Article

Galvanic Sensor for Detecting Corrosion during Acid Cleaning of Magnetite in Steam Boilers

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Abstract: A simple galvanic sensor was developed to determine the onset of iron corrosion under conditions similar to those used for removing the iron oxide (magnetite) layer from steam boilers with a hydrochloric acid solution. Since the potentials of magnetite and iron are different, the initiation of the dissolution of the magnetite layer without corroding the base metal can be determined by monitoring the potential of a sensor made of magnetite layers of different thicknesses that can be placed directly on the iron surface. Moreover, the time at which the addition of corrosion inhibitors is required to protect the base metal can be specified using this sensor. It has been shown that the time required for the iron base metal to start was dependent on the magnetite layer thickness in the sensor. With this sensor, the onset of the steel corrosion during the cleaning can be detected in real-time which makes the oxide removal process less harmful to the base metal.

Keywords: sensor; steam boiler; acid cleaning; magnetite; oxide

1. Introduction

Steam, generated from boilers of different sizes and types, is used in many industrial plants for process applications and power generation. Industrial boilers are considered critical parts of industrial facilities, as they are directly linked to production to make the business profitable. Steam boilers are made of carbon steel and the inner side of the boiler tubes are in contact with water. Thus, the formation of solid deposits on that side of the tubes is a progressive and inevitable process, even when the water and steam chemistry is carefully controlled, leading to reduced boiler efficiency and increased fuel consumption. In particular, a 2.8 mm thick deposit can increase fuel consumption by 16% [1]. Moreover, steam at a certain temperature can react with iron, forming iron oxide and particularly magnetite (Fe₃O₄) when the environment inside the boiler is reductive. Thick magnetite layers may also lead to deposit corrosion, reduce the water circulation inside the boiler, and overheat the tubes. Therefore, the inner surface of the boiler tubes must be cleaned and kept free of unwanted deposits to ensure that the temperature of the tube wall will not cause damage to the boiler. Chemical cleaning is usually preferred compared to other cleaning methods (e.g., mechanical) to ensure that all deposits are removed from the boiler’s internal surfaces, while an inhibited acid solution is commonly used depending on the composition and thickness of the deposits. When the deposit is magnetite, hydrochloric acid (HCl) is the most commonly applied solvent [2]. Previous studies have shown that HCl is more effective than other inorganic and organic acids in dissolving scale deposits collected from the tubes of an industrial water tube boiler at a specified time [3]. In a typical procedure, the boiler is filled with 5–10% HCl at around 65 °C in a static condition. As HCl is very corrosive, it takes about 500 min to remove the deposits [4]; the cleaning process can also cause corrosion unless carefully controlled [5]. Moreover, iron has shown a high corrosion rate during the removal of magnetite sludge with a solution containing 20% ethylenediamine tetraacetic acid (EDTA) at 120 °C [6].
However, due to the high aggressiveness of HCl, the use of corrosion inhibitors is required during chemical cleaning to control the base metal corrosion [2,7]. In recent years, several studies have investigated the development and application of corrosion inhibitors for iron corrosion [7–9]. Among them, compounds based on amine and thiourea derivatives and cinnamaldehyde have been evaluated as corrosion inhibitors for descaling solutions [7,8]. Moreover, the removal of magnetite grown on iron has been achieved using a buffer solution containing HCl, disodium citrate, and thiourea as the corrosion inhibitor at 80 °C [10].

Nevertheless, there is still a need for monitoring the rates of the two processes occurring during chemical cleaning, i.e., the oxide dissolution and the corrosion of the base metal, to identify the process with the highest rate. In addition, the appropriate time for the injection of the corrosion inhibitors to control the corrosion of the base metal needs to be determined, as the corrosion inhibitors may delay or interfere with the oxide dissolution process [11].

Furthermore, the acid cleaning of the boiler needs to be closely monitored, because, at the beginning of the process, the deposit and the protective oxide are removed, exposing the coated bare metal to the solution. When removing the magnetite layer from the iron surface, a galvanic coupling between them is possible, affecting the kinetics of the magnetite and iron dissolution. Due to this coupling, the dissolution of magnetite takes place chemically according to the following reaction [12], which shows that the oxidation of the base metal is part of this reaction.

\[
\text{Fe}_3\text{O}_4 + \text{Fe} + 8\text{H}^+ \rightarrow 4\text{Fe}^{2+} + 4\text{H}_2\text{O} \quad (1)
\]

Moreover, the iron content in the acid used for washing is chemically analyzed to monitor the cleaning process, which is considered to be an indirect method. The corrosion of the underlying metal can be detected in two different ways: either by detecting the agent that causes corrosion, such as chloride ions or by detecting the products of the corrosion process, such as hydrogen. Moreover, the corrosion can be directly detected on the entire or part of the corroded material, which is also considered to be an indirect method. In previous studies, a coupled multielectrode array sensor has been used successfully to detect the onset of localized and non-uniform corrosion in many applications such as evaluation of corrosion inhibitors, corrosion of alloys in chemical plants, microbial corrosion, and corrosion under salt deposits [13–18]. Moreover, fiber optical sensors have been used to measure the scaling in the heat exchanger of a cooling water tower in power generation and paper mill plants [19].

The purpose of this study was to simulate the cleaning process of a magnetite layer over iron in HCl and determine the time required to dissolve this layer using a sensor consisting of a two-layer electrode made of magnetite and iron. Also, the sensor was used to determine the onset of the corrosion of bare iron. Therefore, the developed sensor could be used to determine when the magnetite layer dissolves without the contribution of the underlying metal and when it is necessary to add a suitable corrosion inhibitor to protect the underlying metal.

2. Experimental

Magnetite powder (BDH) was mixed with a polyvinyl alcohol solution, which was used as a binder, forming pellets by applying a pressure of 7 tones/cm². The pellets were then sintered in the presence of N₂ gas flow. Afterward, the temperature was gradually increased by 50 °C, held for 30 min at 900 °C, and reduced gradually. The iron samples were prepared from an iron rod with the following composition: C 0.2%, Mn 0.94%, Si 0.31%, and Fe 98+% (Goodfellow, England). The magnetite layer was formed on iron coupons in an autoclave as described in a previous study [20].

The electrodes were formed by attaching the prepared magnetite pellets with different thicknesses to iron cylinders with the same diameter. An epoxy resin was used to cover the electrode, exposing only magnetite to the solution, as shown in Figure 1. The X-ray diffraction (XRD) measurements of the magnetite powder and pellets were performed
using a MiniFlex-600 (Rigaku) instrument with Cu Kα irradiation (voltage: 40 kV, current: 15 mA). The potential and linear polarization measurements were conducted in 5% HCl at 60 °C using a saturated calomel electrode as the reference electrode and a platinum electrode as the auxiliary electrode. The solution was stirred using a magnetic stirrer. The potentials of the individual electrodes were also measured under the same conditions. Moreover, the linear polarization resistance ($R_P$) was measured using a Gill AC potentiostat (ACM instruments, Cumbria, UK) with a scan rate of 0.16 mV/s and a range of ±10 mV from the corrosion potential.

![Figure 1](image1.png)

Figure 1. Schematic diagram of the two-layer (magnetite/iron) electrode.

3. Results and Discussion

3.1. Electrochemical Measurements with the Magnetite/Iron Couple

The electrochemical measurements were performed using electrodes as illustrated in Figure 1.

![Figure 2](image2.png)

Figure 2. XRD patterns of the magnetite powder, magnetite pellet, and magnetite film formed on the iron surface.

The variation of the potential of magnetite and iron as single electrodes over time in 5% HCl at 60 °C was also measured (Figure 3). The values in Figure 3 are the average of three measurements with a standard deviation of 0.002–0.08 V. Moreover, the potential of the magnetite electrode was nearly constant and different from that of the iron electrode. It is known that magnetite dissolves according to the reaction [21–24]:

$$\text{Fe}_3\text{O}_4 + 2e + 8\text{H}^+ \rightarrow 3\text{Fe}^{2+} + 4\text{H}_2\text{O} \quad (2)$$
with a potential (E) that can be calculated as follows:

\[ E_{Fe_3O_4/Fe^{2+}} = E^0 - \frac{RT}{2F} \ln \left( \frac{[Fe^{2+}]}{[H^+]} \right)^3 \]  

(3)

where \( E^0 = 0.98 \) V vs. NHE. In contrast, iron corrodes according to the reaction

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e \]  

(4)

and its free potential can be calculated by the following equation

\[ E_{Fe/Fe^{2+}} = -0.440 + \frac{RT}{2F} \ln [\text{Fe}^{2+}] \]  

(5)

Figure 3. Potential–time curves of the iron (a) and magnetite (b) electrodes in 5% HCl at 60 °C.

Reactions (2) and (4) represent the free dissolution of magnetite and iron, respectively, without interference from each other.

Further measurements were also performed, where the magnetite pellets with variable thicknesses were attached to the iron electrodes, and the potential was measured as a function of time. As shown in Figure 4, the measured potential was initially (~60 min) similar to that of the magnetite electrode (Figure 3), whereas, after an amount of time which depended on the thickness of the magnetite pellet, the potential started to change significantly until it reached the potential of the iron electrode (Figure 3). Similar results have been observed in a previous study on iron samples obtained from the magnetite-coated inner surface of a boiler [4].
Figure 4. Potential–time curve of the magnetite pellets of different thickness values attached to the iron electrode in 5% HCl at 60 °C.

The potential observed during the first hour of immersion indicated that magnetite dissolved freely and without the contribution of iron dissolution. However, as the dissolution progressed, the magnetite thickness was reduced or magnetite became more porous, exposing a small area of iron to the solution. Thus, the measured potential deviated from the initial potential value of magnetite, depending on the extent of the relative exposed iron area. Consequently, a mixed potential was measured for the magnetite/iron couple, which was controlled by the rates of all the processes occurring at the same rate at this potential, i.e., the dissolution of magnetite and iron and the evolution of hydrogen gas. These results agreed with the results of earlier studies, where it was also shown that the potential of a galvanic magnetite/iron coupling depended on the area ratios between magnetite and iron and tended to be closer to that of iron as its relative area increased [25–28]. As the process progressed and the relative exposed area of iron to the medium increased, the potential of the short-circuited magnetite/iron couple became similar to that of iron. The variation of the potential of the galvanic couple over time could be explained by the schematic Evans diagram (Figure 5a). More specifically, the change in the potential depended on the kinetics of the anodic and cathodic reactions and the ratio of the relative exposed areas of magnetite and iron to the solution. When the experiment was completed, a severe iron attack was observed, which was significantly dependent on the magnetite/iron area ratio, as shown by the photo in Figure 5b which shows the formation of cracks on the magnetite surface that allows the acid to reach the iron base metal which coincides with the shift of the potential towards that of iron. In particular, the iron attack was enhanced when the relative exposed area of iron was small due to the large shift of its potential in the anodic direction when it was galvanically coupled to magnetite. Moreover, the variation of the time required for the potential to shift toward that of iron was different from one electrode to another when the thickness of the magnetite pellet was kept constant due to the variations in the characteristics of the magnetite pellets. In addition, when the magnetite thickness increased, the time needed for the potential shift toward that of iron also increased (Figure 6), suggesting that the dissolution or penetration of thicker magnetite pellets was more time consuming.
Figure 5. (a) Schematic Evans diagram for the magnetite/iron galvanic couple and the change in its potential by changing the relative magnetite and iron areas exposed to the solution. (b) An optical photo of the magnetite layer (thickness 0.8 mm) was taken before and after exposure of the sensor to the acid for 2 h at 60 °C where visible cracks can be seen on the surface.

Figure 6. Effect of magnetite thickness on the time required to reach the potential of iron in 5% HCl at 60 °C.

Although these results cannot indicate the minimum time needed for the complete removal of the oxide from the iron surfaces, they can indicate the tendency of the removal process, and most importantly, specify when the iron is attacked by the acid used for cleaning. To further confirm the increased corrosion attack on the iron substrate when the galvanic potential of the magnetite/iron couple was between that of magnetite and iron (Figure 3), a series of Rp measurements were performed at different times using an electrode made of a 0.85 mm thick magnetite pellet coupled with the iron electrode. In the initial stage of the cleaning process, the Rp values were high (Figure 7), close to the potential of magnetite. However, the Rp values tended to decrease over time, reaching very low values at around 400 min, indicating the corrosion of iron. This large decrease in the Rp value was observed when the potential of the galvanic couple was close to the iron potential.
3.2. Application of the Sensor in a Boiler Tube

The sensor used in this study was fabricated from a magnetite pellet, which was prepared by pressing and sintering magnetite powder and subsequently attached to an iron electrode. To simulate the actual operating conditions in a steam boiler, we suggest incorporating the prepared sensor as part of the internal boiler surface. To that end, a small part of the internal boiler surface was isolated from the remaining surface by a suitable insulator, thus exposing the iron surface to the waterside, as illustrated in Figure 8 [29]. More specifically, the corrosion sensor was integrated into a suitable part of the steam boiler. As shown in Figure 8a, an opening (2) was formed through the iron panel (1) and a hollow insulator (3) was secured to the iron panel inside the opening (2), isolating the sensor (4), which was mounted within the hollow insulator (3). Thus, the sensor (4) and the iron panel (1) were electrically isolated by the hollow insulator (3). The first surface of the iron sensor (5) was positioned in the opposite direction of the waterside, whereas the second surface of the iron sensor (6) was facing the waterside in the steam boiler. It should be mentioned that (6) should be aligned with the second surface of the iron panel (7), which was part of a larger iron structure of the steam boiler. Hence, the hollow insulator (3) and the iron sensor (4) formed a structurally sound and continuous set of the iron surface. Moreover, the iron surface (6) and the second surface of the iron panel (7) were in contact with the waterside of the steam boiler wall, leading to the formation of the magnetite layers (8) and (9) through the electrochemical reaction between iron and steam (Figure 8b). The thin layers of magnetite (8) and (9) were expected to have the same nature and thickness. As described in a previous study, a magnetite layer can be formed on an iron specimen surface when heated in the absence of oxygen [20]. In this study, the characteristic peaks for magnetite were observed in Figure 2. The agreement of the peaks of the magnetite powder with those of the oxide layer formed on the iron surface indicated that the oxide grown on the iron surface was mainly magnetite. The potential of the sensor was also measured against the reference electrode (10), which was positioned near the iron sensor surface using a voltmeter (11) connected through an electrical wire.
This simulation process ensured that the magnetite layer covering the iron surfaces (6) and (7) can be grown under actual operational conditions, making our study and results more realistic. In addition, it was revealed that monitoring the potential of the prepared galvanic sensor can provide essential information on the dissolution of the magnetite layer without the risk of an underlying metal substrate attack during the chemical cleaning process. In particular, when the sensor potential is close to that of magnetite, as shown in Figure 3, the base metal does not corrode. However, when the observed potential shows a shifting tendency toward the potential of iron, other precautions should be considered such as using corrosion inhibitors.

4. Conclusions

A simple galvanic sensor was fabricated by coupling iron with a magnetite layer to determine the onset of iron corrosion under conditions similar to those used to remove the magnetite layer in steam boilers using a cleaning solution composed of 5% HCl at 60 °C. The measurement of the potential of this galvanic couple using a magnetite layer with different thicknesses revealed a correlation between the thickness of the magnetite layer and the onset of iron corrosion. It has been shown that the time required for the iron base metal to start corroding ranges between 6 and 14 h depending on the magnetite layer thickness. Also, the $R_p$ measurements of the galvanic sensor during the dissolution process presented a correlation between the potential and the $R_p$ value which showed a large decrease in its value as the potential starts to shifts to that of iron. The potential of the galvanic couple tended to shift negatively to that of iron base metal as the relative area of iron exposed to the solution increased. Under such conditions, a strong attack on the iron is expected because of the anodic shift of iron due to its galvanic coupling with magnetite. Therefore, this sensor can be applied to determine the time at which the magnetite layer dissolves without dissolving the base metal and when the base metal should be protected by adding corrosion inhibitors in the solution.
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