The Dissolution Rate Constant of Magnetite in Water at Different Temperatures and Neutral or Ammoniated Chemistry Conditions

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Abstract

In this study, the dissolution rate constants of magnetite were measured at various water chemistry conditions and different temperatures, corresponding to several feedwater conditions of water-cooled reactors. Sintered magnetite pellets were used as the dissolving material and these were mounted in a jet-impingement apparatus in a recirculating water loop. Exposures were carried out at temperatures of 25, 55 and 140ºC and pHs of neutral and 9.2 in which many FAC (Flow Accelerated Corrosion) studies have been conducted. Average dissolution rate constants were estimated by measuring the volume of lost material with a profilometry technique. The excellent correspondent between the calculated value of dissolution rate constant of 2.20 mm/s for the synthesized magnetite and 2.05 mm/s for the single crystal of magnetite at neutral condition shows that the particle removal from the synthesized pellets is not an obstruction in this technique. Also, good agreement between the values calculated in duplicated runs at neutral condition at room temperature supports the accuracy of the method.

1. Introduction

In cooling-water systems with low oxygen in which carbon steel is used as the structural material, magnetite is the most common iron oxide generated as the corrosion product over a range of temperatures. It acts as a protective layer and reduces further corrosion of the underlying steel. In the corrosion process, some of the iron dissolved as ferrous species precipitates as magnetite at the metal-oxide interface and takes up the volume of the corroded metal while the remaining ferrous species diffuse through the developing magnetite film to the solution. When the water is saturated with dissolved iron, magnetite precipitates at the oxide-solution interface and builds up the second outer layer. Wherever the solution is not saturated with dissolved iron there is no precipitated outer layer and the single layer formed at the metal-oxide interface by corrosion dissolves at the oxide-solution interface. The undersaturation in feedwater and other coolant systems commonly occurs through temperature gradients (since the solubility of magnetite depends on temperature [1]) and through the condensation of steam [2,3]. This dissolution of the magnetite layer in unsaturated water reduces its protective nature and causes higher corrosion rates. To be able to predict the corrosion rate accurately the dissolution rate of magnetite should be known.

Unfortunately, there are very few reported measurements of the dissolution rate of magnetite at system temperatures. Moreover, the results of the two determinations of the dissolution rate of magnetite in alkaline water at 300ºC show large discrepancies [4, 5]. Therefore, to obtain dissolution rate constants under a range of conditions, an experimental apparatus for installation in a water loop was designed and built. The results for a preliminary run at 300 ºC were reported elsewhere [6]. Here, the results obtained at several other temperatures and water chemistry conditions are presented.

2. Methodology

The first step was to provide magnetite of the right form to simulate corrosion-product films found on corroded carbon steel. Magnetite samples were made by solid-state mixing and vacuum sintering of hematite and iron powder mixtures followed by compaction to pellets and sintering in an argon atmosphere. Details of these steps can be found in reference [6].

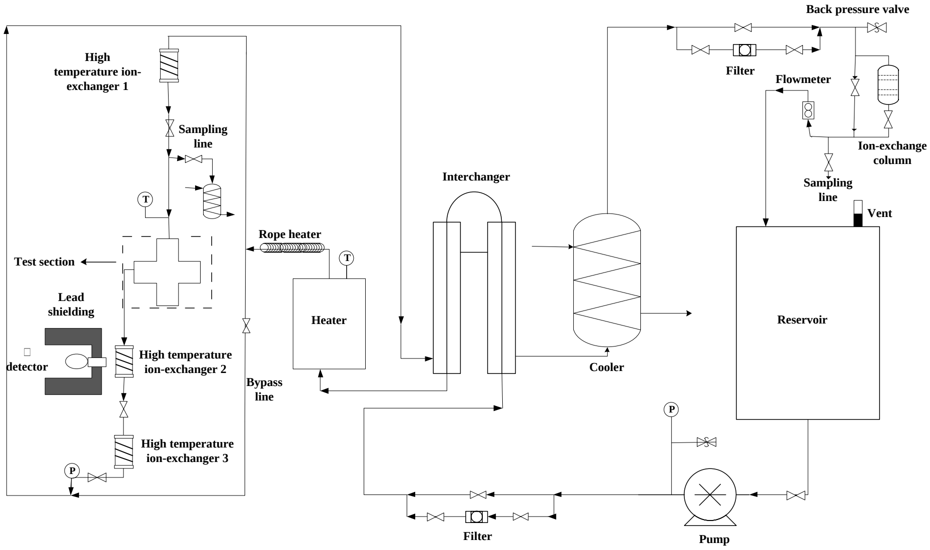


Figure 1 Schematic diagram of the recirculating loop adapted from [6].

The dissolution experiments were conducted in a recirculating loop (Figure 1). In this loop, de-ionized water with the required chemistry (neutral or $\text{pH}_{(25^{\circ}\text{C})}$9.2 with ammonia) is pumped from a 60-litre reservoir through the interchanger, heater and ion-exchange column to the test section. The circulating water returns to the tank after being cooled in the interchanger and then the cooler. The test section is a Swagelok union cross with a 0.5 mm diameter jet in the upper arm facing downward. The water impinges onto the magnetite pellet inside the cross and leaves it from one of the horizontal arms. The distance between the jet and the pellet is between 1-3 mm (2-6 times jet diameter). For electrochemical measurement purposes, three electrodes are connected to a Gamry PCi4/300 potensiostat/galvanostat: a silver ring around the jet with a silver wire lead is the counter electrode, the pellet with an embedded platinum wire is the working electrode and a high-temperature Ag/AgCl electrode (Corr Instruments) is the reference electrode. The pellet and all the wires inside the test section are electrically isolated from their surroundings with a Teflon holder and heat shrinks respectively. Two high-temperature ion-exchange columns are located after the test section and a high-purity Ge gamma detector is placed in front of the upstream one in case of need for conducting radio-tracing experiments on irradiated magnetite in future steps of the work. This will count the gamma radiation emanating from the column as dissolved radioactive species accumulate on the ion-exchange material, giving instantaneous dissolution rates accurately. In the non-radioactive experiments, average dissolution rates were calculated by measuring the total volume of the craters created by magnetite dissolution. Crater volume was calculated from a series of surface profiles of the pellets made of small intervals with a mechanical profilometer. These profiles were then integrated to give the overall volume. Having the crater volume along with the density of the magnetite and the area of the dissolution made it possible to calculate the average dissolution rate. Subsequently, the dissolution rate constant of magnetite at each condition was calculated by dividing the dissolution rate by a literature-value of the solubility. The profile measurements were carried out with several different instruments: a Trioptic 0812; an Ex-cello.0 Milling Machine with Acu- Rite.5 digital reading; a NewView7300 laser instrument with Zygo MetroProTM analysis software (which gave a 3D picture of the crater and its volume); and, for most determinations, a Taylor-Hobson Surtronic 25 profilometer. The results from all the above instruments showed good agreement.

3. Results and discussions

Table 1 summarizes the experimental runs which have been conducted so far.

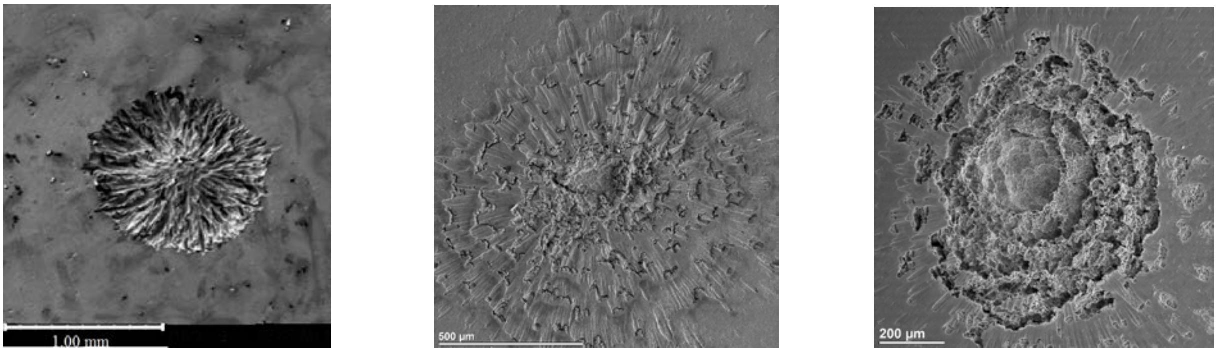
Run	Time (hour)	Temp. (° C)	pH (25°C)	Purging gas	Mean oxygen concentration (ppb)	Mean hydrazine concentration (ppb)	Potential (V vs SHE)
1	187.5	140	Neutral	Hydrogen	0	0	-----
2.1	146	140	9.2	Argon	20	20	-----
2.2	504	140	9.2	Argon	0-5	40	-----
2.3	506	140	9.2	Argon	0-5	30	-----
2.4	504	140	9.2	Argon	-----	40	-0.421
2.5	504	140	9.2	Hydrogen	10	40	-0.30 (OCP)
3.1	239.5	25	Neutral	Hydrogen	5-20	0	0-+0.9 (OCP)
3.2	242.5	25	Neutral	Hydrogen	5-15	0	+0.4 (OCP)
4	360	55	Neutral	Hydrogen	5	0	+0.4 (OCP)
*5	263	140	Neutral	Hydrogen	0	0	-----

*Run 5 was conducted on a single crystal of magnetite

Table 1 Experimental conditions of different runs.

Neutral conditions (Runs 1,3 and4) correspond to the conditions of feedwater in BWRs while the alkaline condition of Run 2 is similar to that of the feedwater of dual-cycle reactors and fossil-fuelled power plants. At 140^0 C, magnetite has a high solubility in neutral conditions and has a correspondingly high FAC rate. In alkaline water, solubilities and FAC rates are much lower.

In Runs 1, 3 and 4, a circular area with a diameter of about 1mm (twice the jet diameter) showed the highest impact of the dissolution. Outside this region, precipitates on the surface were observed in SEM pictures. The conditions of the Run5 are identical to Run1 other than using a single crystal of magnetite as the dissolving sample instead of a synthesized pellet. No sign of dissolution was detected in the Run2 experiments and the pellet retained its original surface throughout the exposure (except for Run2.2). The dissolved area in Run 2.2 was the lower half of a torus and the dissolution rate constant calculated for this case was unusually high; sub-surface voids in the pellet that opened under the impact of the jet could have been responsible. The result could not be repeated and therefore, disregarded. The Run3.1 and Run3.2 experiments were done under identical conditions and produced consistent results.



a) b) c)

Figure 2 SEM picture of the dissolved area on the pellets after exposure in
a) Run1 b) Run3 c) Run4

Table 2 summarizes the calculations of dissolution rate constant of magnetite at each experimental condition. The mass transfer coefficient (k_m) is also calculated for each condition using the correlation given in [7] for impinging jets. In all conditions, the calculated mass transfer coefficient is higher than the calculated dissolution rate constant (k_d), indicated that the process is not limited by mass transfer.

	Temp. (° C)	pH (25°C)	Reynolds No.	k_m[1](mm/s)	Solubility (g/cm^3)	k_d[2] (mm/s)
Run1	140	Neutral	45000	13.90	$1.29*10^{-7}$	2.20
Run2	140	9.2	45000	13.90	$1.30*10^{-8}$	<0.02[3]
Run3	25	Neutral	10000	2.79	$8.90*10^{-8}$	0.25±0.05
Run4	55	Neutral	20000	5.26	$1.03*10^{-7}$	0.85
Run5	140	Neutral	45000	13.90	$1.29*10^{-7}$	2.05

[1] Calculated from the correlation in [7]
[2] Calculated from the total lost volume of magnetite, using the solubility value from Tremaine and Leblanc [1].
[3] from SEM pictures

Table 2 Summary of calculated values for dissolution rate constant and mass transfer coefficient.

4. Conclusion

The calculated dissolution rate constants at three temperatures in neutral chemistry vary as the solubility of magnetite at those temperatures, both increasing with increasing temperature up to 140°C. The dissolution rate was below the detection limit for the ammoniated condition of Run 2. The radio-tracing technique which is more sensitive could be employed to get the dissolution rate constant at this condition. These results indicate that oxide film dissolution is the process controlling in FAC in the feedwater of the power plants, although under neutral conditions mass transfer will have some influence.

Acknowledgment

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5. References

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