



Electrochemical properties of pyrite, pyrrhotite, and steel: effects on grinding and flotation processes

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Synopsis

Metal sulphides are usually semiconductor and their electrical conductivity is low; therefore they are sources of electrons and promote electrochemical reactions. This phenomenon is of significant importance in sulphide flotation. The formation of a hydrophobic surface on the sulphide minerals is the result of various electrochemical reactions. Potential difference in the mineral-liquid interface plays an important role in the kinetics of the reactions, and consequently, on the flotation behaviour of sulphides. The value of the potential difference is influenced by different oxidation-reduction reactions at the interface area, and is measured by a two-electrode system in which an electrode is applied as reference electrode. In this study, we attempted to measure open-circuit potentials of pyrite, pyrrhotite, and steel electrodes with respect to the reference electrode. To verify the results, two reference electrodes, saturated calomel and gold, were used. Time-potential relations with respect to both reference electrodes show that the potential of both pyrite and pyrrhotite increases with time; however, this trend decreases for steel except when at pH 12. The results show a potential drop by an increase in pH value, except for steel, for which the opposite holds. This paper discusses galvanic interactions between minerals and grinding media in the grinding circuits, as well as among other minerals in the flotation processes.

Keywords

mineral processing, froth flotation, oxidation, reduction, pH control.

Introduction

Electrochemical mechanisms have been used for more than five decades to elucidate some phenomena in flotation operations. It has been found that absorption of collectors onto sulphide minerals occurs via an electrochemical mechanism^{1–7}. Grinding also results in modification of the sulphide minerals surface composition⁸. It has been suggested that iron oxidation species play an important role in depressing mineral flotation^{9,10}. The oxidation-reduction environment is very sensitive to iron with which it is in galvanic contact¹¹. Electrochemical potential is therefore considered an important parameter in controlling the recovery and selectivity of sulphide minerals during flotation². The potential at a solid/solution interface is

determined by the presence of oxidizing and reducing species in solution¹². The change in pulp potentials indicates the involvement of additional electrochemical reactions¹³. Pulp oxidation potential (Eh) controls the formation of surface species responsible for mineral flotation¹⁴. It is therefore expected that it might be possible to optimize flotation performance, in terms of both bulk recovery and selectivity, by control of the oxidation-reduction or redox potential¹. To attain this objective, it is necessary to define the electrochemical properties of minerals and grinding media more precisely, and to investigate in greater detail the applied electrochemical reactions at their surfaces.

Applied studies in pulp potential determination from 1972 to 1988 showed that through the use of noble metals and minerals, valuable information can be obtained about the behaviour of minerals in milling and flotation circuits, and the application of this information in the field of electrochemistry¹⁵.

One of the most important separation stages in flotation circuits is the separation of pyrite and pyrrhotite from other sulphide minerals. Understanding of activation and depression of sulphide minerals, such as pyrite and pyrrhotite, as well as grinding media such as steel balls, under both acidic and alkaline conditions, is necessary to improve recovery and to design process strategies for cost reduction. These parameters can be determined through studies of electrochemical, oxidation, and reduction reactions on the surfaces of minerals and milling media.

In this investigation, the electrochemical properties of pyrite, pyrrhotite, and steel and their open-circuit potentials were measured at different pH values with respect to two

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reference electrodes,. The results of these studies generated further investigations of the oxidation reactions of minerals and grinding media, as well as the galvanic interactions between, them in grinding and flotation processes, and their effects on the recovery and selectivity of minerals during flotation.

Methods and materials

Figure 1 shows the circuit that was used to measure open-circuit potentials. In this circuit, potential differences between mineral and metal electrodes in different electrolytes were determined by the use of a digital multimeter (Hioki³² Model) with respect to the reference electrode. Potentials were read promptly after submerging the electrodes in the solution, and readings were taken at five-minute intervals until the resulting potential was constant or the difference between two successive readings was negligible. These results are reported with respect to the standard hydrogen electrode. Therefore, values of 0.242 V and 1.68 V were added to the measured potentials with respect to the saturated calomel and gold electrodes, respectively. Experiments were carried out at a temperature range of $25\pm1^{\circ}\text{C}$ in an exposed condition (exposed to air). Mild abrasive and distilled water were used to clean the electrodes after every experiment to remove any possible coating by oxides and hydroxides.

Electrolytes

The open-circuit potentials of pyrite, pyrrhotite, and steel electrodes were measured in distilled water electrolyte at six different pH values: 2, 4, 6, 8, 10, and 12. In these experiments, 1 N sulfuric acid was used to set acidic pH values and 1 N sodium hydroxide was used to set alkaline pH values.

Electrodes

The source of pyrite and pyrrhotite electrodes was pure and bulk specimens of the minerals. Pyrite, pyrrhotite, and steel were selected from a Mexican mine, Wards Institute (Canada), and the steel mill balls of Chadormalo iron mine in Iran, respectively. The type of steel used in this experiment was 70Cr₂.

In Figure 2, a general scheme of the operative electrodes is shown. To produce these electrodes, first the sample was cut in $1\times1\text{ cm}$ dimensions with 0.5 cm thickness. A copper wire was used to connect the electrode to the digital multimeter. This wire passed through a plastic tube and connected to the polished surface of the sample. Next, the sample was placed in a polystyrene mould. The end of the plastic tube and the junction of wire and sample were placed in the mould. Finally, to ensure the contact between the copper wire and the sample, a small amount of mercury was added at the point of connection. Since the uneven surfaces would act as anodes and cathodes, leading to possible measurement errors, the part of electrode surface that was exposed to the solution was polished by mechanical devices until a flat surface was obtained.

Results

Pyrite open-circuit potential

Figure 3 shows the open-circuit potentials of the pyrite electrode versus time at different pH values for saturated

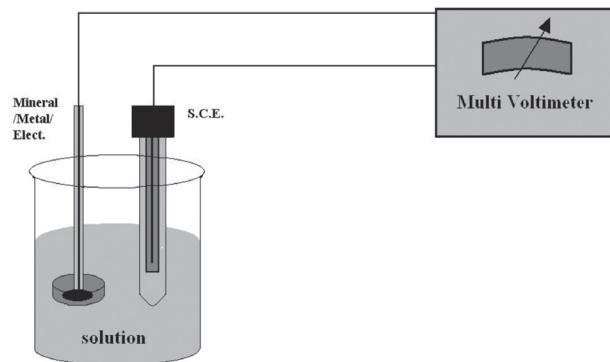


Figure 1—Experimental setup for open-circuit potential measurements

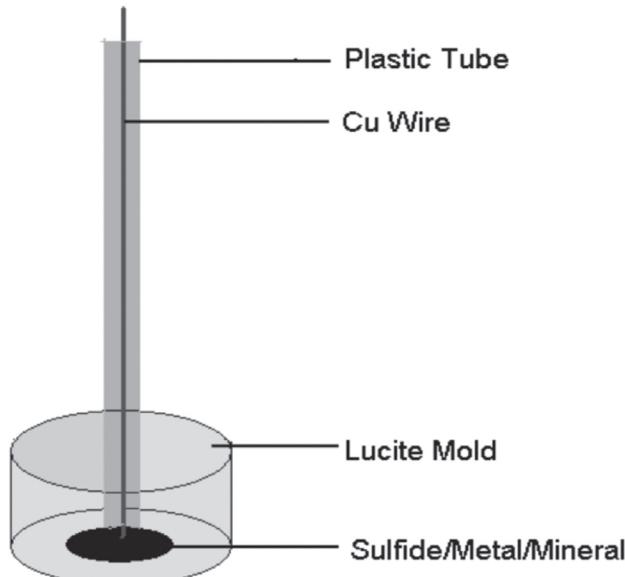


Figure 2—Structure of mineral/metal electrode

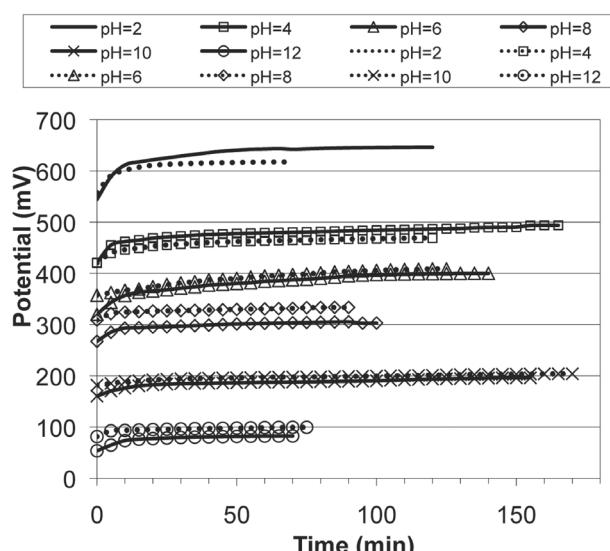


Figure 3—Time-potential relationships of pyrite with respect to saturated calomel reference electrode (solid line) and to gold reference electrode (dotted line)

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calomel and gold reference electrodes. It can be clearly seen that there is an inverse relationship between pH and potential, with potential dropping with an increase in pH. The greatest increase from the start to the end of measurement occurs at pH=2, which is equal to 101.6 mV for the saturated calomel electrode and 59.9 mV for the gold electrode. With increasing pH (passing from acidic to alkaline conditions), the amount of increase in the potential becomes less; i.e. at pH=12 it reaches 28.9 mV and 18.2 mV for the saturated calomel and gold electrodes respectively.

The measured potential values with respect to the saturated calomel reference electrode at pH values from 2 to 12 are equal to 646.1 mV, 493.8 mV, 400.1 mV, 303 mV, 196.1 mV, and 82.5 mV. These values for the gold reference electrode were recorded as 617.5 mV, 468.9 mV, 408.6 mV, 333.7 mV, 203.9 mV, and 99.5 mV. A small difference was observed in the measured potential values with respect to saturated calomel and gold reference electrodes. Additionally, it should be noted that many similarities are observed from the diagrams, and this demonstrates the high accuracy of the results obtained.

Pyrrhotite open-circuit potential

Pyrrhotite open-circuit potentials with respect to the saturated calomel and gold reference electrodes were measured at different pH values, and the results are shown in Figure 4. It can be clearly seen that the greatest increase in potential for saturated calomel and gold reference electrodes is equal to 88.2 mV and 69.2 mV respectively at pH=2. As pH increases, the potential variation decreases until it reaches 17.8 mV with respect to the saturated calomel electrode and 14.1 mV with respect to the gold electrode at pH=12. These observations indicate the strong impact of acidic pH values on the electrochemical reactions of sulphide minerals.

Pyrrhotite open-circuit potentials at pH values of 2, 4, 6, 8, 10, and 12 for saturated calomel electrode were 516.7 mV, 389.5 mV, 323.7 mV, 221.9 mV, 131.4 mV, and 36.2 mV respectively, whereas in the case of gold electrode, these values were 489.9 mV, 355.6 mV, 311.9 mV, 249.2 mV, 130.8 mV, and 35.1 mV. From Figure 4, it can be easily understood that open circuit potential decreases with increasing pH. The recorded open-circuit potentials for saturated calomel and gold electrodes and the diagrams show that the results are of high accuracy in this case as well.

Steel open-circuit potential

The results of the steel open-circuit potential measurements are shown in Figure 5. These results are relative to the saturated calomel and gold reference electrodes. It can be seen that steel has a completely different electrochemical behaviour compared to pyrite and pyrrhotite. As shown in Figure 5, open-circuit potentials of steel increase with increasing pH, in contrast with the behaviour of pyrite and pyrrhotite. Based on our observations, open-circuit potentials of steel at all the measured pH values (except pH=12) decrease with time. The time required to reach a constant and stable point at all pH values is less than that for pyrite and pyrrhotite. It can be concluded that the electrochemical activity of steel is much higher than that of pyrite and pyrrhotite. Figure 5 clearly shows that at pH=12 the

behaviour of steel is the reverse of that at other pH values, in that the potential increases with time, similar to pyrite and pyrrhotite.

The steel used in these experiments exhibited a voltage of -373 mV, -331 mV, -279 mV, -237 mV, -201 mV, and -17 mV for open-circuit potentials with respect to the saturated calomel reference electrode at pH values of 2, 4, 6, 8, 10, and 12 respectively. The corresponding voltage values with respect to the gold reference electrode were -345 mV, -311 mV, -285 mV, -229 mV, -218 mV, and -20 mV. Comparing the values and diagrams obtained by two reference electrodes (saturated calomel and gold) confirms the high accuracy of the results.

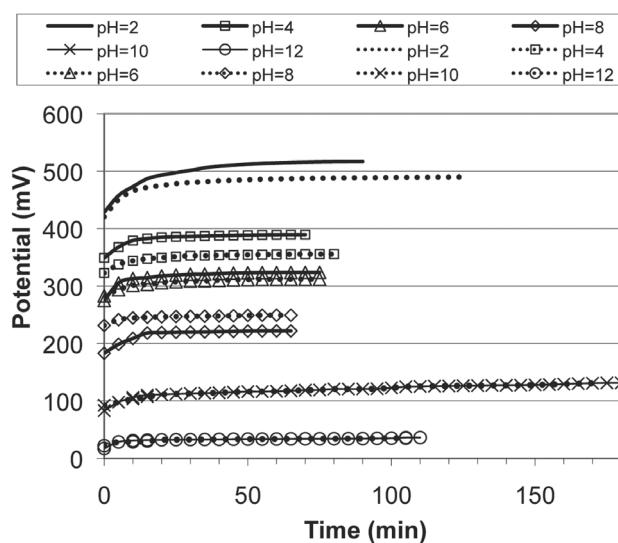


Figure 4—Time-potential relationships of pyrrhotite with respect to saturated calomel reference electrode (solid line) and to gold reference electrode (dotted line)

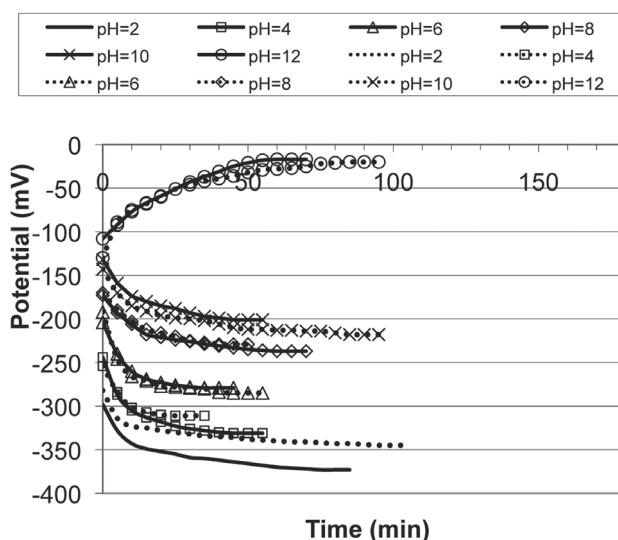


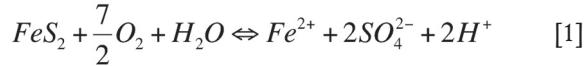
Figure 5—Time-potential relationships of steel with respect to saturated calomel reference electrode (solid line) and to gold reference electrode (dotted line)

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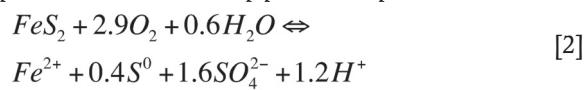
Discussion

Pyrite oxidation

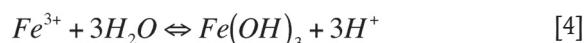
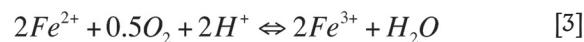
Pyrite, with chemical composition of FeS_2 , is a semiconductor mineral, and if it is completely oxidized, it will alter to ferrous iron and sulphate ions^{16,17}. Pyrite oxidation takes place according to the following reaction¹⁸:



Laboratory observations show that the pyrite oxidation reaction is not a complete reaction, and that ferrous iron and sulphate ions react further to produce sulphur¹⁹.



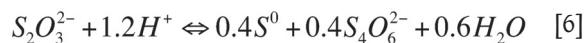
Sulphur is altered from S_2^{2-} (in pyrite) on the inner surface to S^0 (elemental sulphur that is suitable for electrochemical reactions) on the external surface²⁰. It has been reported that the surface sulphur layer remains associated with the sulphide lattice, i.e. as a metal-deficient sulphide^{21,22,23}. The ferrous iron produced by Equation [2] undergoes the following reaction that precipitates iron hydroxide²⁴:



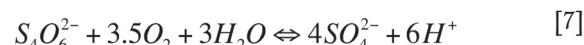
Iron hydroxide produced in Equation [4] is precipitated as a coating on the mineral's surface and prevents further oxidation of the pyrite. This phenomenon obtains more momentum in alkaline solutions rather than acidic solutions. Pyrite oxidation (which produces ferrous iron and sulphate ions) causes seven electrons to be lost from each atom of sulfur, which is converted from S^{-1} in pyrite to S^{6+} in sulphate ions. Since one or two electrons are transferred in every reaction, the oxidation process is complex and multi-stage²⁰. The most important stage includes breaking the strong bond between iron and sulphur, and also formation of the thiosulphate ions as intermediate product, as in the following reaction.



The thiosulphate ions produced are unstable in the acidic electrolytes, whereas they are relatively stable in the alkaline electrolytes²⁵. Also, thiosulphate ions are distinguished in the non-acidic conditions¹⁹. The sulphur-enriched layer formed on the pyrite is not a direct product of pyrite oxidation, but it is obtained from the thiosulphate ion (direct product of pyrite oxidation) through the following reaction¹⁹:



While thiosulphate ions are reacting, sulphoxy species like $\text{S}_4\text{O}_6^{2-}$ may be produced during the oxidation process as an unstable intermediate product. The $\text{S}_4\text{O}_6^{2-}$ produced in Equation [6] is converted to sulphate ions by the following reaction²⁵:



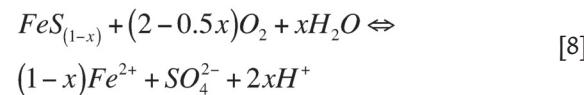
Higher pyrite open-circuit potential is due to the strong bond between iron and sulphur in the pyrite lattice²⁵. In the diagrams of pyrite electrode potential versus time, it is observed that the potential increases with time until it reaches a stable state. The reason for this increase may be explained by sulphate production in several stages. That is, in each stage of reaction, the potential increases by a defined amount until it reaches its maximum limit and stable state.

Intermediate products are less stable in the acidic solutions. Additionally, iron oxides and hydroxides are produced in lesser amounts due to the lower stability. Therefore, the potential increases by a greater amount. In the alkaline solutions, unlike the acidic solutions, the intermediate products, iron oxide and hydroxides, are more stable. Therefore the reaction does not continue, and the potential in these solutions increases by a lower amount and reaches a stable state in a shorter time.

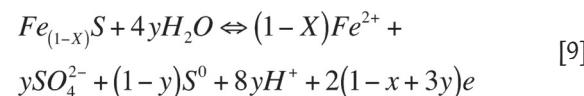
Pyrrhotite oxidation

Pyrrhotite, with chemical composition of Fe_{1-x}S , in which X varies from zero to 0.125, has different relative values for iron and sulphur. Any increase in the sulphur/iron ratio and decrease in metal content in the pyrrhotite structure results in an increase in the oxidation rate of pyrrhotite²⁴.

If pyrrhotite is oxidized by oxygen, it will produce ferrous iron and sulphate ions, similar to pyrite²⁴:

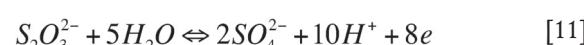
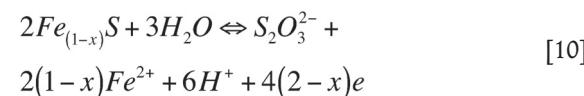


Pyrrhotite oxidation, like pyrite oxidation, does not proceed to completion. By incomplete oxidation of pyrrhotite, elemental sulphur along with sulphate ions and ferrous iron is produced. The reaction is:



The ferrous iron produced in Equation [9] is converted to ferric iron and finally to iron hydroxide by other reactions. The related reaction is in accordance with reactions [3] and [4]²⁴.

Iron hydroxide layers passivate the electrode surface and protect the pyrrhotite from further oxidation. It has also been proved that pyrrhotite oxidation is similar to pyrite, in that the utmost two electrons could be transferred in every reaction²⁰. The reaction therefore takes place in several stages, with the production of intermediate products such as thiosulphates. Due to the instability of these products, especially in the acidic solutions, other reactions occur and eventually sulphate ions are produced²⁴. The following reactions are applicable in terms of thermodynamics:



In the diagrams of pyrrhotite open-circuit potential versus time, it is obvious that pyrrhotite is oxidized at a lower potential compared to that of pyrite. Also, in contrast to

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pyrite, pyrrhotite exhibits a lower open-circuit potential and greater reactivity. Studies show that the specific area of different size fractions of pyrrhotite samples is 2 to 10 times greater than for pyrite samples. This difference could be the result of fracture and roughness of the pyrrhotite surface²⁶. The higher specific area of pyrrhotite in comparison to pyrite is one of the reasons that pyrrhotite is more reactive and oxidized more easily than pyrite. It has also been shown that the crystalline structure of pyrrhotite, which is deficient in iron and lattice vacancies, has less symmetry than that of pyrite. This nonsymmetrical crystalline structure causes an increase in the reactivity and oxidation rate of pyrrhotite.

The increase in open-circuit potential of pyrrhotite versus time and its reduction versus rise in pH can be related to intermediate products and iron hydroxides that are less stable in the acidic solutions. This is why pyrrhotite oxidation reaction continues and its open-circuit potential increases.

Steel oxidation

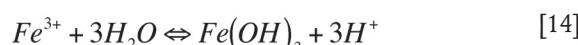
Steel has a very high electrochemical activity, and studies also show that it is more sensitive to ambient condition changes. Steel exposed to air is oxidized in a very short period of time (nanosecond scales). Our results indicate that the oxides formed in the process have very low stability in solutions with pH values less than 10, and are eliminated from the steel surface rapidly. The elimination of these oxides from the steel surface causes its rapid oxidation; therefore, the potential changes very rapidly with time. The product of steel oxidation is ferrous iron:



Further oxidation produces ferric iron⁴:



In aqueous solutions at ambient temperatures, ferric iron is converted to ferric hydroxide by following reaction²⁴:



The iron hydroxide layer passivates the steel surface and prevents further oxidation.

At very high pH values, steel exhibits a different behaviour compared to other pH values. At high pH values, the iron oxide formed on the steel surface is relatively more stable in air as an incomplete film coats the surface. Therefore, the electrochemical activity of steel decreases and its rate of oxidation decreases sharply. Also, due to the rapid reaction of steel with oxygen in alkaline solutions, iron hydroxides are formed at higher rates. The iron hydroxides in these solutions are more stable and cause the more rapid and extensive passivation of the steel surface. Therefore, the electrochemical activity of steel decreases considerably at very high pH values.

Effect of open-circuit potential on the galvanic contact in grinding and flotation processes

During grinding and flotation processes, galvanic contact is made between the minerals and grinding media as well as between different minerals. Redox reactions therefore take place at the surfaces of minerals and grinding media due to differences in their rest potentials²⁷. Galvanic reactions in the

milling and flotation processes include the oxidation of grinding media or mineral, which act as anodes. The reactions also include the reduction of oxygen on the mineral surfaces that act as cathodes.

The results of open-circuit potential measurements show that under all conditions, pyrite has a greater rest potential compared to pyrrhotite and steel. The potential for steel is the least. The mineral or metal that has greater rest potential plays the role of the cathode, and the mineral or metal with lower rest potential plays the role of anode²⁸. Therefore, in the galvanic contact between pyrite and steel, pyrite acts as cathode, which results in reduction on its surface. Pyrite is a proper electrocatalyst for oxygen reduction and formation of hydroxides; and its activity for oxygen reduction is considerably greater than that of other sulphide minerals^{29,30}. Oxygen reduction in the pyrite surface, as well as the release of the iron ions from the steel surface, causes formation of ferric hydroxide in the pyrite surface, and this is the action that passivates its surface³¹. Due to greater rest potential of pyrrhotite in comparison to steel, pyrrhotite also acts as a cathode, like pyrite. Since the potential difference between pyrrhotite and steel is less than that between pyrite and steel, the oxidation and reduction reactions are less intense. Therefore, the rates of steel corrosion and hydroxide coating on the pyrrhotite surface are slower compared to those between pyrite and steel. The effect of hydroxides can be reduced or eliminated by complexing the iron ions³ and thereby preventing precipitation. The use of small quantities of iron-complexing agents, such as polyphosphates and organic acids, can counteract the harmful effect of iron³². Galvanic contact between sulphide minerals such as pyrite or pyrrhotite with milling media is illustrated in Figure 6 (a). In the galvanic contact between pyrite and pyrrhotite, the cathode and anode are pyrite and pyrrhotite, respectively. Due to its lower rest potential, pyrrhotite is oxidized and iron ions are produced, and as a result the pyrrhotite becomes enriched in sulphur layers. Pyrite also causes oxygen reduction on the pyrrhotite surface and produces hydroxide ions, which together with iron ions released from the pyrrhotite surface produce ferric hydroxide. This material passivates the pyrite surface. Galvanic contact between pyrite and pyrrhotite is schematically shown in Figure 6 (b). As shown in Figure 6 (c), in galvanic contact between pyrite, pyrrhotite, and steel, the simultaneous oxidation of steel and pyrrhotite (which act as anode) releases large quantities of iron ions. In this case, compared to the other states, the pyrite surface is widely passivated by iron hydroxide layers.

Electrochemical potential is an important parameter for controlling recovery and selectivity during flotation of sulphide minerals³⁴. The formation of oxide, hydroxide, or iron sulphate types by reduction of oxygen on the surface of cathodic polarized pyrite causes selective depression of pyrite during the flotation process. Oxidation of sulphide minerals with lower rest potential (such as pyrrhotite) forms hydrophobic species on the minerals' surface and enhances flotation. Further evidence for the formation of hydrophobic species of elemental sulphur on sulphide mineral surfaces under simulated flotation conditions was presented by Walker³⁵. Abrasion between pyrite, pyrrhotite, and steel in the milling process eliminate hydroxide species from the surface of the minerals, which results in a considerable

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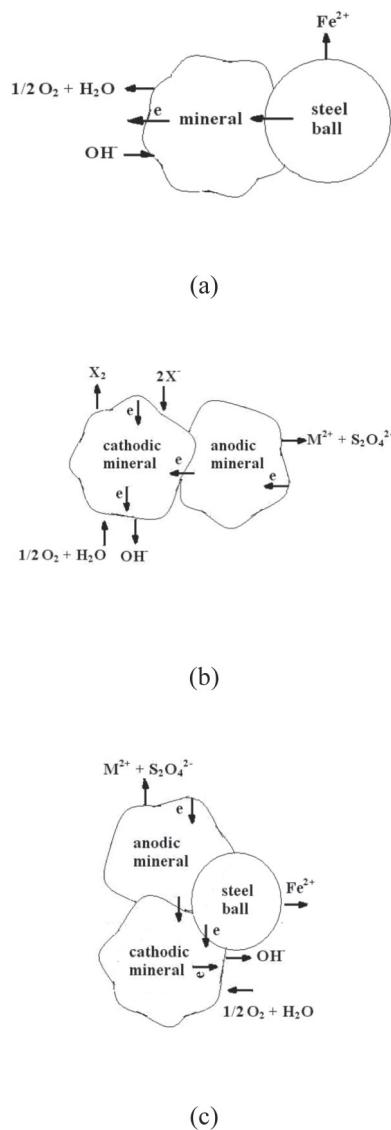


Figure 6—Schematic representation of galvanic interactions between (a) mineral and grinding medium, (b) two different minerals, (c) different minerals and grinding medium³³

degree of oxidation of steel or the mineral with lower potential, which acts as anode. Increased oxidation of steel results in its corrosion and in the case of an anodic mineral, this phenomenon causes the formation of sulphate ions and results in the elimination of hydrophobic species from its surface.

As mentioned above, any increase in potential difference causes an increase in the intensity of galvanic interactions and increases the rates of electrochemical reactions. Figure 7 indicates that the highest potential difference between minerals and steel occurs at acidic pH values, such that with an increase in pH, the potential difference between minerals and steel decreases. Thus, it is clear that electrochemical reactions and galvanic interactions take place at higher rates at lower pH values compared to higher ones. That is why acidic pH values cause more changes in the superficial properties of minerals and result in increased corrosion of grinding media.

There is ample evidence suggesting that a change in grinding media type will have an influence on the pulp chemistry of the system, which will change the flotation behaviour of the sulphide minerals present³⁶. Thus, to reduce galvanic contact effects on the corrosion of grinding media, the grinding media with higher rest potential should be used. According to the Nernst equation, the partial pressure of oxygen in the mill can also influence the grinding environment³⁷. Since oxygen acts as an electron acceptor and forms OH⁻ on noble minerals, the presence of dissolved oxygen in the solution is of vital importance for galvanic interaction²⁸. Oxygen purging causes the grinding environment to be more oxidizing, while nitrogen purging induces the opposite effect³⁸. It is also possible to prevent galvanic reactions by eradicating oxygen and replacing it with nitrogen. By taking into consideration the probable influence of the ratio of surface area of mineral to grinding media on the degree of galvanic interaction³⁸, it may then be possible to control the cathodic or anodic reactions by adjusting the anode-to-cathode surface area ratio. A small anode contacting with a larger cathodic surface promotes the rate of anodic oxidation³⁹.

Conclusions

Based on the results of open-circuit potential measurements, it can be stated that the electrochemical reactions at lower pH values take place at a higher rate and intensity. In the case of pyrite and pyrrhotite, the increase in the intensity of electrochemical reactions causes the removal of hydrophobic species from the surface of the minerals, while in the case of steel, it causes corrosion to increase.

Diagrams of open-circuit potentials versus time showed that for pyrite and pyrrhotite, the potential increases with time. This increase in potential is due to completion of oxidation reactions in several stages and also the formation and oxidation of intermediate products. This issue results in

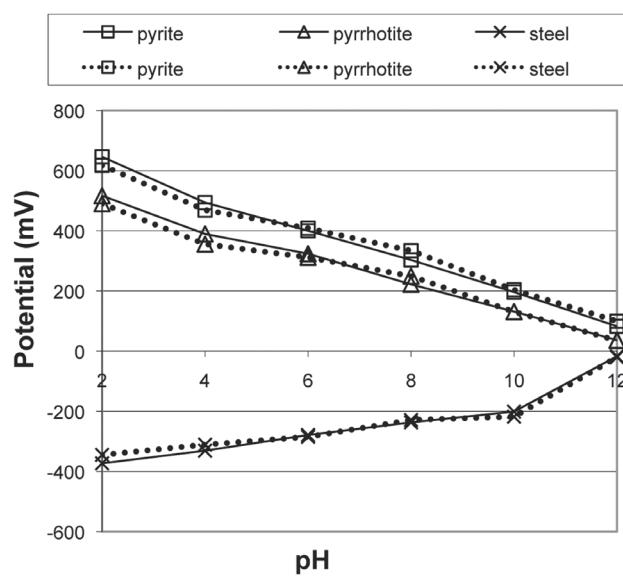


Figure 7—pH-potential relationships of pyrite, pyrrhotite, and steel with respect to saturated calomel reference electrode (solid line) and to gold reference electrode (dotted line)

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continuous changes in superficial properties and also irregularities in the selective flotation of minerals. Therefore, it is necessary that the flotation process is conducted during the preliminary stages of oxidation.

Based on the results of our experimental work, it was determined that among pyrite, pyrrhotite, and steel, pyrite has the highest open-circuit potential and steel has the lowest. Therefore, in galvanic contacts between pyrite and pyrrhotite or steel, pyrite act as the cathode, and in galvanic contacts between pyrrhotite and steel, pyrrhotite takes the role of cathode. While the surfaces of cathodes are passivated by oxide or hydroxide compounds, the mineral with lower open-circuit potential acts as anode and is oxidized. In the case of pyrrhotite, the oxidation process makes it hydrophobic, and in the case of steel, the oxidation causes it to corrode.

Because an increase in potential difference results in an increase in the intensity of galvanic interactions, pH changes have significant impact on galvanic interactions. With reduction in pH, the potential difference and subsequently galvanic interactions between minerals and steel increases. This results in more irregularities in the selective flotation of the minerals.

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