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Dissolution behaviour of magnetite film formed over carbon steel in dilute organic acid media

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Abstract

Magnetite is the major corrosion product formed over the carbon steel in the primary heat transport system of the pressurized heavy water reactor (PHWR). This magnetite usually accumulates radioactivity during reactor operation. The dissolution of the host magnetite is achieved by chemical formulations in order to get rid of the radioactivity trapped in the oxide; the underlying base metal also participates in the process by contributing electron to reduce the ferric ion or by undergoing corrosion. In the present study, the role of base metal in the dissolution of magnetite in various chelating agents has been investigated. The liberated hydrogen was measured by using an amperometric hydrogen sensor. The magnetite dissolution rate and the corrosion rate of carbon steel in the formulations were calculated. The effect of temperature, pH and concentration of the chelating agents on the magnetite film dissolution was studied in detail. The mechanism of base metal aided magnetite dissolution is discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Magnetite (Fe_3O_4) film is formed over the carbon steel (CS) surface by Schikorr's reaction under the reducing and alkaline conditions and at temperatures more than 180°C [1]. The CS is used in the primary heat transport (PHT) system of pressurized heavy water reactor (PHWR) as structural material. The heavy water coolant is used in single phase at 240–300°C under alkaline (pH 10–10.5) and reducing conditions. The magnetite layer formed under these conditions traps radioactive corrosion products and fission products that are transported by the coolant [2]. The build-up of radioactivity on the primary circuit pipelines in water-cooled reactors poses problems during maintenance. Removal of this radioactivity involves the dissolution of the magnetite film. This can be achieved by using appropriate chemical decontamination formulation. The essential requirement of a chemical decontaminant is that it should remove the magnetite or other oxides without causing excessive corrosion of the underlying base metal [3].

Organic chelating acids such as ethylenediaminetetraacetic acid (EDTA), hydroxyethylethylenediaminetriacetic acid (HEEDTA), nitrilotriacetic acid (NTA), citric acid (CA), 2,6-pyridinedicarboxylic acid (PDCA) etc. are employed for removing the contaminated magnetite film from the CS surfaces. These organic acids are used either individually or in combination with another complexing agent (an organic reductant) such as citric acid (and ascorbic acid). The dissolution behaviour of magnetite and other oxides in powder form has been reported in the literature [4]. The dissolution kinetics of

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magnetite powder in many of the organic acids has been reported to follow the inverse cubic rate law which is derived from the shrinking core model. In oxalic acid and EDTA, it has been reported that the time vs percentage dissolution curve exhibit an induction period and progresses along a s-shaped curve indicating the catalysis by the dissolution product such as $[\mathrm{Fe(oxalate)_2}]^{2-}$ [5]. It was also observed that before the chelating agent brings the iron into solution, it is adsorbed on the surface of the oxide particle and the adsorbed complexing agent loosens the iron atoms from the lattice and finally released into solution [6]. Organic reductant helps to reduce the Fe^{3+} in the lattice to Fe^{2+} thus aiding the dissolution process. It was also found that other factors such as the stability of the complex formed during the dissolution, pH and concentration of the formulation and temperature affect the dissolution kinetics [7].

The knowledge of the dissolution behaviour of powder form of magnetite is very useful to arrive at a suitable decontamination formulation. However, the data obtained in the powder dissolution studies cannot be directly extrapolated to derive kinetic information for the dissolution of magnetite film formed over carbon steel. The main difference between the magnetite powder and the magnetite film is the presence of the carbon steel base metal in the latter. The carbon steel base metal has been found to actively participate during the dissolution of the magnetite film, as suggested in the following scheme:

$$\text{Fe (base metal)} \rightarrow \mathrm{Fe^{2+}} + 2\mathrm{e^-} \tag{1}$$

$$\underline{\mathrm{Fe_3O_4} + 8\mathrm{H^+} + 2\mathrm{e^-} \rightarrow 3\mathrm{Fe^{2+}} + 4\mathrm{H_2O}} \tag{2}$$

$$\mathrm{Fe_3O_4} + 8\mathrm{H^+} + \mathrm{Fe} \rightarrow 4\mathrm{Fe^{2+}} + 4\mathrm{H_2O}. \tag{3}$$

This base metal aided dissolution is also termed as 'autoreduction process' [8]. Not much work has been carried out on the dissolution behaviour of magnetite film formed over CS. Shoesmith et al. [9,10] have carried out some electrochemical investigations on CS having 1 μm thick magnetite layer. The variation in the potential as the magnetite film progressively dissolves has been recorded by some authors [11]. Still several questions remain to be answered unequivocally. The thickness range to which the base metal extends its capability to reduce the magnetite film, the law governing the film dissolution and the dissolution of the magnetite at a stage when the base metal is partly exposed, are questions requiring investigations. In addition, the relative rate of dissolution of magnetite and base metal and the role of the Fe^{2+} formed at the metal to oxide interface are the questions that are addressed in this work. The magnetite film formed over the carbon steel surfaces at the high temperatures, under reducing and alkaline conditions is a protective layer with low defect concentration. During the process of corrosion and oxide formation, transportation of ions through the pores in the oxide and along the oxide grain boundary has been reported. When this magnetite coated carbon steel is exposed to organic acid and complexing agents the magnetite film is progressively dissolved followed by complexation of iron ions. The carbon steel base metal, in the absence of magnetite film, has been found to undergo corrosion by the anodic dissolution of the metal due to the acid present in the medium [12]. The wall thinning taking place in the absence of magnetite film can be accurately quantified by simple methods such as weight loss or electrochemical methods. But quantification of wall thinning that takes place when the magnetite film undergoes dissolution is difficult. However, the knowledge is important in deciding the number of decontamination applications to which a system can be subjected. Using an amperometric hydrogen sensor, the onset of the corrosion reaction (that evolves hydrogen), as the dissolution of magnetite film formed over the carbon steel progresses in the medium containing the complexing agent was determined. The variation in the corrosion rate as a function of time was also followed by measuring on-line the hydrogen released till all the magnetite is dissolved and the material corroded like plain metal.

The rates of magnetite film dissolution and the base metal corrosion were calculated from the solution iron values and from the hydrogen release behaviour. The metal loss by hydrogen discharge as measured by this method gives the overall average. Selective/specific attacks cannot be identified or quantified by this method. The effect of pH, temperature, the nature and the concentration of the complexing agent, co-complexing agent and the reductant on the dissolution of magnetite film and on the corrosion of carbon steel are discussed. The study also gave an insight into the process of magnetite film dissolution.

2. Experimental

2.1. Oxide film characterisation

CS pipe specimen that was exposed to a loop simulating the PHT system of PHWR (pH 10.0 maintained by LiOH at 290°C) was used for this experiment. XRD analysis of the oxide film scrapped from the CS specimen indicated that the film is essentially made of magnetite. The XRD line observed at $d = 2.700$ corresponded to the maximum intensity line of $\alpha\text{-}Fe_2O_3$ but its relative intensity was very low.

The thickness of the magnetite film was measured by using a descaling solution (Clarke's solution) prepared by dissolving 2 g Sb_2O_3 and 5 g $SnCl_2$ in 100 ml of concentrated HCl. A 2 cm^2 (2 cm × 1 cm) size of a coated CS and a blank CS were weighed and suspended in Clarke's solution for 1 min, then washed with water and acetone and dried. From the weight loss and after making appropriate correction for the blank, the thickness of the magnetite layer was calculated by assuming the density of magnetite layer to be 5.3 g/cm^3. The thickness was estimated to be 5 μm that corresponds to 3 mg of magnetite per cm^2 of CS.

These specimens were cut to a size with an oxide area of about 2 cm^2 and the other sides were polished to remove any air formed oxide layer and coated with an impervious organic coating. The effectiveness of the latter was tested by exposing a polished carbon steel specimen, whose surfaces were covered with the organic coating, to the EAC formulation at 85°C. It was found that the above specimen did not release any hydrogen even after several hours.

Specimens having different magnetite film thickness viz. 41 and 19 μm were collected, the latter from the same engineering system from which the 5 μm specimens were obtained and the former from another engineering system operated at pH 9.5–10.5 and reducing conditions. The thickness values reported were the average value of three measurements carried out by Clarke's solution de-scaling method. The oxide film was scrapped from a portion of the specimen having 41 μm thick magnetite film and was analyzed by XRD. The result showed it to be 100% magnetite.

A CS pipe specimen obtained from a heavy water plant was found to have a 37 μm oxide layer and the oxide layer was analyzed by XRD and was found to be haematite (α-Fe_2O_3).

2.2. Measurement of hydrogen evolved

The hydrogen gas evolved while exposing the carbon steel specimen having magnetite film was measured using an amperometric hydrogen sensor. The schematic of the experimental arrangement used for the measurement of hydrogen liberated by the CS having magnetite film is given in Fig. 1. The sensor was calibrated by passing argon gas containing known concentrations of hydrogen. The hydrogen concentration during calibration was varied using a microprocessor controlled mass flow controller. Before the actual measurement, the sensor was calibrated by passing known concentration (from 25 to 100 ppm (volume/volume)) of H_2 and a calibration graph was made by plotting the concentration of hydrogen (H_2) vs current. The H_2 evolved from the coated CS was determined from the relationship established by the calibration. The sensor was connected to a current integrator and the value of current as a function of time (with time resolution of seconds) was obtained on-line using a computer.

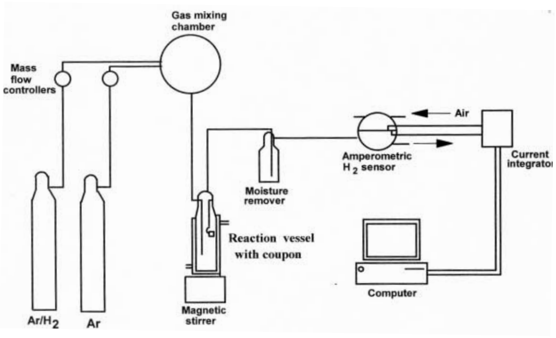

Fig. 1. Schematic diagram of the H_2 measuring system for on-line corrosion measurement.

2.3. Dissolution studies

Experiments on magnetite film dissolution were carried out in the double walled glass vessel. A 500 ml volume of the complexing agent/ formulation was taken in the concentration range of 1–3 mM. A thermostat controlled the temperature of the vessel and argon gas was passed through the reaction vessel for 1 h to remove the dissolved oxygen. Most of the experiments were carried out at 85°C and a few at 60°C. When the experimental vessel attained the set temperature, hydrogen measurement was started, the magnetite coated CS was introduced into the vessel after 100 s from the time the hydrogen measurement was started. All the graphs that give the variation of hydrogen concentration with time include this 100 s. The hydrogen measurement was carried out at every second using a pc controlled amperometric sensor. The time at which the hydrogen started evolving was also noted and the experiment was continued till saturation in the hydrogen concentration was reached. Solution samples were taken at the time when hydrogen started to evolve and also at the end of the experiment. The iron concentration was estimated by complexing it with o-phenanthroline and measuring the absorbance at 510 nm by UV–Vis spectrophotometer. The specimen was then removed from the vessel and washed with water, then with acetone, dried and weighed. The weight loss was noted. The iron released to the medium and the weight loss were compared. The same coupon was polished using 400-grade emery paper and exposed to a fresh formulation to determine the corrosion rate of the CS.

The corrosion rate was calculated using the formula

$$\text{Corrosion rate } (\mu\text{m/h}) = \frac{\text{weight loss (g)} \times 10^4}{A\rho t}, \qquad (4)$$

where A is the surface area of the coupon (cm^2), ρ is the density of CS (7.8 g/cm^3), and t is the time of exposure (h).

Magnetite film dissolution rate was calculated using the formula

Magnetite film dissolution rate

$$= \frac{[M - 1/4(M)] \times 232 \times 10^4}{A \times \rho \times t \times 167.7}, \qquad (5)$$

where M is the amount of iron released to the solution when H_2 liberation started. 1/4 (M) corresponds to the contribution of iron from the base metal, A is the surface area of the coupon (cm^2), ρ is the magnetite density (5.3 g/cm^3), and t is the time of exposure (h).

2.4. *Quantifying the release of Fe^{2+}/Fe^{3+} from the magnetite film during dissolution*

During the dissolution of magnetite film, the amount of Fe^{2+} and Fe^{3+} released to the solution were estimated by measuring iron as Fe(II)-*o*-phenanthroline in presence and absence of hydroxylamine hydrochloride [13]. The concentration obtained while carrying out the analysis in the absence of hydroxylamine hydrochloride corresponds to Fe^{2+} and the value obtained in its presence corresponds to the total iron. The concentration of Fe^{3+} was obtained from the difference.

3. Results and discussion

3.1. *Exposure of carbon steel*

By measuring the evolved hydrogen using the on-line amperometric hydrogen sensor, the base metal corrosion reaction that occurs during the magnetite film dissolution process was followed. The argon gas acted as a carrier for hydrogen besides providing the inert, oxygen-free atmosphere required for the experiment. Measurement of the evolved hydrogen due to the interaction of a polished CS coupon with EDTA at 85°C indicated that the concentration of hydrogen increased rapidly and saturated after exhibiting a small hump (Fig. 2). The time taken for hydrogen to reach the saturation value was only 180 s (3 min). The integrated value after conversion to its iron equivalent corresponded with the base metal corrosion loss obtained by weight loss method. When the experiment was repeated with other complexing agents, it was observed that the time taken to reach the saturation value did not change. However, the value of the saturation concentration of hydrogen varied from one complexing acid to another. This is due to the difference in the corrosion behaviour of the complexing acid and to a small extent to the difference in the size of the CS specimens used in the experiments. The corrosion rate values for carbon steel and measured by the weight loss method and corroborated by the hydrogen measurement, for the various complexing acids and their combinations (formulations) are given in Table 1.

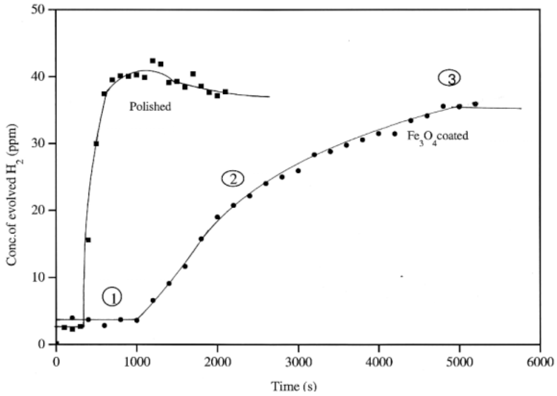

Fig. 2. Compression of hydrogen evolution behaviour of Fe_3O_4 coated CS and a polished CS in 1.37 mM EDTA at 85°C. Region 1 only base metal aided Fe_3O_4 dissolution, region 2 base metal aided Fe_3O_4 dissolution and corrosion reaction, region 3 only corrosion reaction $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$ takes place.

Table 1
Corrosion rate of carbon steel in various complexing agents at 85°C

Complexing agent	Concentration (mM)	Initial pH	Corrosion rate (μm/h)
PDCA	2.75	2.7	4.2
EDTA	1.37	2.6	3.1
CA	3.00	2.5	1.4
HEEDTA	1.37	2.7	0.8
NTA	1.37	2.6	2.5
DTPA	1.37	2.7	3.4

3.2. *Exposure of magnetite coated carbon steel*

When the measurement of corrosion was repeated with the carbon steel having 5 μm thick magnetite film in pure EDTA medium, for several minutes during which dissolution of magnetite film occurred, there was no evolution of hydrogen. After 20 min from the commencement of the experiment, hydrogen started evolving and slowly reached a saturation value that was the same as that observed for polished carbon steel indicating the complete removal of magnetite film. There are three regions in the plot of concentration of evolved H_2 vs time graph namely region 1, where only the magnetite dissolves with the participation of the base metal. Region 2 in which reductive film dissolution and corrosion take place. In region 3, base metal corrosion alone takes place as the oxide is completely removed. The non-zero value for the hydrogen concentration observed in region 1 with many of the complexing acid is attributed to the sluggishness with which the H_2 sensor approaches the zero value after the calibration is carried out. Measurement of iron dissolved in the solution immediately after the hydrogen started evolving revealed that about

2.85 μm thickness of magnetite film has been dissolved. Thus, it is clear that the solution containing EDTA does not corrode the base metal by the hydrogen evolution reaction till the thickness is reduced to about 2 μm. Till this thickness is reached only magnetite dissolution take place. During this magnetite dissolution process, base metal is consumed but the 'corrosion' that we refer here is the corrosion reaction that releases hydrogen. One can get the magnetite film dissolution kinetics by measuring the iron released to the solution as a function of time. After the thickness of oxide left on the coupon was reduced to about 2 μm both the magnetite dissolution and base metal corrosion occur simultaneously. The longer duration taken, in the case of magnetite filmed carbon steel to reach the hydrogen saturation value from its initial evolution (low slope), is indicative of the presence of magnetite on its surface during this intervening period. Also, it indicated that once the corrosion reaction starts, the corrosion reaction dominates and the magnetite dissolution rate comes down significantly.

Solution sample from the reaction vessel was taken immediately after the hydrogen signal started rising. Till that time, only base metal aided magnetite film dissolution occurred. Experiments carried out with several chelating agents and formulations indicated that the iron brought into solution at this stage corresponded to a constant value of 2.85 μm of magnetite film (Table 2). While calculating the magnetite film thickness dissolved at this stage correction for the iron that was released from the base metal to aid the magnetite dissolution reaction has been taken into account (Eq. (5)). The scatter in the value is mainly attributed to the error in the measurement of the area of the oxide-covered surface that is small and curved. From the value of iron released to the solution at this stage and from the area of the oxide covered surface, the magnetite film dissolution rate was calculated. The experiment was repeated with citric acid, ascorbic acid and mixtures of acids such as EDTA–citric acid and EDTA–Ascorbic acid–Citric acid (EAC) and the time vs hydrogen concentration curve plotted in Fig. 3. It had been observed earlier that under the pH condition in which citric acid was used, magnetite in powder form underwent dissolution at extremely slow rate whereas in EDTA medium it was very fast. This is in contrast to what was observed in the case of magnetite film that is present over the carbon steel. The time to evolve H_2 was found to be the same in pure CA solution medium and in EDTA solution medium. Thus, the magnetite film dissolution rates for citric acid (3 mM) and EDTA (1.37 mM) are equal. The difference in dissolution behaviour between the magnetite powder and magnetite film is attributed to the participation of the underlying base metal in the latter case that significantly alters the kinetics of the dissolution as well as the products of dissolution. In the case of magnetite powder, both ferric and ferrous ions are released to the solution as per the reaction

$$Fe_3O_4 + 8H^+ \rightarrow 2Fe^{3+} + Fe^{2+} + 4H_2O \qquad (6)$$

whereas in base metal aided dissolution, only ferrous ions are produced as given in Eq. (3). Thus, the base metal (Fe) acts as an effective reductant and converts the Fe^{3+} present in the film to Fe^{2+} enabling faster dissolution. It is expected that addition of an external reducing agent would similarly enhance the dissolution rate. Measurements with EDTA–citric acid (EC) formulation and EAC formulation (containing ascorbic acid) indicated that the magnetite film dissolution rate enhancement did not occur. This observation indicated that the ascorbic acid poorly competes with the base metal in reducing the Fe^{3+} in the magnetite film. The oxide dissolution rates observed with the EDTA and EDTA based formulations are given in Table 3.

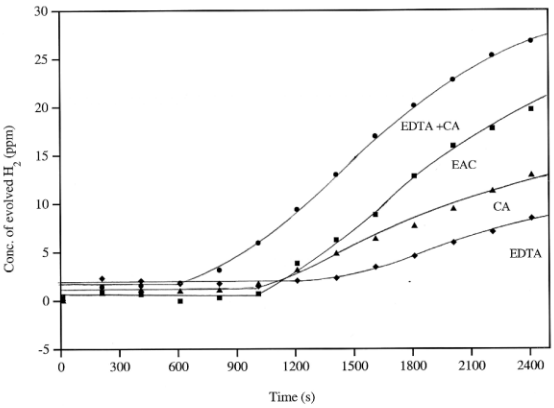

Fig. 3. H_2 evolution from CS having 5 μm thick Fe_3O_4 film in EAC formulation (EDTA – 1.37, AA – 1.7 and CA – 1.4 mM) and its constituents at 85°C.

Table 2
Magnetite film thickness lost at the time of hydrogen liberation at 85°C in various formulations

Formulation	Concentration (mM)	Magnetite dissolved (in thickness equivalents) (μm)
EAC	1.37 + 1.7 + 1.4	2.5
HEEDTA	1.37	2.54
CA	3.00	3.13
PDCA + AA	2.75 + 1.7	3.09
PDCA + CA	2.75 + 1.4	2.99
Mean		2.85

As expected, the temperature was found to have significant effect on the film dissolution in organic acid medium. Dissolution carried out in the temperature range 40–85°C indicated that at temperatures about 40°C the dissolution of magnetite film in EAC formulation was very poor (Fig. 4). Thus, temperature is a crucial parameter for magnetite film dissolution.

Table 3
Magnetite film dissolution rate and corrosion rates of carbon steel in EAC formulation and its constituents

Formulation	Concentration (mM)	Oxide dissolution rate (μm/h)	Corrosion rate (μm/h)
EDTA	1.37	7.8	3.1
Citric acid	3.00	12.1	1.4
EDTA + CA	1.37 + 1.4	16.3	5.6
EAC	1.37 + 1.7 + 1.4	13.7	6.6

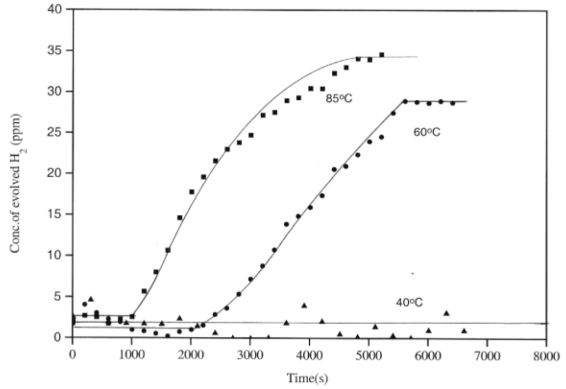

Fig. 4. Effect of temperature on Fe_3O_4 film dissolution and corrosion of CS in EAC formulation.

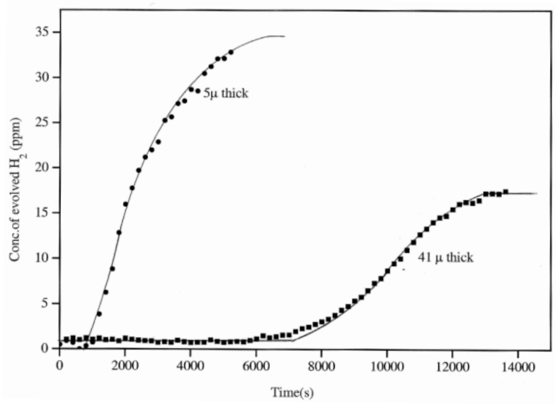

Fig. 5. H_2 evolution behaviour from CS specimen having 5 μm and 41 μm thick Fe_3O_4 films when exposed to EAC formulation of 85°C.

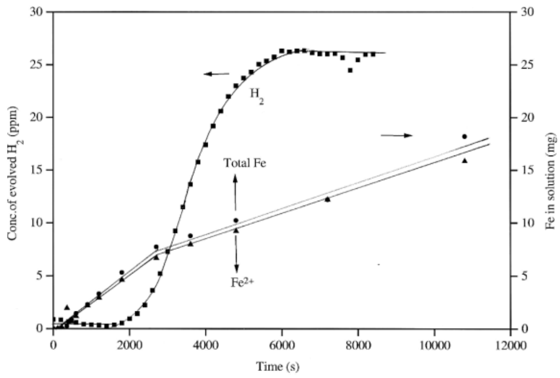

Fig. 6. A plot of H_2 evolved vs time when a CS specimen having 41 μm thick Fe_3O_4 films when exposed to 10 mM PDCA medium at 85°C. The plot also gives concentration of Fe^{2+} and total Fe (Fe^{2+} and Fe^{3+} released to the solution as a function of time.

The dissolution study carried out with a carbon steel specimen having a 41 μm thick magnetite film in EAC formulation at 85°C indicated that the dissolution rate does not vary much with the thickness of the film. For the 5 μm film, a dissolution rate of 13.7 μm/h was observed whereas for the 41 μm thick film, the estimated dissolution rate was 18 μm/h. The CS with the thick magnetite film exhibited a corrosion behaviour that is similar to that of the specimen having a thin film. (Fig. 5). It took 122 min for the hydrogen evolution to start (ca. 13 min for dissolving the 2.85 μm in the 5 μm film). Similar dissolution rates indicate that the thick film also undergoes base metal aided reductive dissolution from the beginning. Estimation of iron in solution at the time when hydrogen started to evolve indicated that iron equivalent to 37 μm magnetite film has been brought to solution.

In order to quantify the extent of base metal aided dissolution, the amount of Fe^{2+} and Fe^{3+} released to the solution during the magnetite film dissolution was estimated. Experiments carried out with the CS specimen with 19 μm thick magnetite layer in 10 mM PDCA solution indicated that the entire iron released during the dissolution was in the form of Fe^{2+} (Fig. 6). Absence of Fe^{3+} in the solution indicated the absence of simple acid dissolution reaction that would release Fe^{3+} from the oxide without the involvement of base metal. The above figure also gives the hydrogen release curve as a function of time. The slope of the iron vs time curve decreases as soon as the hydrogen started evolving thereby indicating the reduction in the iron release rate after the base metal corrosion reaction starts. During the period, in which only the magnetite dissolution occurs, the iron vs time curve is quite linear indicating that the film dissolution rate and in turn the iron release rate remains constant from the beginning of the film dissolution till the corrosion reaction liberating H_2 starts. During this stage, the estimation of iron in solution indicated that 17 μm equivalent of magnetite has been dissolved, thereby confirming that hydrogen starts to evolve only after reaching a thickness value of 2 μm.

3.3. Dissolution of haematite film formed over CS

The above observation was confirmed by a study carried out using a carbon steel specimen with a haematite (α-Fe_2O_3) coating of 37 μm thickness. The haematite contains only Fe^{3+} ions in the oxide lattice, however, when it was exposed to a solution containing 1.37 mM EDTA at 85°C under inert condition and the solution analyzed for Fe^{2+} and Fe^{3+} indicated that more than two third of the iron released was in Fe^{2+} state. Fig. 7. This experiment when repeated in PDCA medium indicated that during the dissolution of haematite film, iron was released only in Fe^{2+} state Fig. 8. The two lines in Fig. 8 representing the amount of Fe^{2+} and the total iron lie one over the other indicating that only base metal aided dissolution take place from the beginning hence only Fe^{2+} was released. The observation of small amount of Fe^{3+} in the case of haematite dissolution in EDTA medium is attributed to the presence of some oxygen impurity in the argon gas which is known to convert rapidly the Fe^{2+} existing in the form of Fe(II)-EDTA to Fe(III)-EDTA. Also, some oxidation is expected while taking the sample for analysis. An experiment was carried out to understand the stability of Fe(II)-EDTA and Fe(II)-PDCA in solution at 85°C. These complexes were prepared individually in solution under deaerated condition. The concentration of Fe^{2+} and total iron concentration in solution was estimated as a function of time. The results showed that by purging the solution with the argon gas, the Fe(II) concentration in EDTA medium decreased to 60% of the initial value with in three hours. When the Fe(II)-EDTA solution was exposed to air, the entire Fe(II)-EDTA was converted to Fe(III)-EDTA with in two hours. Same experiments when repeated with PDCA indicated clearly that Fe(II)-PDCA is quite stable to oxidation by air. Neither under the argon purged conditions nor under the aerated conditions, conversion of Fe(II)-PDCA to Fe(III)-PDCA was observed. Thus, only results of experiments carried out in PDCA medium represent the actual iron release behaviour during dissolution.

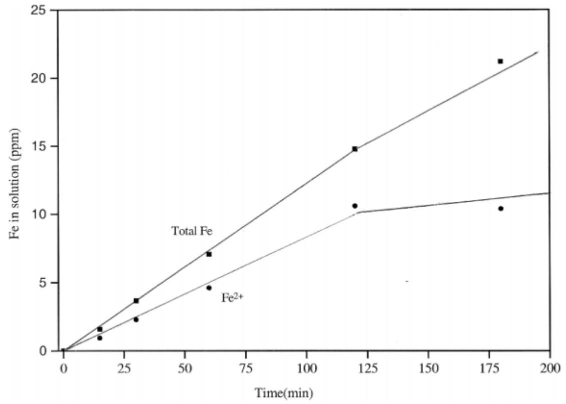

Fig. 7. Comparison of Fe^{2+} and total Fe (Fe^{2+} and Fe^{3+}) released to the solution when a CS specimen having 37 μm α-Fe_2O_3 was exposed to 1.37 mM EDTA solution at 85°C.

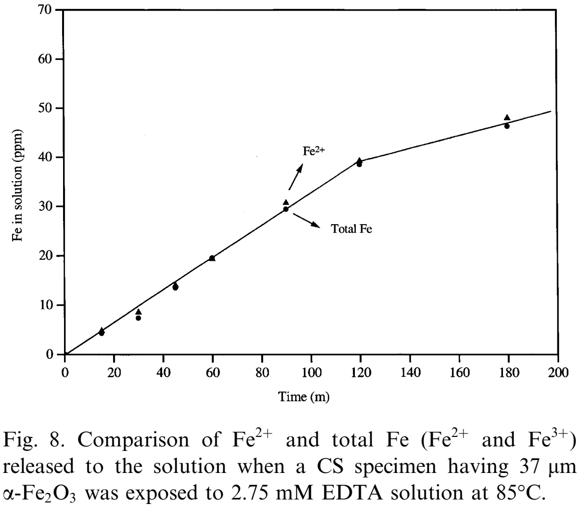

Fig. 8. Comparison of Fe^{2+} and total Fe (Fe^{2+} and Fe^{3+}) released to the solution when a CS specimen having 37 μm α-Fe_2O_3 was exposed to 2.75 mM EDTA solution at 85°C.

3.4. Effect of loading the formulation with iron on the dissolution of Fe_3O_4 film

Dissolution of magnetite powder in organic acid medium was found to depend very much on the pH of the medium. In the case of magnetite powder maximum dissolution was observed in the pH range 2–3 [14]. To understand the role of pH in the dissolution of magnetite film, experiments were carried out using EAC formulation at 85°C. The pH of the formulation was altered by dissolving iron powder to get iron concentration in the solution of 100–300 ppm to get the variation in the pH from 2.7 to 4. The results showed as the pH of the solution increased there was a noticeable decrease in the oxide dissolution rate (Fig. 9). One exception to this rule was, with the 100 ppm iron containing EAC formulation, the film dissolution rate was slightly faster than in simple EAC formulation. This may be attributed to the enhancement in the dissolution rate observed in the presence of Fe (II)-EDTA that acts as a better reductant than the ascorbic acid. At higher iron concentration in solution, the pH effect outweighs the effect due to Fe(II)-EDTA. At 300 ppm iron concentration the complexing capacity of the complexing agents present in the EAC formulation viz. EDTA, ascorbic acid and citric acid are exhausted, hence no magnetite dissolution took place. However, when a polished carbon steel coupon was exposed to 300 ppm iron containing EAC formulation, hydrogen evolution

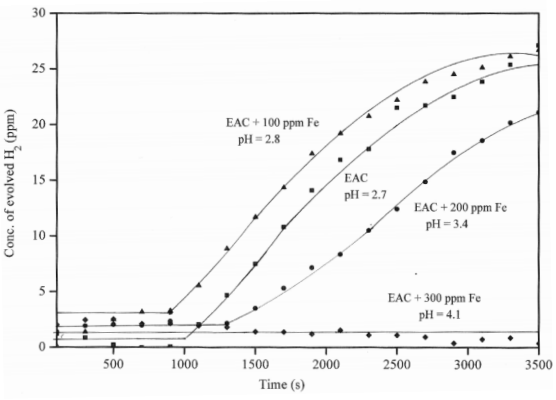

Fig. 9. Effect of loading EAC formulation with iron on the dissolution of 5 μm Fe_3O_4 coated CS and on the H_2 evolution at 85°C.

was observed indicating that at this concentration base metal corrosion can take place.

3.5. *Dissolution of magnetite in PDCA medium*

Pyridinedicarboxylic acid (PDCA) is effective in dissolving the magnetite film [15] by the autoreduction process. Experiments were carried out with PDCA, PDCA–citric acid and PDCA–ascorbic acid–citric acid formulations. The hydrogen evolution behaviour was very much akin to that observed in EDTA and EDTA based formulations. The oxide dissolution rates and the corrosion rates observed with PDCA and PDCA-based formulations are given in Table 4. The effect of concentration of PDCA on the magnetite film dissolution was studied. Within the concentration range studied, it was observed that the dissolution rate increased with increase in the concentration of PDCA in solution (Fig. 10).

3.6. *Influence of CA in the dissolution of magnetite film*

A set of experiment was carried out with various chelating agents and in presence of CA and the results are given in Table 5. It was found that PDCA, EDTA, CA and HEEDTA, when tested individually, exhibited almost similar dissolution rate for magnetite film whereas NTA and DTPA showed higher dissolution rates. The presence of CA along with NTA showed a decrease in the magnetite dissolution, the rate was reduced from 22.5 to 5.7 μm/h. Addition of CA to HEEDTA was found to enhance the dissolution rate significantly. The rate increased from 12.7 to 90 μm/h. Similar increase in dissolution rate was observed in experiments carried out with powder and the effect was attributed to the adsorption of HEEDTA and citric acid together on the magnetite surface favouring the dissolution process.

Table 4
Magnetite film dissolution rate and corrosion rate in PDCA based formulations

Formulation	Concentration (mM)	Oxide dissolution rate (μm/h)	Corrosion rate (μm/h)
PDCA	2.75	10.0	4.2
PDCA + CA	2.75 + 1.4	18.7	6.3
PDCA + AA	2.75 + 1.7	23.0	2.5
PDCA + CA + AA	2.75 + 1.4 + 1.7	16.9	6.3

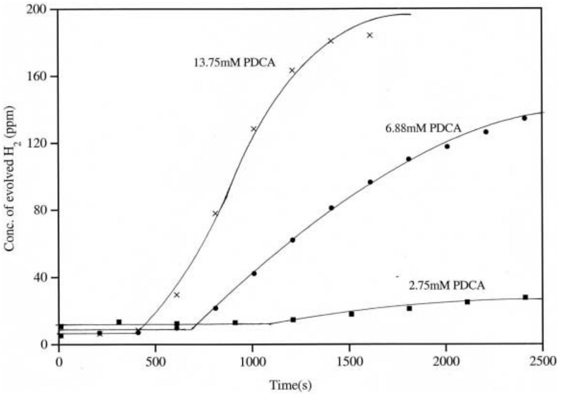

Fig. 10. Effect of varying the concentration of PDCA in the dissolution of Fe_3O_4 at 85°C on 5 μm thick magnetite film formed over CS.

Table 5
Influence of 1.4 mM CA in the dissolution of magnetite film in various complexing agents at 85°C

Formulation	Concentration (mM)	Magnetite dissolution rate (μm/h)	
		Absence of CA	Presence of CA
CA	3.00		12.1
PDCA	2.75	10.0	18.7
NTA	1.37	22.5	5.7
EDTA	1.37	7.8	16.3
HEEDTA	1.37	12.7	90.0
DTPA	1.37	19.6	21.7

3.7. *Mechanism of magnetite film dissolution*

The magnetite dissolution rates observed with various chelating agents when employed in the concentration range 1–3 mM lie in the range 7–23 μm/h, whereas the corrosion rates were found to vary in the range 2–7 μm/h. These data clearly indicate that for any single complexing agent or for any combination of complexing agents, the magnetite film (when coated over CS) dissolution rates are always higher than the base metal corrosion rate, by a factor of 2–3. After applying the correction for density and the oxygen contribution, the rate of iron release from magnetite film is larger than the iron release rate from the base metal corrosion reaction. This will ensure complete dissolution of magnetite even in a thin film where simultaneous magnetite film dissolution and base metal corrosion reaction take place.

It is evident that even in carbon steel having thick magnetite film, the base metal aided dissolution takes place from the beginning. Also, till the magnetite film is reduced to about 2 μm, no hydrogen liberation takes place.

This implies that when base metal aided dissolution is taking place, the corrosion reaction that evolves hydrogen is not favored. The absence of the corrosion reaction during most part of base metal aided dissolution is attributed to the fact that the base metal aided magnetite dissolution reaction is thermodynamically more favorable than the corrosion reaction. The EMF value for the base metal aided dissolution reaction (Eq. (7)) is +400 mV vs SCE and for the corrosion reaction (Eq. (8)) that evolve hydrogen is −400 mV. These EMF values suggest that the former reaction is favorable as compared to the latter.

$$Fe_3O_4 + 8H^+ + 2e^- \rightarrow 3Fe^{2+} + 4H_2O \tag{7}$$

$$2H^+ + 2e^- \rightarrow H_2. \tag{8}$$

The other possibility is that the formulation does not get access to the base metal and hence it does not react with the base metal. The mechanism of dissolution of oxide films, proposed by several authors, invoke the existence of pores in the oxide film leading to the base metal. It is assumed in these models that the organic acids come in contact with the base metal through these pores and enable the base metal aided dissolution reaction. The Fe^{2+} released from the base metal is transported through the solution in the pore and the electrons (e^-) through the conducting oxide layer. It is anticipated from these models that the higher the thickness of the oxide layer, the more difficulty for the acids to get access to the base metal, as the number of pores leading to the base metal decreases with thickness. Thus, base metal aided dissolution is expected to decrease with increase in thickness. However, it was observed in our experiments that the dissolution rate is more or less same with 5 and 41 μm thick magnetite films. Also, the data on iron release obtained in the experiments carried out to observe the iron release as a function of time indicated that during the dissolution of film the concentration of iron in solution was found to linearly increase with time (Fig. 6). This indicated that the rate of film dissolution remained constant till the hydrogen started evolving.

The model of magnetite formation as proposed by Robertson [16] envisages that the oxide layer as consisting of grains and the Fe^{2+} formed during the oxide formation reaction is transported through the grain boundary of the oxide and the electron through the oxide layer. The observations made in this work favour the latter model for the transport of Fe^{2+} formed in the metal-oxide interface during the base metal aided magnetite film dissolution reaction.

4. Conclusions

(1) The corrosion reaction in the magnetite filmed CS sets in only after the thickness of the magnetite layer is reduced to about 2 μm.

(2) The magnetite film dissolution rate remained constant till the corrosion reaction set in, and thereafter, the rate decreased considerably.

(3) The magnetite film dissolution rate in the various organic complexing acid media were greater than the corrosion rate of carbon steel base metal in the corresponding acid.

(4) The dissolution behaviour of magnetite film in organic chelating medium was found to be very much different from magnetite powder. The film dissolution was affected only marginally with the nature of the chelating agent. Ascorbic acid, an organic reducing agent, hardly had any effect on the film dissolution.

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