

Pyrite Leaching Behaviour under CESL Process Conditions

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ABSTRACT

The amount of pyrite in copper concentrates fed to the CESL Process can vary appreciably. The fraction of pyrite that oxidizes influences both capital and operating costs and is therefore an important variable. The present paper explores operating conditions that influence the extent of pyrite oxidation and the probable overall reaction chemistry under CESL conditions.

KEYWORDS

Pyrite, leaching, CESL, enargite

INTRODUCTION

A key defining difference of the CESL Copper Process for the hydrometallurgical treatment of copper concentrates is the limited extent of sulphur (S) oxidation occurring during the leaching step. This is important because extra S oxidation:

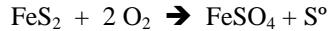
- uses additional reagent, namely oxygen (O_2), requiring a more costly, higher energy consuming O_2 Plant;
- generates unwanted heat in the leach vessel making the autoclave larger for a given operating temperature constraint and therefore more expensive to construct; and,
- produces unwanted acid which must be neutralized resulting in higher limestone neutralization costs and unwanted additional residue as well as extra wash water requirements adding further constraints on the overall process water balance.

Pyrite merits attention because, unlike most other sulphide minerals, it reacts in the CESL leaching step to preferentially form sulphate rather than S. If no elemental S forms, the generally accepted reaction under the autoclave's oxidizing conditions has been:



This reaction indicates an $O_2:\text{FeS}_2$ stoichiometric requirement of 1 ton O_2 per t of pyrite. The acid requiring neutralization is 1.64 t/t of pyrite when Fe_2O_3 is the form of Fe in final residue. When lime or limestone is the acid neutralizing agent, the extra residue production is ~2.9 t/t of pyrite. Pyrite levels in copper concentrates, which can range to as much as 50%+, can therefore have significant process, material handling, environmental and permitting implications resulting in important economic consequences. Understanding the correct stoichiometry also enhances the value of modeling systems such as Metsim.

Papangelakis and Demopoulos (1991) reported on the reaction kinetics of pyrite under pressure leaching conditions in the sulphate- O_2 system. Their paper included a review of earlier work that indicated the products of the reaction included only ferrous and ferric ions, sulphate ions, and elemental sulphur. Two parallel reactions were presented:



The first reaction converts all S in pyrite to sulphate while the second converts only half. It was indicated that higher oxidation potentials typically found in leaching conditions favoured the sulphate forming reaction. Long and Dixon (2004) extended earlier work to the 170 to 230°C range, but again in the sulphate- O_2 system, examining the roles of particle size, oxygen partial pressure, pulp density and copper (Cu) addition on the kinetics of pyrite leaching. The present work focuses more on the stoichiometry of the pyrite leaching reaction under conditions specific to CESL's mixed sulphate-chloride system operating at 150°C.

The CESL Copper Process typically comprises the steps of concentrate regrinding, the oxidation of sulphide concentrates at elevated pressure and temperature in the presence of catalytic chloride ions, leach residue separation and washing, and Cu recovery via solvent extraction and electrowinning. Additional steps in the flowsheet include neutralization of any acid generated across leaching, bleed stream processing to control the build-up of impurities occasioned in the leach step, and an evaporation step to maintain the water balance which is critical to hydrometallurgical flowsheets. An example of a general CESL flowsheet is presented in Figure 1.

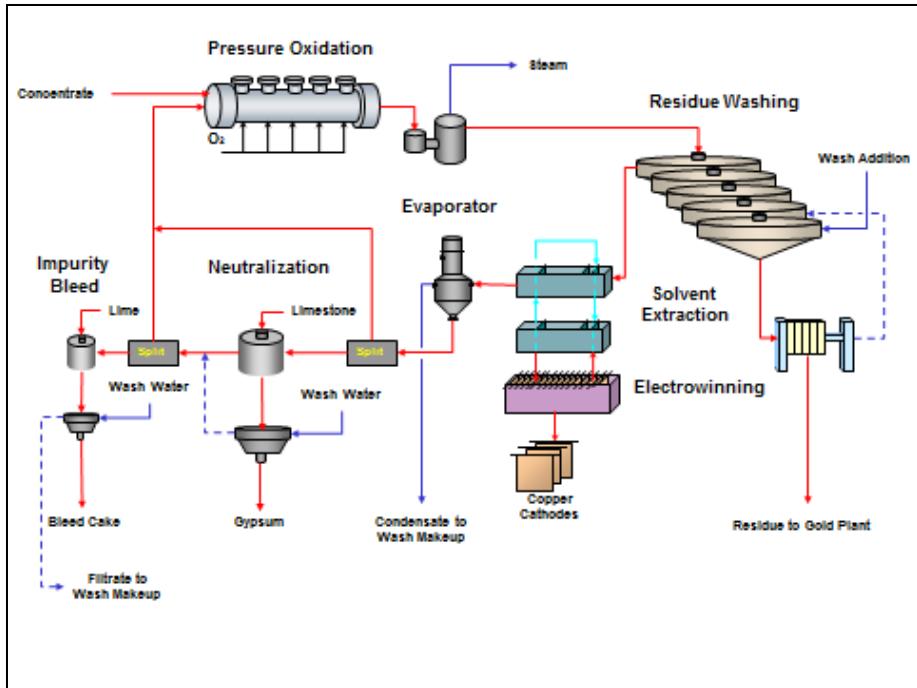


Figure 1 – General CESL flowsheet showing main unit operations

Most of the sulphur in the concentrate in the CESL Process is not oxidized to sulphate, but instead is converted to elemental sulphur. This is a key cost driver for the process and accounts partly for its low costs compared to some other hydrometallurgical processes for copper concentrates. It turns out that pyrite is a key determinant in sulphur oxidation to sulphate.

Given the operational penalties associated with pyrite, it may seem logical to pursue improved rejection of pyrite from copper concentrate in the upstream flotation step. However, this may not be practical due to mineralogical characteristics of the ore or it may be discouraged because of appreciable precious metals locked in the pyrite lattice.

EXPERIMENTAL

The objective of the present work was to characterize and quantify the stoichiometry of pyrite leaching under typical CESL Process conditions.

A relatively pure pyrite sample was used as concentrate. An implicit assumption being made was that pyrite interactions with other sulphides had little impact on the overall pyrite leaching chemistry that was observed under these conditions. The pyrite mineral used was purchased from Ward's Natural Science and originated in Zacatecas, Mexico. About 1 kg of pyrite "rocks" assaying 47.3% Fe, 53.2% S with minor Cu values (0.04%) were crushed and then ground in a rod mill to produce a product with the following screen size:

+325 mesh (>45 um)	4%
-325 mesh + 400 mesh (38 to 45 um)	2%
-400 mesh (<38 um)	94%

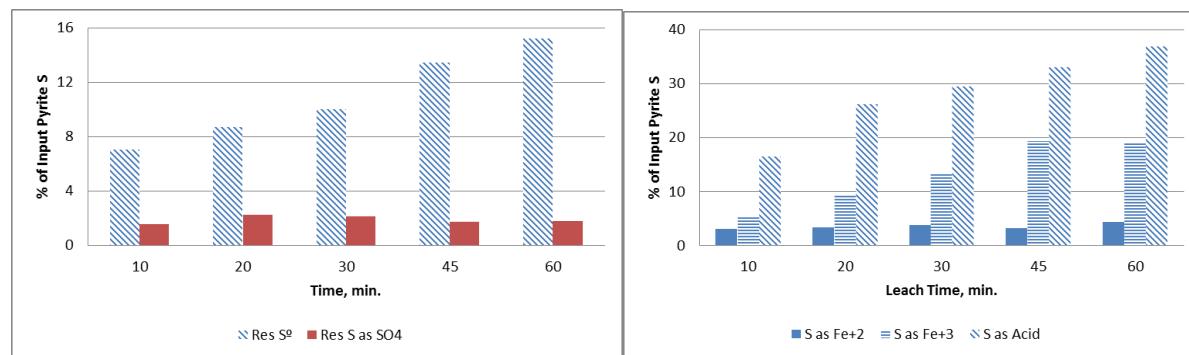
Standard batch leach tests were performed in a 2 L, titanium body Parr autoclave using 30 g/L of the ground pyrite and 1.1 L of a feed solution assaying 15 g/L Cu, 12 g/L Cl⁻ and zero acid. The procedure involved charging the autoclave with the appropriate materials, clamping the head of the autoclave including internals onto the top of the body of the autoclave, and sliding the unit into a vertical, electrically heated jacket. The autoclave internals attached to the head of the autoclave included the agitator, cooling coils for temperature control, and a

sparger for supplying the oxygen from an external compressed gas bottle. The head provided for a gas bleed line as well as a secondary line which was outfitted with an emergency rupture disk.

Temperature was controlled automatically. The electrical jacket heated the autoclave slurry to the operating temperature in about 20 minutes at which point O₂ was introduced. The moment of introduction of oxygen defined time = 0. Thereafter, cooling water and electrical heat alternated and maintained the temperature at the desired set point to within +/- 3°C. At the conclusion of the test, cooling water dropped the temperature of the autoclave to 60°C within 5 minutes and the unit was depressurized and the autoclave opened and the slurry filtered. Leach filtrate, wash water and residue were analyzed for their Fe, S and acid constituents. No sampling was conducted while tests were in progress to allow for stricter mass balances in each of the tests.

RESULTS & DISCUSSION

Identical tests were performed for different periods of time (10, 20, 30, 45 and 60 minutes). The resulting distribution of the reacted S from pyrite is shown in Figures 2 & 3.



Figures 2 & 3 – Deportion of reacted pyrite S to solid and solution constituents respectively

Figure 2, on the left, shows the fraction of reacted pyrite S going to elemental S and the fraction going to sulphate in residue presumably as some basic iron sulphate phase. It is interesting to note that this latter phase does not change significantly with time unlike elemental S which is continually increasing.

The reacted S that goes to solution is either present as acid, ferrous sulphate or ferric sulphate. Figure 3, on the right, shows that the ferrous level does not change appreciably as a function of time while both ferric and acid levels increase as extra pyrite leaches. The curves suggest that ferric iron in solution may hit a limit after 45 minutes as Fe precipitation reactions balance the rates of ferric generation.

The data of the various S products listed in Figures 2 & 3 may be used to calculate the proportion of S reacted that goes to form elemental S.

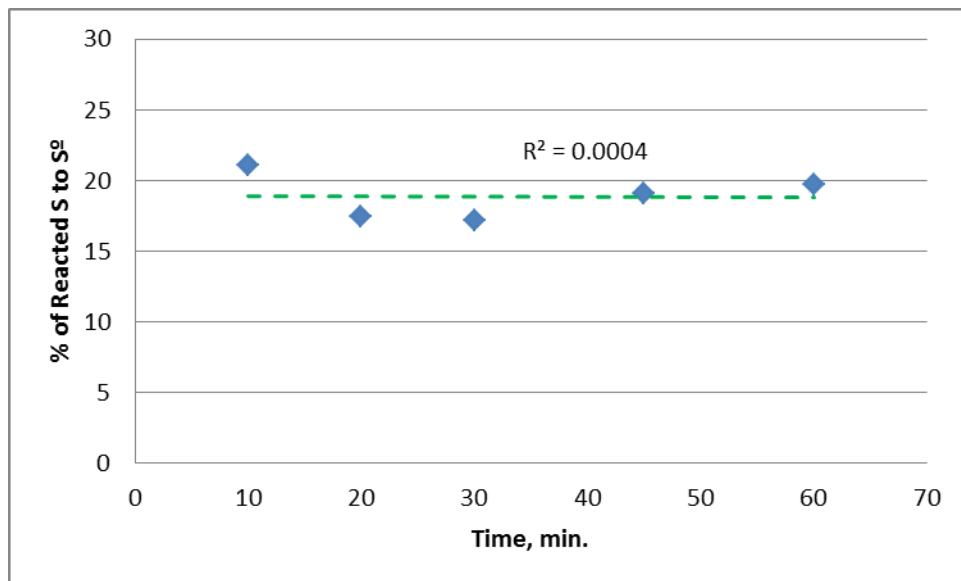
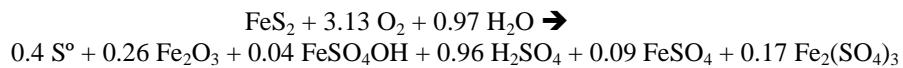


Figure 4 – Fraction of reacting pyrite S going to S°

Within experimental error, and independent of time, about 19% (+/- 1%) of the S that is reacted ends up in the elemental form when pyrite is leached under standard CESL conditions (Figure 4). The 60 minute experiment was analyzed in greater detail to arrive at an equation that might typify what occurs overall in a standard CESL leach. The equation:



predicts an O₂ requirement of 0.84 g/g of pyrite reacted versus a measured value of 0.85 indicating reasonable independent confirmation. It is estimated that 80% of S leached from pyrite is converted to sulphate in one form or another.

The rate of oxygen consumption is a good indicator of the leaching kinetics and the present data set was combined with additional tests run at shorter retention times (Figure 5) confirming data set consistency.

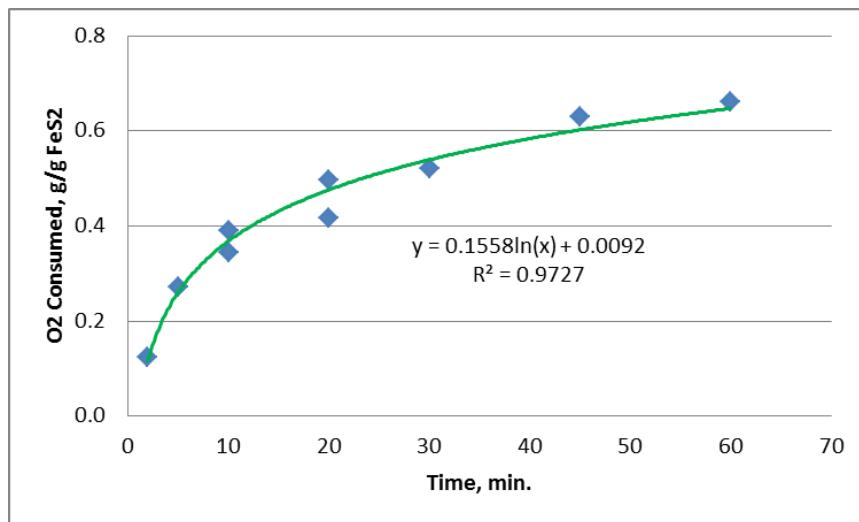


Figure 5 – Oxygen consumption as a proxy for the rate of pyrite leaching

Temperature was shown to have an appreciable effect on the extent of pyrite oxidation as inferred from measured oxygen consumption. Tests were conducted at constant O₂ partial pressure and constant total pressure as shown in Table 1.

Table 1 – Relative roles of temperature and O₂ partial pressure

Temperature (°C)	Pressure (psig)	P O ₂ (psig)	Net O ₂ (g/g FeS ₂)
130	125	85	0.13
140	140	85	0.27
150	155	85	0.38
130	200	160	0.44
150	200	130	0.66

At a constant partial pressure of oxygen, an increase in temperature from 130°C to 140°C doubles the extent of pyrite reaction. Raising the temperature further to 150°C increases the extent of oxidation by nearly the same absolute amount. At higher partial pressures of oxygen, pyrite was shown to react appreciably faster for a given temperature. For example, at 150°C, net oxygen consumption increased from 0.38 to 0.66 g/g of FeS₂ (+74%) when increasing the oxygen partial pressure from 85 to 130 psig (+53%). At 130°C, the difference is even more pronounced. If overall stoichiometry is not significantly affected and other minerals have a different leach response to oxygen partial pressure, this suggests that the control of partial pressure might be used to suppress pyrite leaching without adversely affecting the recovery of the target metal-bearing minerals.

Chloride levels, which are maintained at 12 g/L Cl⁻ in the standard CESL system, have been explored in other internal studies and have been shown to have significant impact on the extent of S oxidation. Figure 6 shows a series of pyrite leaches at varying chloride levels from 0 to 12 g/L Cl⁻. Increasing chloride reduced the extent of pyrite reacted and the amount of acid generated during the leach.

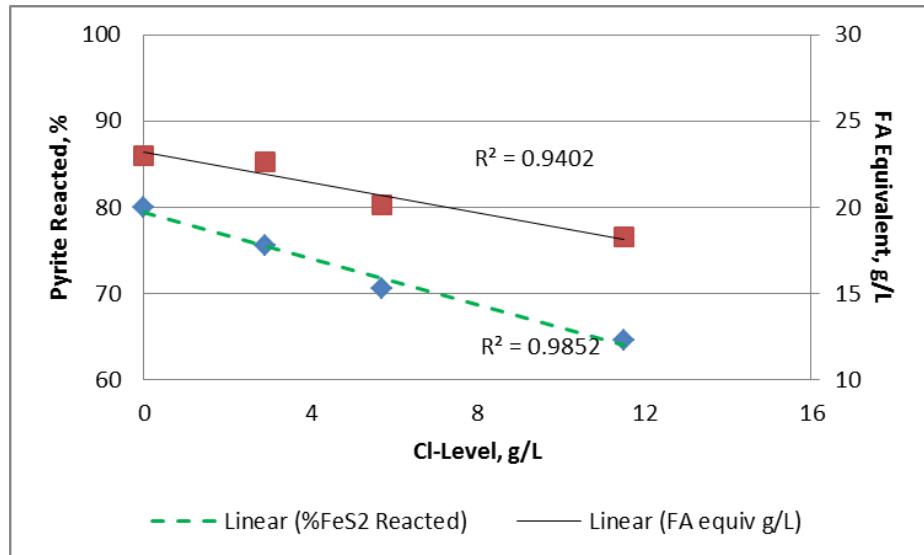


Figure 6 – Higher chloride suppresses extent of pyrite leaching

Data from bench tests performed on different copper concentrates containing varying amounts of chalcopyrite (Figure 7) show that the degree of S oxidation is strongly related to the pyrite content of the concentrate

and that pyrite is responsible for the bulk of the S oxidation seen under CESL Process conditions, where S associated with chalcopyrite deports to elemental S.

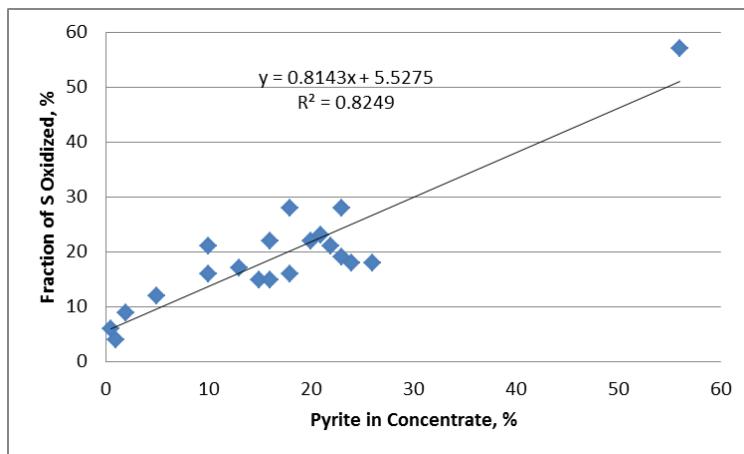


Figure 7 – Chalcopyrite concentrates with varying amounts of pyrite

Other factors such as surfactant type and dosage, and Cu level in solution did not appear to affect the pyrite leach stoichiometry. Initial acid level, however, could be important at low acid concentrations. Although interesting from a theoretical perspective, low acid would not be material in a full scale process as acid would always be present in the first compartment of the autoclave when pyrite in concentrate is at levels greater than ~10%.

These findings can be used to better understand the behaviour of more complex systems. For example, CESL has been doing extensive work with arsenic-rich concentrates with levels of up to 11% As that also happen to contain high levels of pyrite. Oxygen associated with pyrite (and chalcopyrite) leaching can be deducted from the total consumption to get a relationship between O₂ consumption and the arsenic-bearing sulphide minerals (Figure 8).

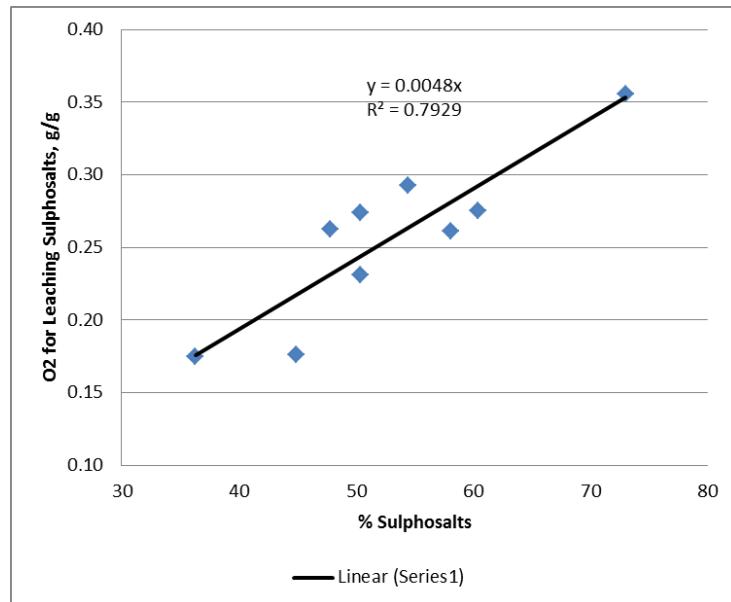
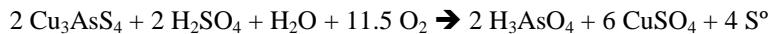


Figure 8 – Estimated consumption of O₂ during leaching by sulphosalts only

Extrapolating these values to 100% sulphosalts gives an oxygen consumption rate of ~0.48 g/g of sulphosalt mineral. The dominant sulphosalt in these tests was enargite so this value can be used to guess at the probable reaction of enargite under CESL conditions. The best fit to the observed data is:



This gives an O₂:enargite ratio of 0.47 g/g which is quite close to the extrapolated value. The equation indicates that 50% of the S in enargite may be recovered as elemental and the balance will be converted to sulphate.

CONCLUSIONS

The pressure leaching of pyrite in sulphate-chloride media was investigated. It was found that:

1. About 20% of the S in pyrite that reacts is converted to elemental S with the balance going to sulphate. This finding, based on detailed chemical analysis of both solutions and solids, is corroborated by oxygen consumption data.
2. Both temperature and oxygen partial pressure significantly affect the rate of pyrite leaching. The effect of oxygen partial pressure was considerably higher than might be expected suggesting its careful control may be useful in selectively suppressing unwanted pyrite leaching.
3. Chloride levels in solution were shown to slow the rate of pyrite leaching.
4. Surfactant types and concentrations and copper levels in solution did not affect the pyrite leaching stoichiometry.

These findings were extrapolated to sulphosalt systems where it was found that enargite leaching under CESL conditions most likely results in 50% conversion of the S in enargite to the elemental form.

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