

The Role of Electrochemistry in Making a Mining Business Work: Why Adequate Particle Liberation is not Enough

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ABSTRACT

In the beneficiation of copper ores, rejection of pyrite is crucial to produce a high concentrate grade. Pyrite has low floatability at alkaline process conditions and, for this reason, control of pH is very important in copper flotation. Under adequate process conditions, pyrite should report primarily to the tailings stream. However, activation of pyrite in copper flotation circuits is quite common, due to electrochemical conditions in the upstream comminution circuit. In grinding, pyrite can easily get activated by the copper species in the system. This activation greatly enhances the hydrophobicity of pyrite, making the mineral act “as if it were a copper sulfide”. As such, pyrite is more easily recovered, which negatively impacts both the overall copper recovery and final concentrate grade.

The electrochemical reactions resulting in pyrite activation can be significant, and at the same time they are poorly understood at many operations. The reason why pyrite gets activated in grinding is because of the electrochemical conditions (in both SAG mills, primary ball mills and re-grinding mills); however, operations, and specifically comminution circuits, focus primarily on throughput, liberation, and specific energy consumption, while little to no attention is given to the electrochemistry of this process.

The current paper presents an executive but complete overview of the different mechanisms that explain pyrite activation in copper concentration plants. Then, based on typical process conditions for large-scale concentration plants in the Andean region, a quantified estimate is given of the impact of pyrite activation on the actual copper concentration process. Finally, different alternatives to either avoid or minimize pyrite activation are identified.

INTRODUCTION

Characteristics of the Andean region

Many sources of water in the Andean region are slightly acidic by nature and thus acid rock drainage (ARD) is a phenomenon that occurs naturally. Given the fact that the Andean region is also rich in copper ore bodies, it is common to observe water sources that are not only naturally acidic but also contain a significant amount of Cu-ions as a result of the partial dissolution of copper species by the acidic water.

Copper ores have varying pyrite (Fe_2S) content, however average values are estimated to be 1-10% on whole rock basis for the Andean region. In copper sulfide concentration plants, this pyrite can get unintentionally activated by Cu-ions in solution and report to the final concentrate stream, resulting in a lower copper grade and/or recovery for the final concentrate. The origin of these Cu-ions can be (I) the copper bearing mineral sulphide species in the ore, or (II) the copper that is present in the acidic Andean water sources.

The fairly unique combination of acidic water sources with the large-scale pyrite-containing copper ore bodies in the Andean region, plus the relatively high energy prices in the region that make operations focus primarily on grind size and not on the electrochemical conditions of the grinding process, make the copper concentration plants especially prone to the undesired activation of pyrite and its detrimental effects on final copper grade and recovery.

The role of particle liberation

Adequate particle liberation is a necessary but not sufficient condition for copper sulphide flotation. A grinding circuit should deliver a product slurry with the right grind size which implies that the copper sulphide grains are sufficiently liberated to be recovered in the next stage of flotation. However, the copper sulphide particles will only report to the concentrate, if there is no other mineral species present in the system that competes with, or even replaces copper sulphide as preferred floatable species. In case pyrite gets activated, then unavoidably (I) either less copper sulphide will float and/or (II) total mass pull will increase as the activated pyrite reports to the concentrate, and hence final copper concentrate grade and recovery will be lower, despite of having adequate particle liberation for the copper sulphide species.

Activation of pyrite

Pyrite activation in simple terms means that the pyrite particles are coated by Cu-ions that are present in solution, and hence the pyrite behaves as if it were a copper sulphide species. Xanthate is widely used as Cu-specific collector, and is added to the system to promote flotation of the copper species; however, xanthate does not distinguish between the actual copper sulphide particles and the Cu-coated pyrite particles, and thus once pyrite is activated, it will float as if it were a copper sulphide.

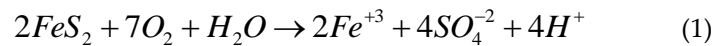
The Cu-ions that coat the pyrite particles can originate (I) from the process water as a result of the natural presence of Cu-ions in case an acidic water source is used, or (II) from the copper minerals that partially release Cu-ions into solution due to the electrochemical conditions of the grinding process.

Interestingly, pyrite activation has been shown to become significantly less for certain types of pyrite (Owusu et al., 2013). Trace impurities such as arsenic can be beneficial in this context as the incorporation of As into pyrite crystals significantly reduces its electrochemical activity and hence As containing pyrite shows significantly lower level of pyrite activation.

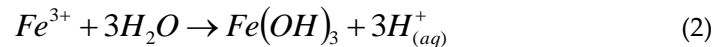
THE MECHANISM OF PYRITE ACTIVATION IN COPPER FLOTATION

Pyrite flotation in the absence of other sulphide minerals

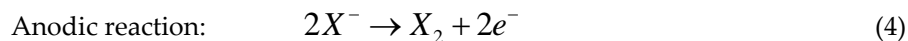
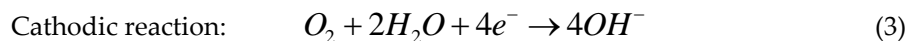
Pyrite (FeS₂) in water is strongly reactive, and tends to oxidize, consuming oxygen and generating acidity, according to the following equation (Scott et al., 2007):



Oxidation of pyrite results in the formation of different species on the surface of the mineral (Nicholson et al., 1990). Temperature and pH dictate which products develop on the surface of pyrite upon oxidation. In acidic conditions (below pH 4) ferric sulphate is the primary oxidation product, while at a near neutral pH or above (above pH 6) the ferric ions generated by the oxidation of pyrite (Eq. 1) will precipitate almost all as iron oxide or hydroxide (Todd et al., 2003; Banks et al., 1997), as depicted in Eq. 2:



The species formed at the surface of pyrite upon oxidation are mostly hydrophilic, and therefore reduce the capacity of the mineral to float. However, pyrite can be inadvertently floated by the collectors commonly used for copper, such as xanthates and dithiophosphates. Xanthate ions in solution can oxidize to dixanthogen on the surface of pyrite (Wang and Forssberg, 1991). Oxygen accepts electrons, while xanthate (X⁻), which is an anionic surfactant, loses electrons and oxidizes to dixanthogen (X₂), as depicted in Eqns. 3 and 4.



The dixanthogen formed adsorbs onto the surface of pyrite and, being highly hydrophobic, causes the mineral to float (Figure 1).

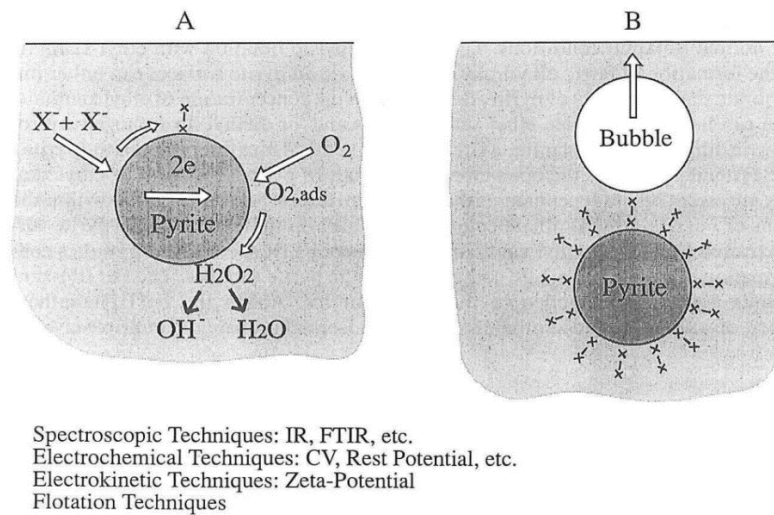


Figure 1 Schematic presentation of classical model of pyrite flotation with xanthate as collector (Wang and Forsberg, 1991)

There is a window for pyrite flotation in the presence of xanthate between about pH 4 and pH 10. Above pH 10, oxidation of xanthate to dixanthogen does not occur, and the ferric hydroxide also competes with xanthate for adsorption, making for pyrite impossible to float (Morey et al., 1999).

Pyrite flotation in presence of other sulphide minerals

When pyrite is present in a flotation pulp together with other sulphide minerals (e.g., chalcopyrite), the chemistry of the system is more complex. Electrochemical interactions occur between the minerals themselves, and between the minerals and the grinding medium.

What drives the actual reactions that take place, is the rest potential of each sulphide mineral. The rest potential indicates the degree of reactivity of each mineral species in the pulp. Pyrite has the highest rest potential, which means that during electrochemical (galvanic) contact in a mixed mineral pulp, pyrite becomes the cathode (receives electrons, and oxygen is reduced on its surface), while the less noble sulphide mineral (generally the copper sulphide) oxidizes, releasing positive metal ions (Cu^{2+} , Fe^{2+}) into solution. As a result, the oxidized copper mineral becomes less floatable, while pyrite can interact with the dissolved Cu^{2+} ions, with the formation of hydrophobic cuprous xanthate on its surface (Voigt et al., 1994).

The order of the chemical reactions that take place when pyrite and chalcopyrite are both present, is described below (Fornaseiro et al., 2008):

1. The bivalent Cu(II)-ions in solution react with the OH-ions present at the alkaline process conditions and form $\text{Cu}(\text{OH})_2$ that absorbs onto the pyrite surface
2. The bivalent Cu(II) ion is then reduced to Cu(I) forming Cu(I)-S on the surface of pyrite, together with the oxidation of sulfide
3. Xanthate (X^-) will react with the Cu(I)-S on the pyrite surface to form $\text{Cu}(\text{I})\text{X}_{\text{surface}}$ and turns pyrite into an easily floatable species

This process mechanism is shown in Figure 2.

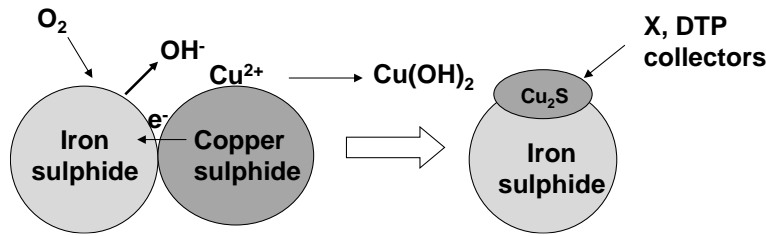


Figure 2 Electrochemical interactions between pyrite and the copper sulphide in flotation pulp

Enhanced pyrite activation with forged steel grinding media

The reaction is enhanced in the presence of forged steel grinding media. Mild steel acts as a catalyst for the galvanic reactions, and also releases Fe^{3+} ions to solution upon oxidation, which can in turn depress the flotation of the copper sulphides further (Huang and Grano, 2005). This latest mechanism, the direct depression of copper sulphide by Fe^{3+} ions in solution, combined with a reduction in the available collector (which is in part adsorbed by the activated pyrite) can cause tangible decrease in Cu recovery. These effects are however not further analyzed in this paper.

Cu-activation of pyrite occurs in particular in the grinding mills, where the amount of fresh surface produced is high. Pyrite can be activated not only by the Cu-ions released to solution upon oxidation of the copper sulphide, but also by Cu^{2+} ions already present in process water (e.g., from previously neutralized acidic process water). This mechanism is very relevant to copper operations, as it is the main cause responsible for the unwanted flotation of pyrite. The net result is that significant more pyrite than expected often reports to the flotation concentrate, even at high pulp pH (Figure 3).

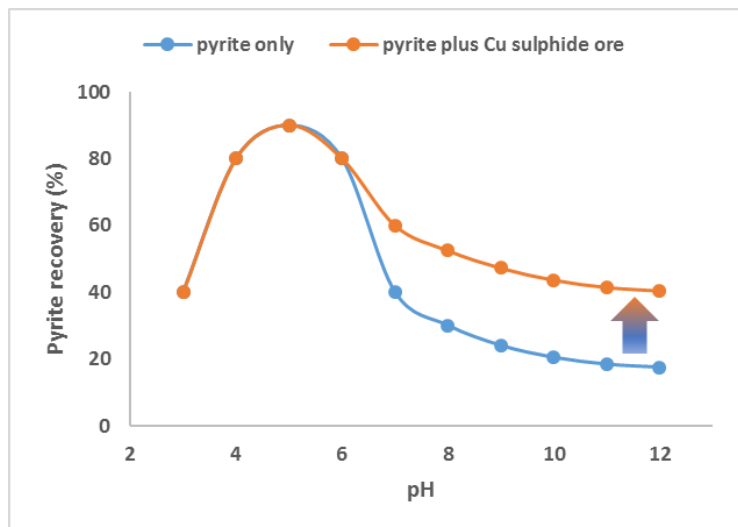


Figure 3 Typical case of pure pyrite vs. pyrite-copper sulphide flotation

QUANTIFICATION OF POTENTIAL IMPACT OF PYRITE ACTIVATION

Base case definition

A theoretical base case was defined, based on typical operational data for large size copper mining sites in the Andean region. Excel based calculations were used, assuming a steady-state operation in which the feed equals the sum of tailings plus concentrate, for both total mass flow (tpd) and for the element of interest (Cu in this case). A feed rate of 100.000 tpd was set for the base case, and Cu grade in feed, rougher concentrate and rougher tailings was set at 0.7%, 8% and 0.1% respectively. These values can be considered typical for large size copper mining operations in the Andean region. Once these values were set, it was possible to calculate rougher recovery (86.8%), rougher mass pull (7.6%), concentrate grade (8%) and tailings grade (0.1%) for the base case. It should be noted that all these values are theoretical, as this study does not involve any industrial experiment, however both the assumed and calculated values as shown in Table 1 are in line with industrial practice. As can be seen, the base case considers a pyrite content of 0%.

Table 1 Definition of Base Case Conditions

	Assumed value	Calculated value
Throughput (tpd)	100.000	
Cu grade in feed	0.7%	
Cu grade in Ro concentrate	8%	
Cu grade in Ro tailings	0.1%	
Ro recovery		86.8%
Ro mass pull		7.6%
Mass flow tailings (tpd)		92.405 tpd
Mass flow concentrate (tpd)		7.595 tpd
Pyrite content	0%	
Degree of pyrite activation	0%	

Quantification of pyrite activation

Subsequently, the impact of pyrite activation was quantified assuming 3 different levels of pyrite content in the feed (2-4-6%) and 3 different degrees of pyrite activation (20-30-40%; apart from the 0% pyrite activation corresponding to the base case). It should be noted that the degree of pyrite activation recognises the fact that some, but not all pyrite, will get activated. For these calculations it was assumed that all copper is present as chalcopyrite. In summary, the following ore and process variables were evaluated:

- Pyrite content: 2%, 4% and 6% total pyrite content (whole rock basis).
- Degree of pyrite activation: 20%, 30% and 40% pyrite activation. The degree of pyrite activation represents the actual amount of pyrite that gets activated by presence of Cu-ions in the system.
- Cu grade in rougher tailings, Cu grade in rougher concentrate and rougher mass pull: these parameters were all calculated as a function of pyrite content and its degree of activation.

It was assumed that the total copper recovery in the rougher stage is not affected by the additional mass pull from the pyrite activation. In other words: it was assumed that the rougher circuit has no physical constraints to handle the additional mass pull due to pyrite activation. In practice, this implies that the cleaner circuit will receive a feed stream (the rougher concentrate) that is significantly larger volume and lower grade than what would be the case without pyrite activation.

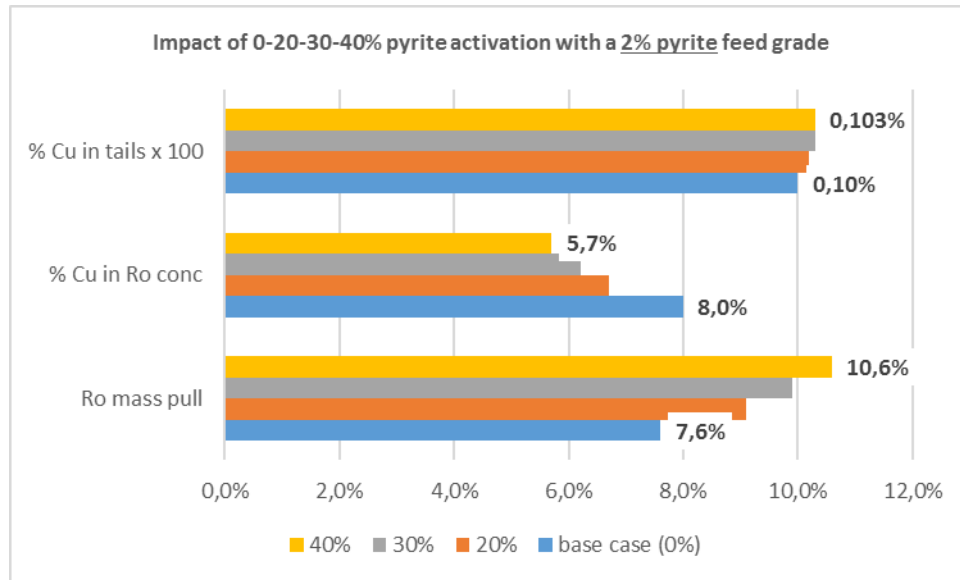


Figure 4 Impact of different degrees of pyrite activation for a 2% pyrite ore

As can be expected, as the degree of pyrite activation increases, the impact on the actual operation becomes more significant. Rougher mass pull increases from 7.6% at base case to 10.6% assuming 40% pyrite activation, at a pyrite feed grade of 2%. The total copper content in the rougher concentrate for these same conditions decreases from 8.0% to 5.7% and the copper content in the rougher tailings increases slightly from 0.10% to 0.103%.

As can be expected, for ores that contain higher amounts of pyrite, the detrimental effect of pyrite activation becomes even more significant. Figure 5 shows the corresponding numbers for a pyrite content of 4%. Total mass pull for the rougher stage increases from 7.6% to 13.6%, rougher concentrate grade decreases from 8.0% to 4.5% and Cu tailings content increases from 0.10% to 0.107%.

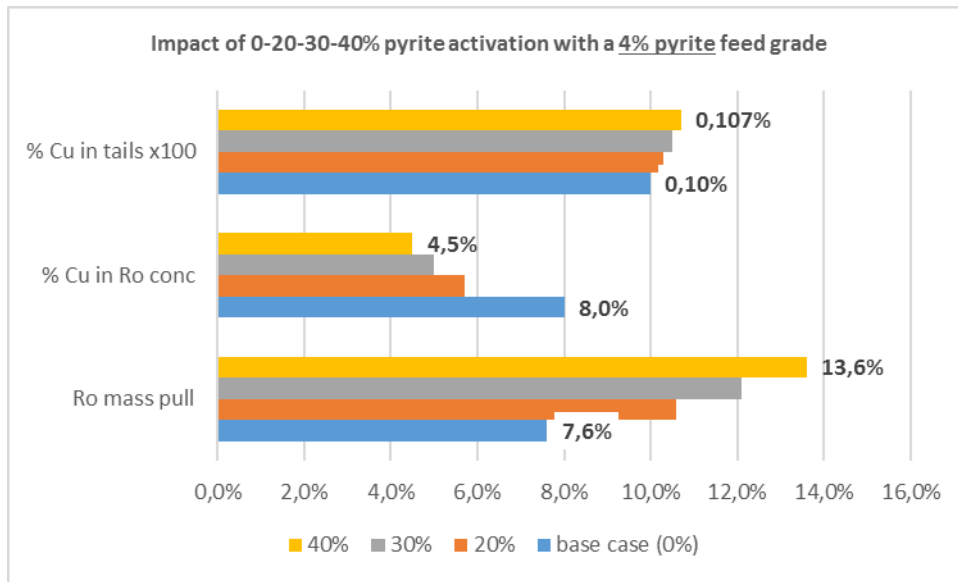


Figure 5 Impact of different degrees of pyrite activation for a 4% pyrite ore

As worst case scenario, the same calculations were done for a 6% pyrite ore, giving the following numbers:

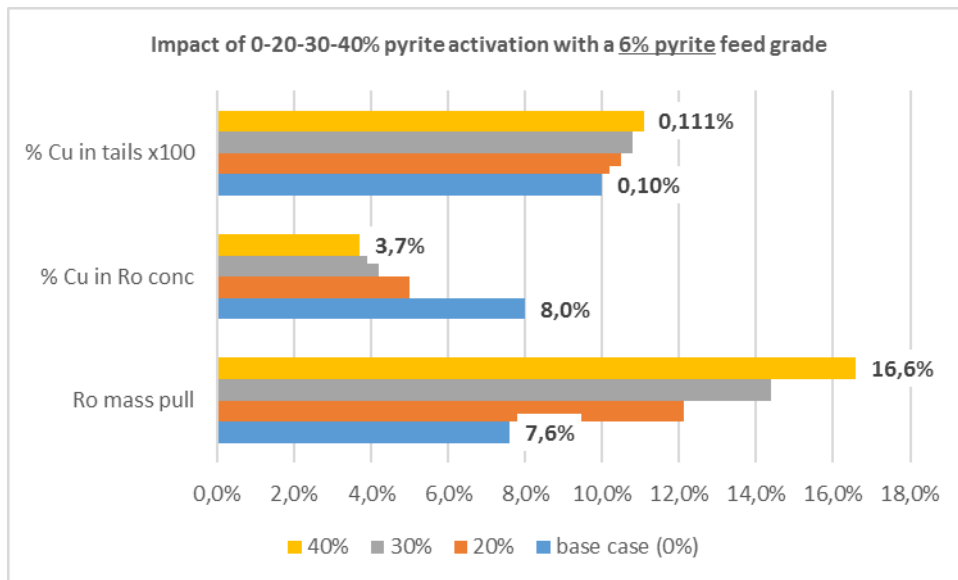


Figure 6 Impact of different degrees of pyrite activation for a 6% pyrite ore

It will be clear that in this worst case scenario – assuming a 6% pyrite content in the feed and a maximum pyrite activation of 40% - the operation of the plant becomes beyond reasonable since mass pull in the roughers would more than double and copper concentrate grade falls back to more than half its original value. In practice this means a clear loss of control of the operation, as the low grade large volume feed to the cleaner circuit would result in lower overall rougher-cleaner recovery, and a low final concentrate grade.

MITIGATION OF PYRITE ACTIVATION

In order to identify options for minimizing the detrimental effect of pyrite activation on overall copper sulphide flotation performance, it is important to distinguish between the different electrochemical conditions that contribute to pyrite activation. This section will briefly describe the alternatives, as presented in existing publications, for minimizing or mitigating pyrite activation.

Natural tendency of pyrite to get activated in copper/iron sulphide system

This is a result of the high rest potential of pyrite in presence of the less noble copper sulphide species. There are three clear alternatives to revert this natural tendency:

- Aeration of the pulp prior to xanthate addition to render the surface of pyrite inactive by oxidation of the surface (Owusu et al., 2015)
- Utilization of reducing agents as pyrite depressant such as sodium sulfite (Fornaseiro et al., 2008)
- Utilization of copper complexants such as TGA that immobilize Cu-ions in solutions and prevent pyrite activation by elimination of “free” Cu-ions (Fornaseiro et al., 2008)

These three alternatives all focus on changing the electrochemical Eh/pH conditions of the grinding/flotation pulp in such a way that pyrite activation becomes less likely as the conditions created by using any of these alternatives are adverse to the natural pyrite activation associated to its high rest potential.

Catalytic effect of forged steel grinding media

The catalytic effect of forged steel grinding media on the pyrite activation results in acceleration of pyrite reduction and copper sulphide oxidation (Greet et al., 2015). In practice, there is one way only to reduce this catalytic effect:

- Use of a less reactive medium, such as high chrome balls

The use of different type of grinding media, such as high chrome balls or ceramic media (used for limited applications only), will eliminate the catalytic effect of forged steel grinding media on pyrite activation, and hence the degree of pyrite activation will decrease.

Xanthate absorption onto activated pyrite surface

The use of xanthate as collector in the copper/iron sulphide system, together with the interaction of pyrite with dissolved Cu^{2+} ions, facilitates the formation of hydrophobic cuprous xanthate on the pyrite surface. The copper activated pyrite is more prone to adsorb xanthate from solution, and reports to the flotation concentrate. A good alternative available to avoid or minimize xanthate absorption onto the activated pyrite surface is:

- Controlled collector addition during grinding to maximize collector absorption to copper sulphide species before pyrite activation occurs (Fornaseiro et al., 2008)

Addition of collector during grinding ensures that the xanthate gets strongly attached to the copper sulfide species and hence “losing” xanthate to pyrite activated by Cu-ions is less likely.

One other possible alternative is:

- Use of a more selective collector as a replacement for xanthate.

Xanthate, and dithiophosphate (DTP), are the most commonly used collectors for copper minerals, also for their lower cost. However, it was shown that other collectors, such as thionocarbamates, have higher affinity for the copper minerals compared to xanthate and DTP, and are less likely to be adsorbed on pyrite (Basilio et al., 1988; Leppinen et al., 1988).

Presence of Cu-ions in process water

The presence of Cu-ions in solution that do not originate from oxidation of Cu species in the ore, “supply” Cu-ions to react with xanthate on the pyrite surface and enhances activation. The way to deal with this presence of Cu-ions in process water is as follows:

- Pretreatment of acidic process water focused on Cu-removal and not on neutralization only

The case of Cu-ions that originate from an acidic process water source is quite unique for Chile. Typically, these acidic water sources get neutralized as grinding is not feasible with acidic water. However, typically neutralization is focused on increasing pH of the water only and little attention is given to whether the Cu-ions in solution are effectively removed. Even if Cu-ions precipitate as $\text{Cu}(\text{OH})_2$, then still this precipitate can be an efficient source for Cu-ions for pyrite activation in the actual grinding stage. Another source of Cu-ions in solution can be from soluble copper minerals such as chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), which has also been observed in the Andean region.

CONCLUSIONS AND RECOMMENDATIONS

Grinding plants tend to focus on achieving the desired grind size in order to assure adequate liberation of the copper sulfide species. However, achieving adequate grind size is a necessary but not sufficient condition for good flotation performance. If pyrite gets activated, then even if grind size is optimum, flotation performance still will be poor with lower-than-expected copper grade and recovery. Assuming a 2% pyrite content in the feed and a pyrite activation of 40%, Cu grade in the rougher concentrate can decrease from 8% to 5.7% and mass pull for the rougher stage increases from 7.6% to 10.6%.

Activation of pyrite causes increased mass recovery or mass pull, decreased Cu concentrate grade and increased Cu tailings grade. In addition, at high levels of pyrite activation, the overall copper recovery likely will decrease. The exact numbers are dependent the specific site characteristics, but doubling the actual mass pull or achieving only half of the expected copper grade in the rougher concentrate, is (unfortunately) totally reasonable in case of pyrite activation.

The way to mitigate the impact of pyrite activation depends on the actual mechanism behind this activation. Different mechanisms exist and each specific site should define, using operational information, solid/liquid feed stream chemical assays, plus additional chemical and surface characterization of the mineral species involved, which mechanisms explain the pyrite activation that is being observed and what would be the best way forward to mitigate its impact.

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