

ELECTROCHEMICAL REACTIONS BETWEEN IRON SULFIDE MINERALS AND THEIR IMPLICATIONS FOR CONCRETE DURABILITY

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Abstract

It is well known that iron sulphides such as pyrite (FeS_2) and pyrrhotite ($(\text{Fe}_{1-x}\text{S}, 0 < x < 0.125)$) are unstable in presence of oxygen and moisture, oxidizing to produce sulfuric acid and iron sulphate. Further reactions in concrete cause the formation of expansive reaction products such as ettringite and thaumasite, potentially leading to structural failure. However, the possibility of accelerated oxidation when pyrite and pyrrhotite come to contact with each other or with a steel rebar has not yet been investigated.

This type of accelerated oxidation is more commonly known as corrosion when it happens in metals such as steel reinforcements. Since both pyrite and pyrrhotite are semiconductors and therefore sources of electrons, they can, however, promote this type of electrochemical reaction. Using electrochemical techniques, the electrochemical properties of pyrite, pyrrhotite, and steel and their open-circuit potentials were measured at different pH values. A zero resistance ammeter was also used to investigate the possibility of an accelerated oxidation reaction when any two of pyrite, pyrrhotite or steel are in electrical contact. The results show that pyrrhotite oxidation is accelerated in the presence of pyrite and both minerals could lead to an increased corrosion rate for steel rebar.

These results are particularly significant as the Maskimo aggregate that was responsible for over \$400 million dollars in damage to concrete in the Trois Rivières region of Quebec, Canada contains significant quantities of both pyrite and pyrrhotite. While pyrrhotite alone will cause damage to concrete through expansive reaction products, the combination of the two minerals may have contributed to both the extent of the damage and the small amount of pyrrhotite that was necessary to cause the damage. In addition to the results of the electrochemical studies, on-going work to investigate the electrochemical behaviour of the two minerals in concrete will also be outlined.

Keywords: Iron sulphide, pyrrhotite, pyrite, electrochemical reaction, concrete

1. INTRODUCTION

Sulfide sulfur has been identified as a potential source of adverse chemical reactions in concrete that produce expansive reaction products since at least the 1970s [1]. Early work focused on the effects of pyrite (FeS_2), often in the bedrock below concrete foundations and basements. In the early 1990s, pyrrhotite ($\text{Fe}_{1-x}\text{S}, 0 < x < 0.125$) was identified as the cause of

cracking in a dam in Spain [2-4]. While considerable research was done to investigate this incident, analysis of the unaltered concrete showed high levels of calcium aluminate hydrate [2], suggesting that the cement used in the dam may not have had a standard composition.

More recently, significant problems related to pyrrhotite in concrete have developed in the Trois Rivières region of Quebec, Canada and in northern Connecticut and southern Massachusetts in the U.S.A. These problems have resulted in an estimated \$400 million worth of damage to date in Canada and have affected more than 1000 home owners. Some estimates from the victim's association in Connecticut suggest 10x the number of households will eventually be affected in the United States. Further details of the damage are given elsewhere [5]. The incident in Trois Rivières resulted in considerable research in terms of understanding pyrrhotite induced failure mechanisms [5] and developing new test methods [6-8].

The adverse reactions that cause pyrrhotite induced cracking in concrete are complex and multi-stage. While the final reaction products associated with pyrrhotite damage in concrete are ettringite [3,4] and thaumasite [4,5], the first reaction is the oxidation of the pyrrhotite in the presence of water, which forms iron hydroxide (goethite, FeOOH) and sulfuric acid. The iron hydroxide is itself expansive and may itself contribute to the cracking. Damage to basements and foundations typically starts with cracking at corners, possibly due to oxygen and water vapour entering the concrete in two directions, rather than one.

While there has been considerable work on the underlying behavior that produces pyrrhotite damage, it has been assumed that the damage to the concrete is solely driven by the presence of the pyrrhotite. The aggregate in Trois Rivières contains, however, both pyrrhotite and pyrite. The two minerals are both semi-metallic and can have very low resistivities, raising the possibility that one mineral might accelerate the oxidation of the other or of steel rebar. The initial results from an on-going investigation of this study are presented here, along with a brief summary of the next steps in the research.

2. MATERIALS AND METHODOLOGY

Pyrite and pyrrhotite cores were taken out of mineralogical samples purchased from Ward's Science (NY, USA). Synchrotron XRD measurements were taken of material from the same samples at the Canadian Light Source in Saskatoon, Saskatchewan, Canada (Table 1), with results quantified by Rietveld analysis. These measurements showed that samples were approximately 70-80% composed of the mineral of interest, but that no pyrite was present in the pyrrhotite sample or vice-versa.

Table 1: Mineralogical composition of pyrite and pyrrhotite samples

Mineral	Pyrite Sample (wt.%)	Pyrrhotite sample (wt.%)
Pyrite	81.4	0.0
Quartz	17.1	0.0
Muscovite-2M1	1.4	0.0
Galena	0.1	0.0
Pyrrhotite-6C	0.0	74.3

Dolomite	0.0	20.2
Sphalerite	0.0	2.2
Chalcopyrite	0.0	1.9
Clinocllore	0.0	1.4

The extracted cylindrical samples were 1.176 cm in diameter with length varying from 1 to 3 cm. The end of the cylindrical samples was attached to 30 cm long conductive copper wires using a conductive carbon adhesive paste. The sample wire assembly was then coated with 3MTM ScotchkoteTM liquid epoxy coating 323 in order to limit the electrolyte contact with an area of 1.086 cm².

Prior to each experiment, the exposed surfaces of the electrodes were ground and polished with wet SiC papers (BUEHLER, IL, USA) from 120 to 600 and 1200 grit finish, washed by de-ionized water and degreased by acetone and dried at room temperature.

The carbon steel rebar sample was passivated by keeping in saturated calcium hydroxide (Ca(OH)₂) solution (pH= 12-13), for at least 48 hours, prior to testing. The passivation process simulates the effect of the concrete pore solution on rebar before exposure to experimental conditions. The elemental composition of carbon steel rebar is presented in Table 1.

Table 2: Chemical composition of the carbon steel provided by the manufacturer (wt%)

C	Si	S	P	Mn	Cr	Mo	Ni	Fe
0.26	0.27	0.03	0.01	1.1	0.05	<0.01	0.07	Balance

Three different solutions with acidic, neutral and basic pH were selected in this experiment. The solutions were 0.1 wt. % NaCl in distilled water (pH 6), saturated Ca(OH)₂ with addition of 0.1 wt.% NaCl (pH 12) and distilled water solution with added H₂SO₄ (pH 4). While the saturated calcium hydroxide solution approximates the pH conditions typically associated with concrete pore water, the other two solutions were included as H₂SO₄ is expected to be produced during oxidation of pyrrhotite, raising the possibility that local conditions in the concrete have a lower than expected pH.

A straightforward and easily measurable electrochemical parameter is the free corrosion potential (E_{CORR}). E_{CORR} was obtained by measuring the potential of a freely corroding specimen with respect to the reference electrode. The potential of specimens in the selected solution was measured against a Fisher brandTM accumetTM epoxy body mercury-free reference electrode (-45 mV vs. Saturated Calomel Electrode). Corrware software (Scribner Associates Inc, NC, USA) was used to set up the electrochemical experiments.

The galvanic corrosion experiments were carried following the basic principles of ASTM G71 (G71 2009) [9]. Galvanic corrosion of two dissimilar specimens can occur if their E_{CORR} values are more than 100 mV apart [10]. This may lead to the accelerated electrochemical reaction between the two specimens. The pyrite and pyrrhotite, pyrite and carbon steel, and pyrrhotite and carbon steel were coupled to investigate their possibility of galvanic corrosion among them. The two selected specimens were connected through a zero-resistance ammeter, and their galvanic corrosion current (I_{Couple}) and galvanic corrosion potential (E_{Couple}) against standard reference electrode were monitored once the two samples were electrically connected.

3. RESULTS AND DISCUSSION

E_{Corr} values are indicative of the level of activity of samples, a more positive E_{Corr} value, indicates a more “noble” material that is less likely to oxidize while a more negative value indicates a more active specimen that will oxidize preferentially when connected with a specimen with a more positive potential [10]. As can be seen in figure 1, pyrite shows the most positive E_{Corr} value of 0.25 V while pyrrhotite has a value of -0.14 V and carbon steel shows the most negative value of -0.20 V. Based on E_{Corr} measurements alone the activity of the measured specimens rank as follows pyrite < pyrrhotite < carbon steel.

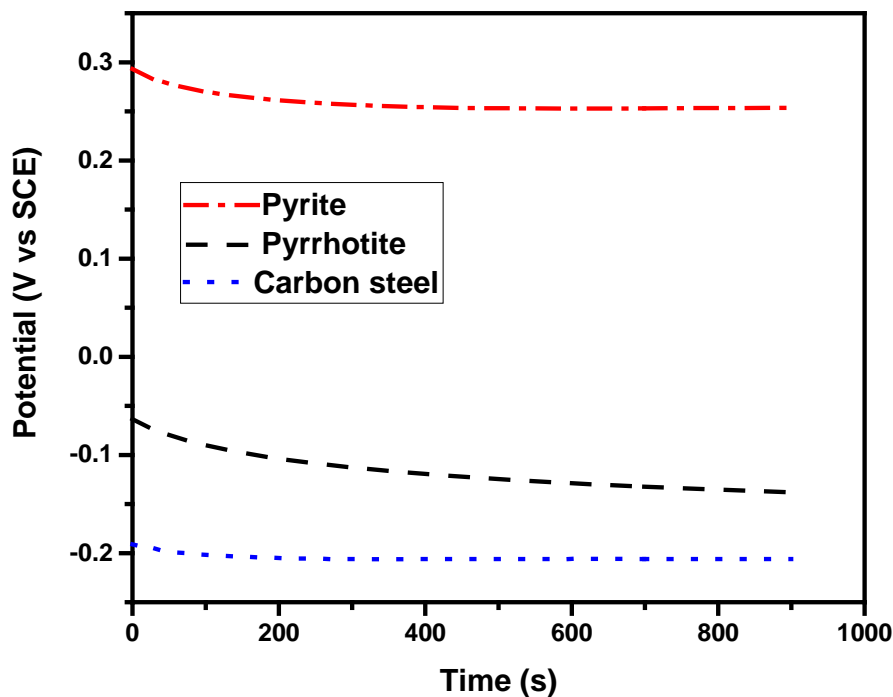


Figure 1: The corrosion potential of alloys measured in saturated $\text{Ca}(\text{OH})_2$ solution containing 0.1 wt.% NaCl for 30 minutes.

The other important information obtained from Figure 1 is the possibility of galvanic corrosion between the specimens. The E_{CORR} difference between pyrite and pyrrhotite is as much as 0.39 V, and the difference between pyrite and carbon steel is about 0.45 V. Both differences would produce a significant driving force for galvanic corrosion to occur, as the pyrite would accelerate the oxidation of both carbon steel and pyrrhotite [11,12]. The E_{CORR} difference between pyrrhotite and carbon steel is, however, only 0.06 V, a potential difference that is often too low to accelerate the corrosion of carbon steel in connection.

The E_{Couple} and I_{Couple} measured while coupling pyrite and pyrrhotite in the pH 12 solution are shown in Figure 2. It is clearly seen that two regions of change are observed. The first phase lasts for about 75-80 hrs, where the E_{Couple} starts at a negative value of -0.1 V, close to the E_{CORR} of pyrrhotite, and gradually increases and reaches 0.056 V, a value between E_{CORR} of pyrite and pyrrhotite. In this phase, initially the I_{Couple} starts at 0.03 mA and over time drop to 0.002 mA in 80 hrs. In the second phase from 80 h to 150 h, both E_{Couple} and I_{Couple} reach a stable value of 0.056 V and 0.0015 mA respectively.

The coupling measurement shown in figure 2 indicates that when pyrite and pyrrhotite are in contact with each other in a conductive environment, an electrochemical reaction can occur between them, the rate of this reaction is high at the beginning as measured by a current of 0.03 mA and it will slow down about 20 times to the negligible rate of 0.0015 mA. The final current indicates almost no ongoing reaction between the coupled specimens.

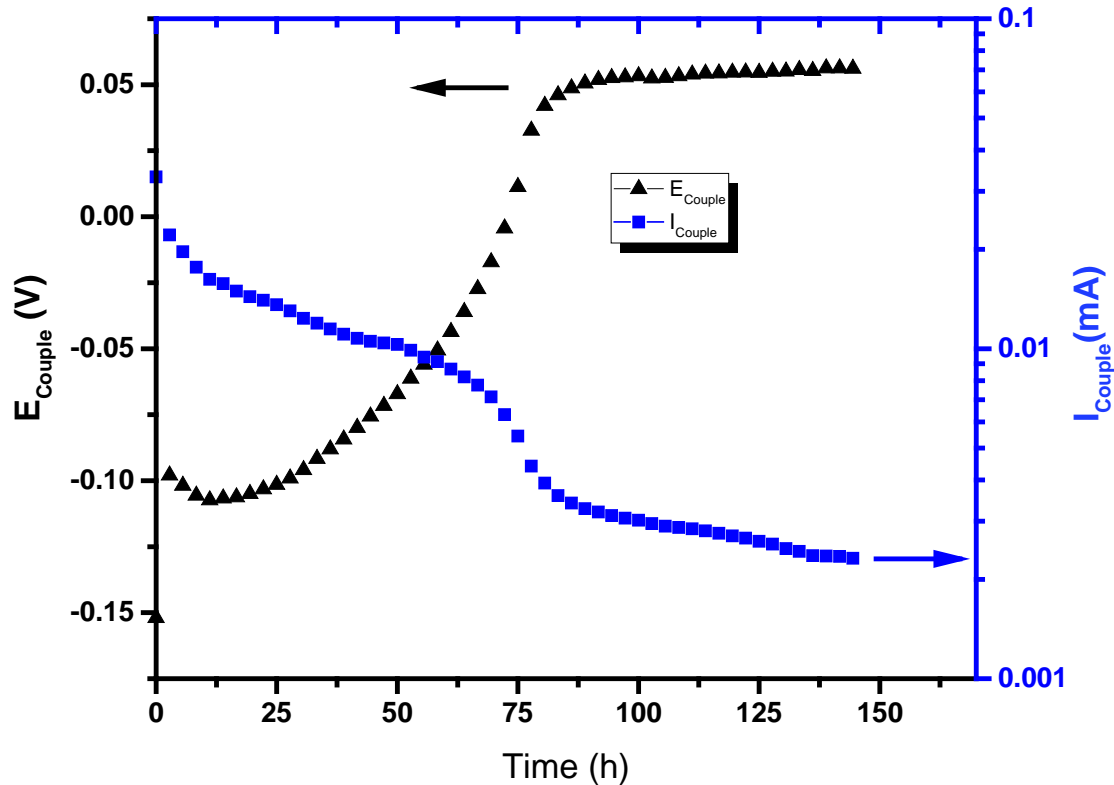


Figure 2: E_{Couple} and I_{Couple} from coupling of pyrite and pyrrhotite in saturated $\text{Ca}(\text{OH})_2$ solution containing 0.1 wt.% NaCl (pH12).

The same coupling measurements were performed for other couples of pyrite/carbon steel and pyrrhotite/carbon steel at pH 12, and for the pyrite/pyrrhotite couple at different pH values. The results are summarized in Table 3.

Table 3: Activity of coupled specimens in varying pH values.

pH	Coupled specimens	Initial I_{couple} (mA)	Final I_{couple} (mA)
4	Pyrite/ Pyrrhotite	2.2E-3	1.2E-3
6	Pyrite/ Pyrrhotite	6.4E-3	1.8E-3
12	Pyrite/ Pyrrhotite	3.3E-2	1.5E-3
12	Pyrite/carbon steel	4.5E-4	5.7E-6
12	Pyrrhotite/carbon steel	1.7E-5	2.4E-6

As seen in Table 3, the magnitude of current measured between pyrite and pyrrhotite depends on the pH, the basic pH of 12 shows the highest initial coupling current of 3.3 E-2 mA. By decreasing the pH to 6, the current drops 5 times to 6.4 E-3 and at pH 4 it reaches 2.2 E-3. The final current however is independent of pH and is close to 1.5 E-3 in all different pH values confirming close to no activity between the couples.

The coupling of carbon steel rebar with pyrite also increases the oxidation of carbon steel with an increased rate of 4.5E-4 mA. The optical examination of carbon steel samples after coupling with pyrite shows signs of corrosion. However, the connection of pyrrhotite and carbon steel did not increase the activity of carbon steel to a level that corrosion be detected. This is in agreement with the E_{corr} measurements shown in Figure 1, where the free corrosion potential difference between pyrrhotite and carbon steel was only 0.06 V.

The pyrite and pyrrhotite specimens prior and post coupling at pH 12 solution are shown in Figures 3 (a) and 3 (b) respectively. The color change on both minerals is clear in the images.

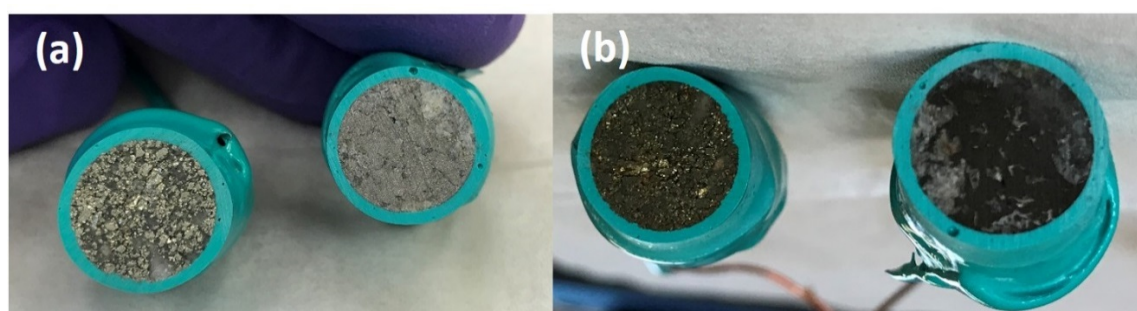


Figure 3: Pyrite (on the left) and pyrrhotite (on the right) electrodes before (a) and after (b) coupling experiment at pH 12.

After coupling, the pyrite and pyrrhotite electrodes were analyzed using Secondary Electron Microscopy (SEM) as shown in Figures 4 (a) and (b) respectively. The pyrrhotite shows an inhomogeneous structure after coupling that is indicative of preferential dissolution of species on the surface, consistent with the results of Figures 2 and 3. Energy Dispersive X-Ray Spectroscopy (EDS) (not shown) were also performed on both electrodes after coupling, with the analysis primarily showing iron, oxygen and sulfur, along with trace elements as seen in Table 1. These results were also consistent with the oxidization seen in Figure 3. Further surface analysis is required to confirm the nature of structure formed on the two electrodes after coupling and exposure to electrolyte.

4. CONCLUSIONS

The results presented here show that the presence of pyrite in concrete aggregate may accelerate the oxidation of both pyrrhotite and reinforcing steel. While the observed effects between pyrrhotite and pyrite are most prominent in the samples measured at a pH of 12, tests at lower pH show the same behaviour. The possibility of acceleration is therefore likely independent of the local pH in concrete samples. It should be noted, however, that the work here was done using standard electrochemical research methods and may not represent the behaviour that actually occurs in concrete in the field.

If the same behaviour does in concrete, then the rate of oxidation of pyrrhotite in concrete aggregate would depend on whether pyrite is present in the same aggregate. It is also possible that other semi-metallic minerals would have the same effect. In this case the production of expansive reaction products would be expected to accelerate as well, causing more rapid deterioration of the concrete. It is also possible that the presence of pyrite would mean that deterioration would occur at lower levels of pyrrhotite content than would otherwise be the case.

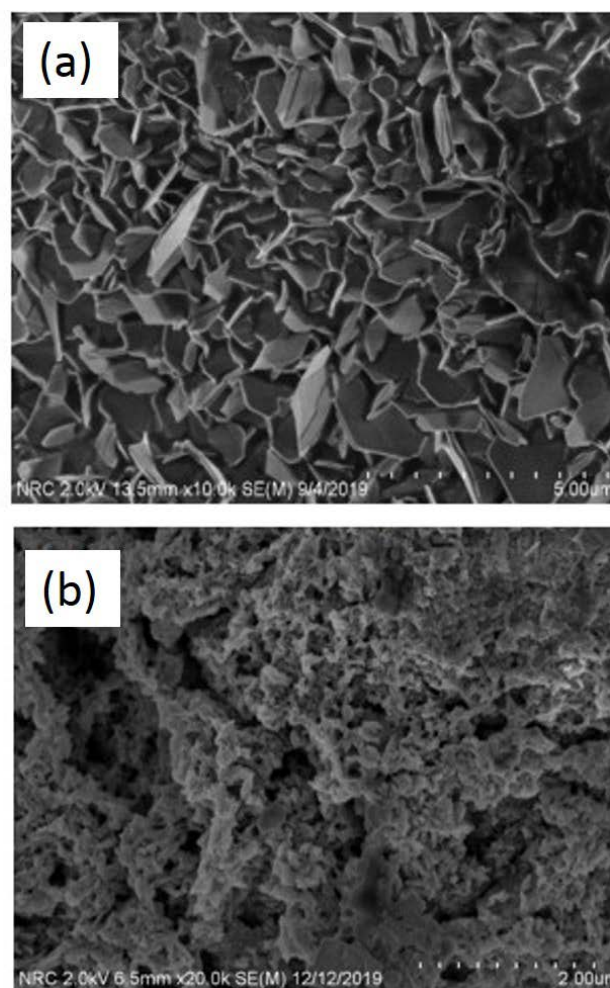


Figure 4 SEM imaging of (a) Pyrite and (b) Pyrrhotite electrodes after coupling at pH 12 electrolyte.

Considerable additional work is underway to explore whether the observed behaviour does occur in the field. Instrumented samples of pyrite and pyrrhotite connected with carbon paste have been placed in concrete and are currently being monitored to see how their potential changes over time. Additional work looking at the coupling of pyrrhotite and other minerals such as chalcopyrite and magnetite are planned. A number of other experiments are also under consideration, including further investigations of the impact of the presence of pyrite on the corrosion of rebar. Once this work is completed the role of mineral-mineral coupling in concrete deterioration will be clarified, potentially supporting changes in North American concrete standards.

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