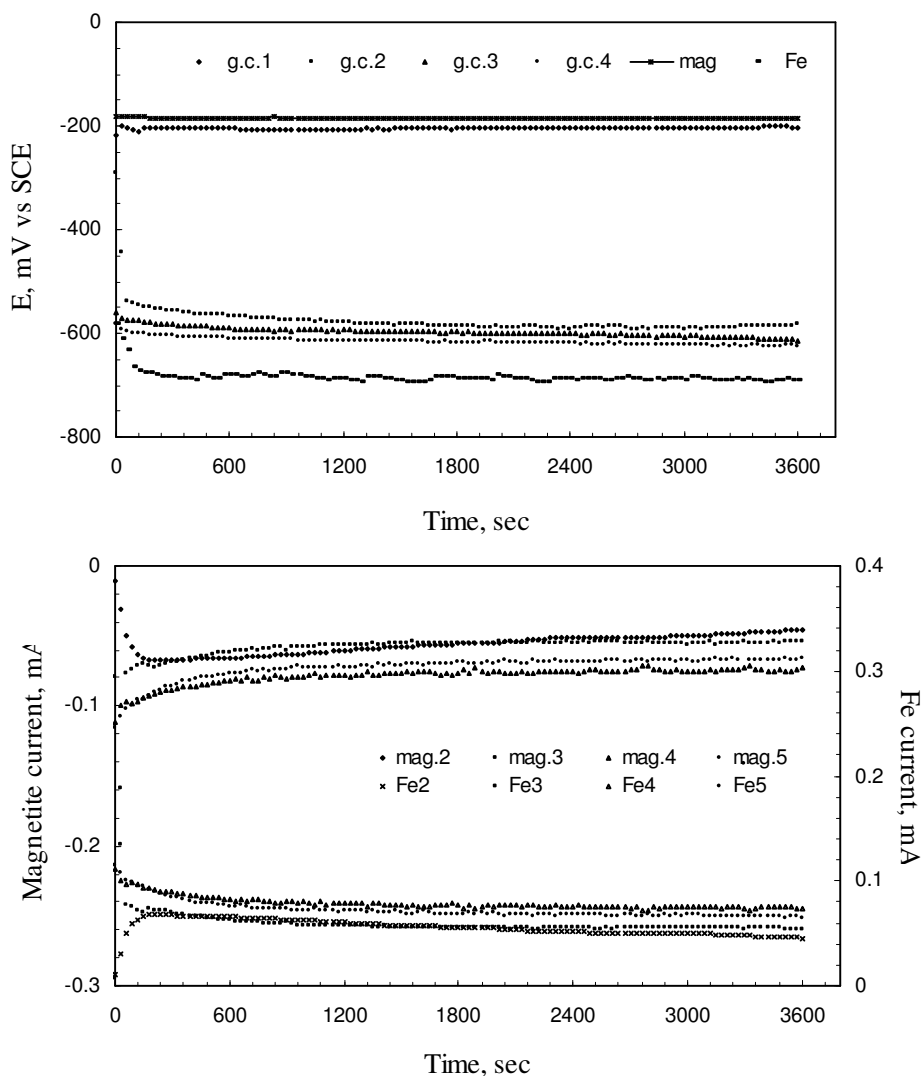


Figure 7. Variation of open circuit potential and galvanic currents with time for magnetite and Iron with and without coupling in different area ratios in 0.1 M $NaClO_4$ solution containing 0.02 M EDTA at pH 3.5 and 55°C

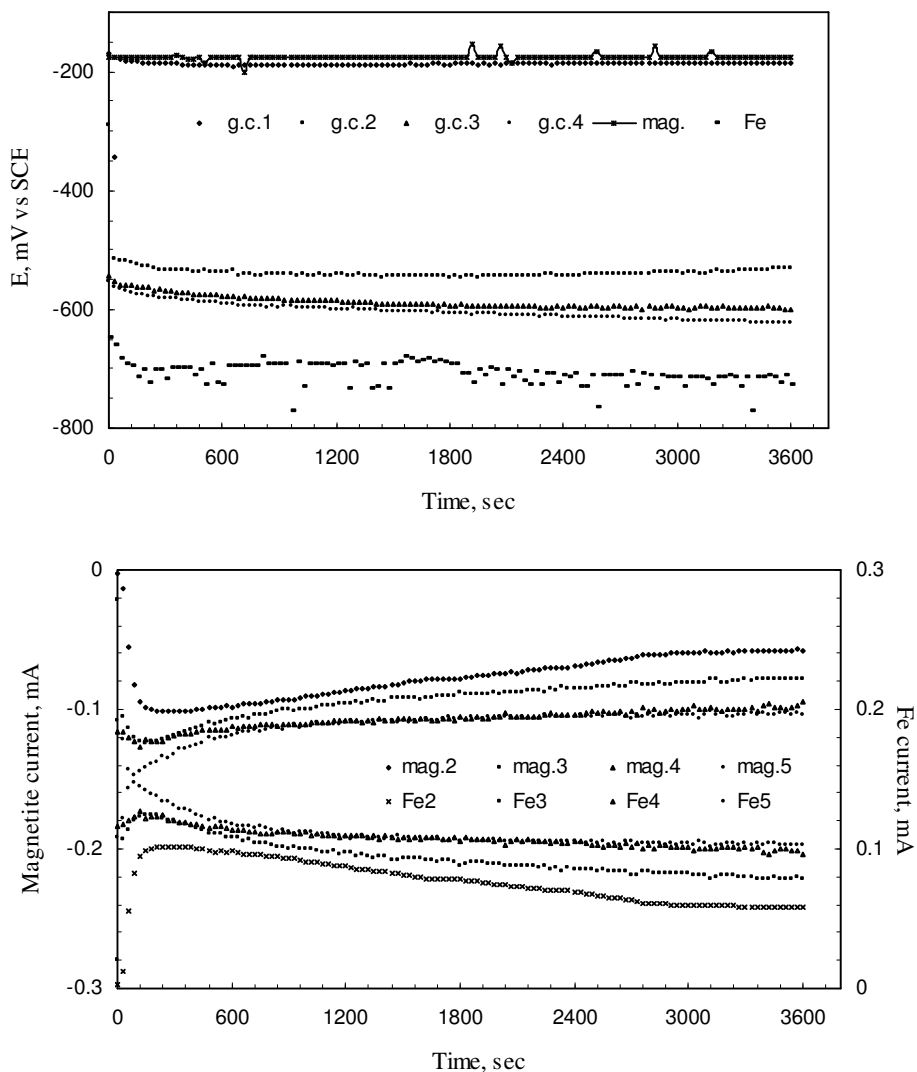
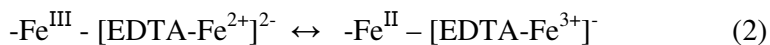


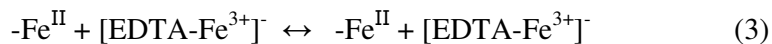
Figure 8. Variation of open circuit potential and galvanic currents with time for magnetite and Iron with and without coupling in different area ratios in 0.1 M NaClO₄ solution containing 0.02 M EDTA at pH 3.5 and 65°C

3.4. The effect of temperature

The second step in magnetite dissolution mechanism is non-reductive dissolution, which is a simple desorption process that removes reactive sites of the oxide surface. This process is usually slow at low temperature but becomes significant at high temperature, thus temperature is considered one of crucial parametered for magnetite dissolution. [17,4]

This step can be represents by the following





To study the effect of temperature, it changes to 55 and 65 °C, and compared with the results at 40 °C at pH 3.5 in presence of 0.02M EDTA and 0.02M Fe²⁺. From fig. 7 & 8, the couple 1 behaves like single magnetite, whereas the other couples behavior revealed a drop in its potential in the first minutes followed by a steady state, with E_{ss.} values close to that for single iron, as shown in table 4. It's clear that the dissolution increase with temperature increase. Activation energy for magnetite dissolution can be calculated by Arrhenius equation

$$K_a = K_o \exp (-E_a/RT)$$

By express the dissolution rate as current, the equation can written as

$$E_a = -(2.3)(1.987) d(\log i)d(1/T) \text{ Kcal mol}^{-1}$$

By plotting the logarithm of current plots vs. reciprocal of temperature, the activation energy values calculated for couples. From table 5, the activation energy increases with iron area in the couple increase. The magnitude of the activation energies associated with dissolution reactions is often used in interpreting the nature of the reaction mechanisms. The values in table are in accordance with those calculated in white et al. work, which attributed to reactions controlled by solute diffusion (10-20 KJ mol⁻¹).

Table 4. 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 NaClO₄ solution containing 0.02 M EDTA + 0.02 M Fe²⁺ at pH 3.5 and different temperature .

°C	parameter	Galvanic couples				Single electrode	
		(g.c.1)	(g.c.2)	(g.c.3)	(g.c.4)	Fe	mag.
40	E	-169	-585	-605	-594	-639	-167
	I _{mag.}	-0.026	-0.027	-0.035	-0.035	-	-
	I _{Fe}	0.025	0.028	0.035	0.035	-	-
55	E	-202	-585	-690	-623	-690	-184
	I _{mag.}	-0.0467	-0.054	-0.0739	-0.074	-	-
	I _{Fe}	0.0467	0.054	0.0743	0.0664	-	-
65	E	-184	-532	-597	-621	-685	-179
	I _{mag.}	-0.057	-0.078	-0.098	-0.104	-	-
	I _{Fe}	0.057	0.078	0.090	0.102	-	-

Table 5. Values of activation energy (Kcal mol⁻¹) for magnetite dissolution in different galvanic couples calculated from fig. (3-35) and equation (3-25)

Parameter	(g.c.1)	(g.c.2)	(g.c.3)	(g.c.4)
E _a	0.604	0.973	1.219	1.325

References

1. S. Brunet, G. Pinard-Legry and G. Turluer, in Proceedings of the International Congress on Metallic Corrosion, Germany, Frankfurt am Main, Dechema 1981, p.1634
2. C. Ramesh, N. Murugesan, A.A.M. Prince, S. Velmurugan, S.V. Narsasimhan and V. Ganesan, *Corrosion Science*, 43(2001)1865
3. A.G. Kumbhar, K. Kishore, G. Venkateswaran and V. Balaji, *Hydrometallurgy*, 68(2003)171
4. A.A.M. Prince, S. Velmurugan, S.V. Narasimhan, C. Ramesh, N. Murugesan, P.S. Raghavan and R. Gopalan, *J. of Nuclear Materials*, 289 (3) (2001)281
5. Do Haeng Hur, Eun Hee Lee, Myung Sik Choi, Han Sub Chung and Uh Chul Kim, *J. of Nuclear Materials*, 299 (3) (2001)271
6. A.L. Rufus, V.S. Sathyaseelan, M.P. Srinivasan, Padma S. Kumar, S.N. Veena, S. Velmurugan and S.V. Narasimhan, *Progress in Nuclear Energy*, 39 (3-4) (2001) 285
7. A.M. Al-Mayouf and N.A Al-Mobarak, A.A. Al-Swayih, accept to press in *Corrosion* (2007).
8. S. Brunet and G. Turluer, in Proceedings of the 5th European Symposium on Corrosion Inhibitors, Italy, Ferrara, Sept. 1980, p.513.
9. Wayne W. Frenier, *Corrosion-NACE*, 40 (4) (1984)176
10. C.M. Das and M. Sudersanan, *J. of Applied Electrochemistry*, 33 (3/4) (2003). 333
11. S.J. Keny, A.G. Kumbhar, G. Venkateswaran and Kamal Kishore, *Radiation Physics and Chemistry*, 72 (4) (2005) 475
12. P. Ananthan, G. Venkateswaran and J. Manjama, *Chemical Engineering Science*, 58(2003) 5103
13. I.H. Plonski, *J. of Applied Electrochemistry*, 27(1997)1184
14. Wayne W. Frenier and Frederick B. Growcock, *Corrosion-NACE*, 40 (12) (1984) 663
15. J. Manjanna, G. Venkateswaran, B.S. Sherigara and P.V. Nayak, *Hydrometallurgy*, 60 (2) (2001)155
16. A.M. Al-mayouf, *Corrosion*, 58 (6) (2002) 519
17. A.M. Al-mayouf, *J. of Nuclear Materials*, 320(2003)184
18. G. Senanayake and G.K. Das, *Hydrometallurgy*, 72(2004) 59
19. I.G. Gorichev, V.S. Dukhanin and N.A. Kipriyanov, *Russ. J. Phys. Chem. (Engl. Transl.)*, 54 (5) (1980)774
20. Miguel A Blesa, in : Decontamination of nuclear facilities, International joint topical meeting ANS-CAN, Niagara Falls, 1982.