The Influence Of Conditioning Environment Of Oxidized Pyrite On Its Hydrophobicity

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ABSTRACT:
A serious problem in the mining industry is the sulfides surface oxidation because it reduces their hydrophobicity, impairing their flotation. A possible solution to this problem is sulfidization, since surface coating of these minerals with Fe-S bonds and elemental sulfur should increase their hydrophobicity. In this study, NaHS solutions were used to promote the formation of a hydrophobic layer on the surface of oxidized pyrite. Contact angle measurements and Raman spectroscopy were the techniques used to verify the nature of the products formed. The conditioning with NaHS at pH 10 and – 500 mV favors the precipitation of elemental sulfur.

Key words: Pyrite, hydrophobicity, conditioning, sulfur.

1. INTRODUCTION:
Surface oxidation of sulfide minerals is a serious problem in mineral processing, once their hydrophobicity is reduced, turning difficult to maintain the flotation performance, or leading to a high collector consumption (Monte et al., 1997; Monte et al., 2002; Newell et al., 2006; Simukanga et al.; 2017). The performance of the oxidized sulfides flotation has been improved by the sulfidisation technique with varying degrees of success. Sulfidisation has significant potential in the treatment of oxidized ore, tailings dam material and smelter slags. A feature common to all the sulfidised surfaces was the presence of metal sulfides, polysulfides or elemental sulfur, which may contribute to selective flotation.

Newell et al. (2007) demonstrated the ability to recover oxidized sulfides such as pyrothite, pentlandite and chalcopyrite, found together in a massive ore, using sulfidisation and flotation. The extent of this effect depends upon the oxidized sulfide mineral type to be remediate. These authors concluded that the floatability of these oxidized sulfides was restored by sulfidization with varying degrees of performance (chalcopyrite> pyrrhotite> pentlandite). A common feature to all of these sulfides surface was the presence of polysulfides and elemental sulfur which also contribute to its flotation. X-ray photoelectron spectroscopy (XPS) analyses revealed that the oxidized pyrrhotite was readily converted to a pyrrhotite-like surface. The pyrrhotite-like phase adsorbs more HS⁻ ions and the surface becomes covered by pyrite (FeS₂) by the reduction reaction of the Fe (III) ions, as shown by equations (1) and (2).

\[
\begin{align*}
\text{Fe(OH)}_3 + \text{HS}^- & \rightarrow \text{Fe(OH)}_3\cdot\text{HS}_{\text{ads}} \quad (1) \\
\text{Fe(OH)}_3\cdot\text{HS}_{\text{ads}} & \rightarrow \text{FeS} + 2\text{OH}^- + \text{H}_2\text{O} \quad (2)
\end{align*}
\]

Wei and Osseo-Asare (1997) have suggested that pyrite formation occurs in two step process stages (3), (4) and (5):

\[
\begin{align*}
\text{Fe}^{2+} + \text{HS}^- & \rightarrow \text{FeS} + \text{H}^+ \quad (3) \\
\text{FeS} + \text{S}^0 & \rightarrow \text{FeS}_2 \quad (4) \\
\text{FeS} + \text{S}^{2-}_n & \rightarrow \text{FeS}_2 + \text{S}^{2-}_{n-1} \quad (5)
\end{align*}
\]
It can be seen from Eqs. (3), (4) and (5) that the species needed in order to precipitate pyrite in the solution are $\text{Fe}^{2+}$, $\text{HS}^-$ and $\text{S}^{2-}$. Many of the previous investigations have focused on the mechanisms of pyrite formation on the oxidized sulfide surfaces. The formation of pyrite was also affected by the pH and redox potential ($E_h$) of the ferric and ferrous in solution. The intermediate products, elemental sulfur and $\text{FeS}$ (or $\text{Fe(HS)}^+$), were identified as precursors for pyrite formation (Wei and Osseo-Asare, 1996).

The sulfidisation mechanism of oxidized minerals is associated with the strong adsorption of $\text{HS}^-$ onto mineral surface followed by the formation of a sulfide surface through an anionic exchange reaction (Castro et al., 1974; Leppinen and Mielczarski, 1986). The oxidation state of sulfide mineral surface, as well as the nature of the surface oxidized species have drove the character of the sulfidisation mechanism.

In this paper, the precipitation mechanisms of hydrophobic species on the hematite (as a reference of the oxide mineral type), oxidized pyrite and original pyrite surfaces, based on $\text{NaHS}$ reactions, for two different pH values was evaluated. Raman spectroscopy surface analysis were employed to verify the sulfidisation. Thermodynamic stability diagrams ($E_h$-$pH$) were built in order to identify the stable predominant species.

2. MATERIALS AND METHODS:

2.1 Materials
A natural pyrite sample was taken from Ward’s Natural Science Establishment, Inc. One sample of massive crystalline hematite from Minas Gerais, Brazil, was also used in this study to simulate a completely oxidized pyrite. Aliquots from two samples were subjected to X-ray diffraction (XRD) and X-ray fluorescence analysis (XRF). The high grade of purity observed in the samples was confirmed by the XRD diffractograms of hematite and pyrite.

All reagents used were analytical grades and all solutions prepared with high purity water. The pH values in some experiments were adjusted with sodium hydroxide and/or hydrochloric acid solutions.

2.2 Methods
The potentiometric titration experiments were based on Wei and Osseo–Asare’s (1996, 1997) methodology and thus a potentiometric titration curve was plotted for a $\text{NaHS}$ solution with a concentration of 0.3 mol/L mixed with a solution of $\text{FeSO}_4$ with a concentration of 0.1M, at pH 8.0 and 10.0. In separate experiments, the pH was measured immediately after two solutions were mixed. The potentials, $E_h$, of the reaction solutions were measured with a platinum plate electrode referenced to a saturated calomel electrode (SCE). The potentials reported in this study were converted to the Standard Hydrogen Electrode scale (SHE).

The potentiometric titration curves and establish favorable conditioning conditions.

Sulfidization of oxidized pyrite, original pyrite and hematite (as reference) was performed using a $\text{NaHS}$ solution with a concentration of 0.3M, at 25°C. The parameters evaluated were pH (8 and 10) and reaction time (24, 48 and 96 hours). The effect of pH and $E_h$, recorded during each experiment, on the polished sections was analyzed. In some experiments, a pre-conditioning step (2 hours) with hydrogen peroxide solution (33% v/v) was carried out, in order to investigate the effect of previous pyrite oxidation on the sulfidization reaction.

The contact angle measurements were carried out using a Dataphysics Goniometer, OCA 15 Plus model, with a CCD video camera, and an electronic syringe unit. In this study, the captive bubble technique was used, where the polished section sample was placed in a rectangular glass chamber containing the $\text{NaSH}$ solution at pH = 8 and 10. At the end of reaction time, the bubble was placed under the sample. Bubbles were formed with $2 \mu l$ of volume and a velocity rate of 5.0 $\mu l/s$. The contact angle results presented in this study always refer to the advancing contact angle.

The SEM used in this study was a Leica Stereoscan 440 with a Kevex Detector for the EDS analyses. Under high magnification oxidized minerals were visually inspected and point-to-point measurements taken to determine the thickness of an oxidized surface layer and recorded photographically. The chemical nature of this layer as well as the bulk and near surface regions were
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determined by EDS for sulfur, oxygen, iron, copper and nickel using an acceleration voltage of 20 kV.

3. RESULTS AND DISCUSSION:

The variation of redox potential of a 0.1 mol/L solution (100mL) with additions of a 0.3 mol/L-NaHS solution is presented in Figure 1. It can be observed that the solution potential drops from -180 mV to -350 mV and the potentiometric titration curve presents clearly two inflection points at -200 mV and -250 mV, which can be attributed to pyrite and sulfur formation, according to the Eh-pH diagrams of S-H$_2$O and S-Fe-H$_2$O at 25°C, presented in Figure 2 (a) and 2 (b) respectively. Both, sulfur and FeS$_2$, are able to restore the hydrophobicity of oxidized pyrite, where a layer of iron oxide/hydroxide is formed on the mineral surface impairing collector adsorption and flotation. The HS$^-$ ion is a reductive species capable to reduce the sulfate ion formed during pyrite oxidation leading to the restoration of its original hydrophobicity through the formation of both pyrite or elemental sulfur, depending on the pH and Eh. Pyrite oxidation leads to the formation of sulfate and Fe$^{2+}$ ions through reaction (6), which can be reduced by HS$, rendering elemental sulfur according to reaction (7), pyrrothite (reaction (8)) and finally pyrite (reaction (9)), depending on the pH.

$$4\text{FeS}_2 + 14\text{O}_2 + 4\text{H}_2\text{O} \rightarrow 4\text{Fe}^{2+} + 8\text{SO}_4^{2-} + 8\text{H}^+ \quad (6)$$

$$3\text{HS}^- + \text{SO}_4^{2-} + 5\text{H}^+ \rightarrow 4\text{S} + 4\text{H}_2\text{O} \quad (7)$$

$$\text{HS}^- + \text{Fe}^{2+} \rightarrow \text{FeS} + \text{H}^+ \quad (8)$$

$$\text{HS}^- + \text{Fe}^{2+} + \text{S} \rightarrow \text{FeS}_2 + \text{H}^+ \quad (9)$$

In order to check the formation of hydrophobic species on oxidized pyrite through the conditioning in a reducing environment, a hematite sample was used to simulate a completely oxidized pyrite, avoiding any interference of sulfur compounds from the original sample. The Raman spectra of hematite and hematite after conditioning in a 0.3 mol/L NaHS solution during 96 hours, at pH 8.0 did not present remarkable differences, but some peak intensities alteration. However the petrographic microscope images revealed clearly the progressive formation of needle shaped sulfur crystals, as showed in Figure 3. In Figure 3 (a) the structure of fresh hematite is presented, while in Figures 3 (b), (c) and (d) the aspect of hematite after conditioning in a 0.3 mol/L-NaHS solution, at pH 8.0, during 24 hours, 48 hours and 96 hours respectively is exhibited. After 24 hours the presence of needle-like sulfur crystals in hematite surface is observed. It can be also observed that the number of sulfur crystals increase with the increase of conditioning time, characterizing a progressive nucleation mechanism. The SEM/EDS analysis also indicated the presence of sulfur needles on hematite.

![Figure 1. Variation of redox potential of a 0.1 mol/L FeSO$_4$ solution (100mL) with additions of a 0.3 mol/L NaHS-solution.](image)

The contact angles of hematite original sample and after a conditioning in a NaHS-0.3 mol/L solution, during different periods of time and pH values is presented in Figure 4. It can be observed that the contact angle is increased with the increase of conditioning time for pH values, 8 and 10. This behavior is explained by the formation of hydrophobic species, as sulfur and sulfur-iron compounds, as shown in Figures 3, which increase throughout the conditioning time. At pH 8 the contact angle is
higher than at pH 10. This behavior agrees with previous results reported in the literature (Buckley and Woods, 1987), and was already expected, since the smaller pH favors the thermodynamic stability of elemental sulfur, as indicated by the diagram of Figure 2 (a). Furthermore, it should be remembered that elemental sulfur is the more hydrophobic species of this system.

![Figure 2. Eh-pH diagrams for the systems S-H2O and S-Fe-H2O.](image)

Furthermore, it should be remembered that elemental sulfur is the more hydrophobic species of this system.

Figure 3 - Raman's petrographic microscope images of hematite before (a) and after conditioning in a 0.3 mol/L NaHS solution, at pH 8.0, during 24 hours (b), 48 hours (c) and 96 hours (d).

![Figure 4. Contact angles of hematite original sample and after a conditioning in a NaHS-0.3 mol/L solution, during different periods of time and pH values.](image)

The influence of conditioning time in NaHS 0.3 mol/L, on the surface of oxidized pyrite at pH 8.0 is presented in Figure 5. Figure 5(a) is a typical SEM backscattered electrons image of oxidized pyrite, while Figures 5 (b), (c) and (d) are images of the same oxidized pyrite after respectively 24, 48 and 96 hours of conditioning in the NaHS solution. It can be observed a progressive increase of elemental sulfur crystals on the oxidized pyrite surface. A detail of a elemental sulfur crystal on the oxidized pyrite surface, with its respective EDS is showed in Figure 6(a) and (b) respectively. The EDS indicates the presence of sulfur only. In the Raman spectra of pyrite and pyrite after oxidation and
conditioning in a 0.3 mol/L-NaHS solution during 48 hours, at pH 8.0 the presence of both pyrite (342, 378, 429) and elemental sulfur (151, 219, 473) peaks indicated the modification of the oxidized pyrite surface, through the formation of those compounds, which restore the hidrophobicity of the oxidized pyrite. These results are in accordance with the stability diagrams of Figure 2, which indicate the stability of pyrite and elemental sulfur, depending on the pH and redox potential conditions.

Figure 5. Influence of conditioning time in NaHS 0.3 mol/L, on the surface of oxidized pyrite at pH 8.0. (a) oxidized pyrite; (b) 24 h of conditioning; (c) 48 h of conditioning; (d) 96 h of conditioning.

Figure 6. Backscattered electron image of oxidized pyrite with sulfur crystals (a) and respective EDS (b) after conditioning in NaHS (0.3 mol/L) at pH 8.0 during 96 hours.

The contact angles of pyrite original sample, oxidized pyrite and oxidized pyrite after a 24-hours conditioning in NaHS (0.3 mol/L), at pH 8 and 10, is presented in Figure 7. It can be observed that the oxidation treatment with hydrogen peroxide reduces the contact angle of the original pyrite sample for the both pH values tested, while the conditioning with the NaHS solution restore the contact angle of pyrite close to their original values through the formation of both pyrite and sulfur crystals on the surface of oxidized pyrite.

4. CONCLUSIONS:
Sulfidisation increased the hydrophobicity of the hematite, pyrite and oxidized pyrite surfaces, although not to the same extent. With the sulfidization potential of -500 mV in a 0.3 M NaSH solution at pH 10, the hydrophocity of oxidized pyrite was significantly greater than that of hematite. A significant production of elemental sulphur/pyrite was observed. Hematite surface became hydrophobic by sulfidization at pH 8.0 due to the precipitation of elemental sulphur species onto its surface.
REFERENCES:
Simukanga, et. al.; 2017, The recovery of oxide copper minerals from a complex copper ore by sulphidisation, Minerals Engineering, 102 ,15–17

Figure 7. Contact angles of pyrite original sample, oxidized pyrite and oxidized pyrite after a 24-hours conditioning in NaHS (0.3 mol/L).