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Research Article

Evaluation of the Selection of Reagents Used in Pyrite Production

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ABSTRACT

In this study, tests were carried out using different collectors in pyrite flotation. According to the flotation tests, Tomamine M73 and Sodium Butyl Xanthate (SBX) and KEX collectors were used to keep the desired sulfur value around 46% and to increase the efficiency value in the system operating with 30% efficiency. Plant-based trials were conducted on the collectors used. Both the efficiency of the circuit exceeding 30% and the sulfur value remaining at 46% were obtained in the Sodium Butyl Xanthate (SBX) collector.

1. Introduction

Pyrite (FeS_2) is an iron-sulfur mineral, also colloquially known as “fool's gold”. It resembles metallic ripening and a brassy yellow color, but is distinguished from gold by its Mohs hardness of 6-6.5 and its brittleness. The crystal system is cubic pentagonal; frequently cubic, octahedral or pentagonal-dodecahedral crystals occur.

Figure 1. Types of the crystal system of pyrite

It is found in hydrothermal veins, igneous rocks, folded rocks and coal deposits. It occurs in association with minerals such as quartz, chalcopyrite and sphalerite. It can also coexist with iron oxide minerals such as magnetite (Fe_3O_4) and hematite (Fe_2O_3). Gangue minerals such as quartz (SiO_2) and calcite ($CaCO_3$) are also frequently encountered in hydrothermal veins. In sedimentary environments, it may occur as fine grains or concretions in organic matter-rich shales and coal beds. The presence of pyrite in these different environments provides important clues about the geologic history and formation processes of that region.[1-2]

Answering the question "what is pyrite for" directly in an ecological context can be a bit complicated because pyrite itself does not have a major ecological function. However, the presence of pyrite and its chemical reactions may indirectly affect some ecological processes.

- Element Cycles: Iron ions and sulfate ions resulting from the weathering of pyrite participate in the iron and sulfur cycles. Iron is an important element in the structure of many enzymes and is important for living organisms. Sulfate is used as an energy source by some microorganisms.
- Acid Mine Drainage (AMD): Uncontrolled pyrite oxidation can lead to the formation of sulfuric acid and thus AMD. This poses a serious threat to aquatic ecosystems, lowering the pH of the water and increasing the solubility of heavy metals. While this is a negative effect, it illustrates the ecological consequences of pyrite reactivity.

$$4FeS_{2(k)}+14O_{2(g)}+4H_2O_{(l)}\rightarrow 8H_2SO_{4(sulu)}+4Fe_2O_{3(k)}$$

Here, it reacts with 4 iron sulfide (FeS_2) molecules, 14 oxygen molecules (O_2) and 4 water molecules (H_2O) to produce 8 sulfuric acid molecules (H_2SO_4) and 4 iron$_{(III)}$ oxide molecules (Fe_2O_3); These molecules are colloquially called rust.

- Microbial Activity: Some microorganisms can live on the surface of pyrite and interact with it to obtain energy (biosolubilization). This process can affect the release of metal ions and thus the environmental chemistry[3-4]

It is difficult to give clear and precise answers to a question like "what would not happen in the world without pyrite" because natural systems are complex and interdependent. But we can consider some possible impacts.

- The formation of metal deposits could be affected: Many important metal deposits are associated with pyrite or the formation of pyrite. The absence of pyrite could affect the formation or enrichment of deposits of some metals, such as copper, zinc, lead and even gold, in different ways. This could indirectly affect industries and technologies based on these metals.
- The Sulfur Cycle Could Change: Pyrite is an important source of sulfur in the Earth's crust. Its absence could have affected the sulfur cycle and thus the formation of sulfate. Sulfate is an important nutrient for plants and a source of energy for some microorganisms.
- The Acid Mine Drainage Problem Would Be Eliminated: AMD, which is formed as a result of the oxidation of pyrite, is an important environmental problem. The absence of pyrite would completely eliminate this problem. However, it would also mean that some of the potential benefits of pyrite, such as biodegradation, would be lost.
- Geochemical Processes Could Work Differently: The reactivity of pyrite plays a role in some geochemical processes, such as rock weathering and mineral transformations. Its absence could have changed the speed or pathway of these processes.[5-6]

In summary, the role of pyrite in nature is indirect and complex. While it does not have a major ecological "role", it can be influential in various processes such as the formation of metal deposits, element cycles and environmental chemistry. Its absence could lead to some significant changes, especially in terms of metal resources and environmental issues.[7-8]

Pyrite is an important active ingredient for the production of sulfuric acid. The tailings of copper flotation contain mainly pyrite minerals. Pyrite is usually together with valuable minerals such as chalcopyrite, galena, sphalerite etc. which are valuable sulfides. In order to recover copper from these minerals, pyrite must be suppressed. For example, when chalcopyrite is separated from pyrite, chalcopyrite is always floated first.

During beneficiation by flotation, the surface properties of pyrite play a critical role in the separation of this mineral from other valuable sulfur minerals. Pyrite flotation is usually applied to suppress or separate pyrite, which has no economic value in the ore. However, in some cases, pyrite itself may be the target mineral; in such cases, flotation conditions are optimized accordingly.

The flotation process of pyrite varies depending on the chemical properties of the medium, the reagents used and the pH of the medium. Generally, the surface of pyrite is easily rendered hydrophobic by xanthate-type collectors and flotation is performed. However, since unintentional dispersion of pyrite next to valuable minerals may cause purity problems in ore dressing, the flotation of pyrite must be suppressed in this case. One of the most commonly used parameters for this is the use of ambient pH. By increasing the pH, especially with the addition of lime (CaO), the surface of the pyrite is coated with iron hydroxides and thus its hydrophobicity is reduced. Under high pH conditions, the flotation efficiency of pyrite decreases while the flotation of valuable sulfur minerals can be maintained.

In the flotation process, pH is a critical control parameter on surface chemistry and ionic interactions. pH changes directly determine the selectivity and efficiency of flotation by influencing the charge status of mineral surfaces, ionization of reagents, and the type and density of ions in solution. [16]

Surface oxidation also has a great influence on pyrite flotation. While slightly oxidized pyrite surfaces can be more active in terms of collector retention, excessive oxidation reduces the flotation ability of pyrite. For this reason, the freshness of the mineral surface and the preparation procedures before flotation are of great importance. Reagent selection also keeps pyrite under control. In addition to xanthates, cyanide, sulfate reagents and some special depressors are available to suppress pyrite.

Effective suppression of pyrite in flotation applications, especially in copper, lead and content ores, reduces both concentrate and processing costs. In addition, the production of raw material for sulfuric acid production by floating pyrite by oxidative flotation can also create an economic value in some private enterprises. [9-10]

2. Materials and Methods

In this study, an enterprise that has achieved 46% sulfur value with 30% yield by pyrite flotation was requested to recover more material with the same sulfur value. Upon this demand, it was aimed to increase the yield value and the amount of material recovered by using different chemicals.

Table 1. Chemicals Used in the Tests

Test No	Collector	Frother
Test 1	Tomamine M73	-
Test 2	Sodyum Bütil Ksantat	Oreprep X133
Test 3	Tomamine-Kex	-

In test 1, the Tomamine M73 collector was used to achieve the targeted 46% sulfur despite large foams as shown in figure 2. For this reason, when it was desired to increase the amount of material gained, when the amount of collectors fed per ton was increased, the foams became larger and overflowed over time, as in figure 3. In this case, the first intervention was to shut down the collector. In this case, it caused imbalances in the flotation system.

Figure 2. State of the foam using Tomamine M73

Figure 3. The state of the foam after an overdose of Tomamine M73

3. Results

In this study, plant-based tests were conducted based on the results of laboratory tests. Test 1 is the Tomamine M73 collector used in the plant under normal operating conditions. During this study, Tomamine M73 chemical was given and the system was followed in detail. However, the results did not change with the desired % Sulfur value with the Tomamine M73 collector, which has been working for a long time. However, due to the small amount of material recovered, studies were carried out for test 2.

Sodium Butyl Xanthate (SBX) ($C_4H_9OH+CS_2+NaOH \rightarrow C_4H_9OCS_2Na+H_2O$) was used only as a collector without changing the working conditions in test 1. In laboratory studies, the % Sulfur value of the material was 46%, which is the value captured with the Tomamine M73 collector. In addition, with the addition of Oreprep X133 frother together with the Sodium Butyl Xanthate collector, the amount of material taken from the system has increased and the % Sulfur value has increased to 47.40%.

The surface activity level and chemical structures of the reagents used in the flotation process have a direct effect on the volume, stability and structure of the foams formed in the system. In particular, the foam characteristics of xanthate type collectors and surfactant amine-based reagents are quite different. While xanthates such as KEX (potassium ethyl xanthate) and SBX (sodium butyl xanthate) enable flotation by making mineral surfaces hydrophobic, their ability to lower surface tension and form foam is quite limited. Therefore, when xanthates are used, low-volume and unstable foams are often observed.[12-13] Short-chain xanthates (e.g. KEX), although providing higher solubility, do not positively affect the foam characteristic.[15] On the other hand, alkoxylated amine surfactants such as Tomamine M73 play an active role at the water-air interface, promoting foam formation. This structure, which is both hydrophilic and hydrophobic thanks to its EO (ethylene oxide) chain, stabilizes air bubbles and causes the formation of high-volume, small-bubble and long-lasting foam.[11] Such reagents are particularly effective in the flotation of oxidized minerals, but excess foam formation can also lead to undesirable sludge transport.[14] For these reasons, when choosing the reagent to be used in the flotation circuit, not only the collection power, but also the type of foam it will form and its stability should be taken into account.

pH value of the Tomamine M73 collector used 1. In the analyzes was not taken into account. However, in laboratory studies, the pH value was also taken into account during test 2. In the analyzes, it was seen that the pH value was beneficial to the % Sulfur value and amount. It has been observed in the field trial studies that the pH value ranging between 10.30 and 11.20 has an effect on the gain of 4 tons/hour pyrite concentrate. But 1. Since the study was carried out without considering the pH value in the test, this issue was evaluated separately. The status of the pH effect in the study is shown in Table 2.

Table 2. Effect of pH value in test 2

pH Value	% Sulphur Value	Amount of Material Acquired
10,30	%46,80	9 t/h
11,20	%47,20	22 t/h

In test 2, when the values after using Sodium Butyl Xanthate as collector and Oreprep X133 as foaming agent without taking the pH value as a basis, it was observed that the %Sulfur value and amount increased compared to the values in test 1. The values are as shown in Table 3.

Table 3. Results of test 2 without the effect of pH value

Test No	% Sulphur Value	Amount of Material Acquired
Test 1	%46,80	9 t/h
Test 2	%47,40	18 t/h

When Sodium Butyl Xanthate used in test 2 was used alone, it caused the formation of coarse foams and overflow, as seen in figure 4, which was experienced in test 1. By using the Oreprep X133 frother, thinner foamed material was gained as shown in figure 5. In this way, it has been observed that both the % sulfur value has been increased and the amount of material gained has increased.

Figure 4. State of the foam when Sodium Butyl Xanthate is used alone

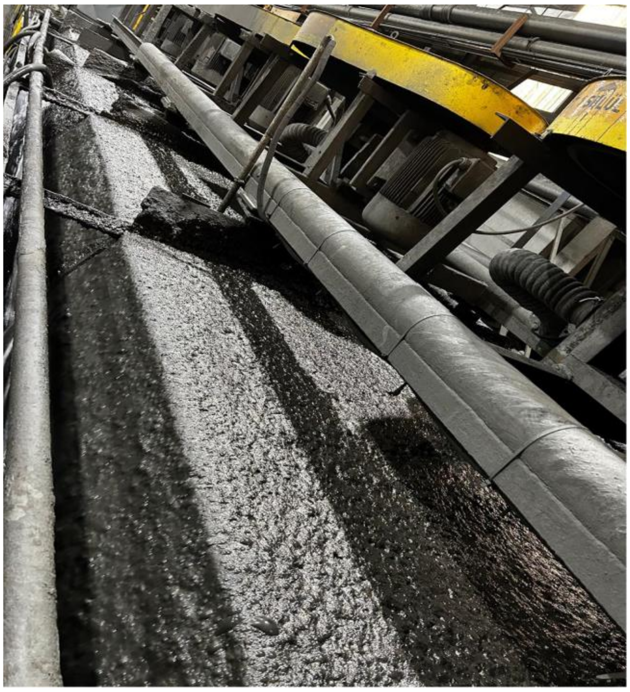

Figure 5. State of the foam when Sodium Butyl Xanthate and Oreprep X133 are used together

Since we have the KEX collector used in copper flotation in test 3, it is aimed to increase both the % sulfur value and the amount of material gained with finer foam recovery by adding an extra KEX collector in order to prevent the overflow of coarse foams with the Tomamine M73 collector in test 1. As can be seen in Figure 6, thanks to the fine foam, there was no overflow and material was gained. An increase in tonnage and % sulfur value was observed when using only Tomamine M73 in the % sulfur value.

Figure 6. State of the foam when Tomamine and KEX are used

When the results of three different test studies are examined, the sulfur rate obtained in each test and the corresponding material recovery amounts differ. In test 1, 9 tons/hour material with 46.80% sulfur content was obtained. In test 2, the sulfur content increased to 47.40% and the amount of material recovered in parallel with this increase reached the highest level with 18 tons/hour. In test 3, the sulfur content was recorded as 46.68% and 12 tons/hour material was obtained. Considering these data, it is seen that the increase in sulfur ratio also positively affects the amount of material recovery. The general status of the values is given in table 4.

Table 4. General results of the Tests

Test No	% Sulphur Value	Amount of Material Acquired
Test 1	%46,80	9 t/h
Test 2	%47,40	18 t/h
Test 3	%46,68	12 t/h

4. Conclusion

In this study, it was aimed to produce more than the desired % sulfur value. As a result of the laboratory study, it was observed that when Sodium Butyl Xanthate was used as collector and Oreprep X133 was used as foaming agent, the amount of material recovered increased and the % sulfur value did not decrease. As a result of the laboratory studies, a plant-based trial was carried out and the results were found to confirm the results of the laboratory studies. Thanks to this study, the amount of material increased without decreasing the % sulfur value thanks to a different collector and frother. In addition, within the scope of the plant-based studies, the pH value was also taken into consideration and working conditions were provided at the appropriate pH value.

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