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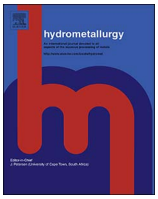

Atmospheric oxidation of pyrite with a novel catalyst and ultra-high elemental sulphur yield

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ABSTRACT

The effectiveness of two different carbon based catalysts, Lewatit® AF 5 (AF 5) a new microporous carbonaceous bead, and a granular coconut shell based activated carbon, in aiding atmospheric oxidation of a gold-bearing pyrite concentrate was tested. Oxidation in ferric sulphate media unassisted by a catalyst was incomplete after 96 h and resulted in only 60% pyrite oxidation, with an elemental sulphur yield ranging between 16% and 28%. Under the same test conditions, oxidation tests assisted by AF 5 saw approximately 96% pyrite oxidation with elemental sulphur yields ranging between 65% and 74%, while activated carbon assisted oxidation reached 100% pyrite oxidation with elemental sulphur yields between 63% and 64%. Testwork indicated that not only were pyrite oxidation kinetics greatly enhanced by the addition of carbon based catalysts leading to almost if not complete oxidation, but drastic increases in elemental sulphur yields and thus reductions in sulphate yields were also experienced.

It is shown that the AF 5 catalyst adsorbs all of the elemental sulphur produced on its surface. The AF 5 beads are large enough (approximately 0.5 mm) that after the leach process they can be screened out of the slurry, resulting in negligible elemental sulphur within the residue after solid/liquid separation. AF 5 also showed much stronger mechanical properties than the activated carbon, resulting in only approximately 0.40% AF 5 loss to fines compared to approximately 21.5% activated carbon loss to fines.

1. Introduction

It is well known that pyrite is an important sulphide mineral within the gold industry due to its affiliation with invisible gold and its ability to contain invisible gold concentrations as high as 132 g/t (Chryssoulis and Cabri, 1990). As a result, ores composed of only a small amount of pyrite still have the ability to contain high gold grades. Unfortunately, this invisible or refractory gold cannot be accessed via conventional gold leaching processes, such as cyanidation, and additional oxidative pre-treatment is required (Marsden and House, 2006).

Some current oxidative pre-treatment processes include high temperature and high pressure (HT/HP) leaching within autoclaves, biological atmospheric leaching and roasting. HT/HP leaching is a proven process reaching desirable recoveries with fast oxidation kinetics (approximately a 1–2 h process), resulting from the increased temperatures and pressures, allowing for an increase in dissolved oxygen (Marsden and House, 2006). The typical reaction for pyrite oxidation within HT/HP autoclaves is presented in Eq. (1).

$$2FeS_2 + {}^{15}\!/_{2}O_2 + 4H_2O \rightarrow Fe_2O_{3(\downarrow)} + 4H_2SO_4 \quad (1)$$

It is evident from Eq. (1), that for the oxidation of 1 mol of pyrite, approximately 3.75 mol of oxygen are consumed and 2 mol of sulphuric acid are produced. The production of sulphuric acid results in a necessary neutralization process prior to downstream cyanidation, adding neutralizing reagents to the operating cost of the process. Neutralization also produces a high volume of gypsum which must be handled. A large cost associated with the operation of the autoclaves is the oxygen consumption, as approximately 4 mol of oxygen are required to convert 1 mol of pyrite. On top of high operating costs associated with autoclaves, the capital costs are also extensively large as autoclaves must be built to withstand temperatures and pressures ranging roughly between 180 and 225 °C and 1500 and 3200 kPa respectively (Marsden and House, 2006). It has become a concern within the gold mining industry that HT/HP autoclave leaching may not remain a viable oxidative pretreatment method with declining gold grades, and a volatile gold price that may lead to an uneconomic process.

Biological atmospheric leaching is another option for the oxidative pre-treatment of refractory sulphides. Biological leaching can take place as heap leaching or atmospheric tank bio-oxidation. Tank bio-oxidation is more applicable to the research involved in this study. The process

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incorporates the use of thermophilic and/or mesophilic iron and sulphur-oxidizing bacteria acting as a catalyst to drive the oxidation of sulphides. Current bacterial oxidation processes include the BIOX® process (Dymov et al., 2004) and the Mintek-BacTech process (Miller and Winby, 1997; Neale et al., 2000), which have been proven to work on the commercial level. Generally, these processes are applied to refractory gold ores with a low sulphide concentration. This is because the overall reaction is acid generating and neutralizing reagents are required. As a result if the sulphide content is too high, the reagent costs to neutralize the acid produced outweigh the profits to be made. The process is only considered economic if the gold grade to sulphide grade ratio is > 0.7, as demonstrated in Eq. (2) (van Aswegen et al., 2007).

$$\frac{\text{Gold grade (g/t)}}{\text{Sulphur grade (\%)}} > 0.7 \tag{2}$$

The type of concentrate being used in this test work has a gold grade to sulphur grade of about 0.07, far too low for this kind of pre-treatment to be economic.

Pyrometallurgical roasting is another oxidative pre-treatment method that has been commercially proven to effectively oxidize pyrite and other sulphidic and/or carbonaceous ores. The overall reaction for pyrite oxidation via roasting is presented in Eq. (3).

$$3FeS_2 + 8O_2 \rightarrow Fe_3O_4 + 6SO_2 \tag{3}$$

The sulphur dioxide generated by roasting can be retrieved and converted into sulphuric acid, reducing gas emissions, however increased environmental legislations and high capital costs associated with roasters, do not make roasting an ideal pre-treatment option.

Given the information regarding the three commonly used oxidative pre-treatment methods above, it is evident that while all are proven to work commercially, all have limitations and flaws. It is well-known that the majority of clean high grade gold reserves have been depleted and that the industry as a whole is moving towards more and more refractory sulphide materials like pyrite, and alongside this, gold grades can be expected to decrease. Knowing the economic limitations of biooxidation processes such as BIOX®, it is clear that these processes will not be applicable for future reserves to be mined. It is also understandable that due to environmental concerns and constraints it will be extremely difficult to construct new roasting facilities, eliminating roasting as a pre-treatment possibility. With the low grades to be expected, it is evident that the high capital and operating costs associated with autoclaves of the HT/HP processes are no longer economical. A new process with lower capital and operating costs than that of the autoclave processes, however with similar kinetics must be developed. That is where the survival of the gold industry lies.

It is difficult to determine the exact mechanism of pyrite oxidation however, elemental sulphur and sulphate are the most stable products resulting from pyrite oxidation with ferric ions acting as the oxidizing agent (Bouffard et al., 2006; Flatt and Woods, 1995; Garrels and Thompson, 1960; Holmes and Crundwell, 2000). Further, the oxidation of pyrite by oxygen present in solution can be disregarded at pH values < 3.0, as the oxidation of pyrite is much more rapid by ferric ions (Nordstrom, 1982). The overall reaction for the process can therefore be represented in Eq. (4), as proposed by previous researchers (Bouffard et al., 2006).

$$\begin{aligned} FeS_2 + 8xH_2O + (2 + 12x)Fe^{3+} \rightarrow (3 + 12x)Fe^{2+} + 2xSO_4^{2-} \\ + (2 - 2x)S^0 + 16xH^+ \end{aligned} \tag{4}$$

Sulphate yield is represented by x in Eq. (4), which can range between 0 and 1, however the goal of this study is to develop a process in which the sulphate yield will be as low as possible.

Regardless of sulphate yield, it is evident that ferric ions are consumed during the oxidation of pyrite, and that ferrous ions are generated. Garrels and Thompson (1960) suggested that the rate of reduction of ferric ions in acidic iron sulphate solutions could be considered as a measurement of pyrite oxidation (Garrels and Thompson, 1960), however this does not apply to the system that will be used in this study because oxygen is being supplied constantly during testing. In the presence of oxygen, the ferrous ions generated will be oxidized to form ferric ions once again outlined as follows (Singer and Stumm, 1970):

$$4Fe^{2+} + O_2 + 4H^+ \leftrightarrow 4Fe^{3+} + 2H_2O \tag{5}$$

Singer and Stumm reported that the rate of pyrite oxidation is controlled by the oxidation of ferrous ions to ferric ions (Singer and Stumm, 1970), which was further validated by research in 2016 (Li et al., 2016).

The use of activated carbon in the assistance of sulphide leaching and oxidation has been reported before. Dixon and Rivera-Vasquez investigated and submitted an U.S. patent application for the use of activated carbon with an acidic ferric sulphate leach solution in the presence of oxygen to assist the copper extraction in enargite. The addition of 100 g of activated carbon to 90 g of concentrate resulted in a complete copper dissolution after approximately 22 h, however the 90 g of concentrate alone experienced < 60% copper dissolution after roughly 35 h (Dixon and Rivera-Vasquez, 2012).

Activated carbons have been studied and researched intensively to determine their capabilities of metal removal, ion oxidation, functional group interactions, and how different pre-treatments affect their properties, among a long list of other studies. Figueiredo et al. investigated the modification of surface chemistry of activated carbons, discovering that gas phase oxidation of carbon increases hydroxyl and carbonyl surface group concentrations, while liquid phase oxidation increases the carboxylic acid surface concentration (Figueiredo et al., 1999). Radzinski et al. confirmed the in-situ formation of hydrogen peroxide in acidic solutions in the presence of activated carbon and oxygen (Radzinski et al., 2016). Rodriguez-Reinoso declared that non-polar molecule adsorption on the surfaces of activated carbon is more dependent on pore size distribution rather than surface chemistry (functional groups) (Rodríguez-Reinoso, 1998).

Ahumada et al. studied the catalytic impact of activated carbons on the oxidation of ferrous ions in the presence of oxygen (Ahumada et al., 2002). In the Ahumada et al. study, the authors outlined the oxidation of Fe^{2+} ions in the presence of activated carbon and oxygen with the following reactions (Ahumada et al., 2002):

$$C^*_{Red} + \frac{1}{2}O_2 + H_2O \rightarrow H_2O_2 + C^*_{Ox} \tag{6}$$

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \tag{7}$$

C^*_{Red} in Eq. (1) represents a functional oxygen surface group such as quinone that has a lower redox potential than the O_2/H_2O_2 couple and C^*_{Ox} represents a functional oxygen surface group with a redox potential greater than that of the Fe^{3+}/Fe^{2+} couple. Hydrogen peroxide generated in Eq. (6) is then used to oxidize ferrous ions seen in Eq. (7), which in turn promotes the overall oxidation of the pyrite viewed in Eq. (4) at a much faster rate than unassisted oxidation.

The focus of this paper is testing the effects of carbon catalysts on an atmospheric leaching process with the intention of the introduction of a viable commercial pre-treatment option for the oxidation of pyrite. The process involves the atmospheric oxidation of pyrite in a sulphuric acid media. Carbon based catalysts are being applied to the atmospheric oxidation in order to increase the pyrite oxidation rates while promoting the production of elemental sulphur rather than sulphuric acid. It is shown that the addition of carbon based catalysts to the atmospheric oxidation of pyrite in acidic ferric sulphate media in the presence of oxygen increases oxidation kinetics and improves elemental sulphur yields. The addition of carbon catalysts promotes the formation of hydrogen peroxide, a strong oxidant, as well as alter the ORP of solutions to benefit elemental sulphur production.