Separation of elemental sulfur from hydrometallurgical residue: A review

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ABSTRACT

Elemental sulfur in mining-related residues represents both a disposal challenge and a by-product opportunity. Sulfur and related sulfur compounds in aqueous environments result in acid generation and pH depression in water bodies. Recovery of sulfur from the residue could not only mitigate the volume and reactivity of the residues but may present opportunities in its sale. As a result, many companies and academic researchers have invested both capital and time into developing a cost-effective and reliable means to separate sulfur of sufficient purity from mining residues. This paper reviews the spectrum of work performed to date on elemental sulfur-containing residues. The generalized procedures currently used in the removal of sulfur from residues, particularly those produced via hydrometallurgical processing, fall into three categories: physical or mechanical separation by flotation, chemical alteration of sulfur hydrophobicity by sulfide addition, and extraction via supercritical H_2O or CO_2. A discussion of the state of present knowledge and recommendations on possible improvements is provided.

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1. Introduction

Mining and metals-refinery waste from sulfide deposits pose significant disposal challenges, the most pressing being proper storage and handling. These wastes are deemed to be acid-producing as their sulfur component reacts with oxygen and water to form thiosalts and sulfuric acid — a phenomenon grouped under the classification of Acid Rock Drainage (ARD) or Acid Mine Drainage (AMD). Typical disposal procedure calls for such mining wastes to be stored subaqueously to mitigate oxidation. While the characteristics of subaqueous disposal for acidic mine tailings are documented (Dave et al., 1997; Li et al., 2000; Roberston, 1991), less has been written on ARD involving the wastes derived from hydrometallurgical refining. Steel et al. (2009) have recently reported results from experiments conducted on residues from Vale's hydrometallurgical demonstration plant located in Argentia, Newfoundland.

The commercial separation and purification of elemental sulfur on a commercial scale has been an ongoing concern for the last half century. Historically, sulfidic ores were treated by pyrometallurgical processes converting sulfides to sulfur dioxide which was then vented atmospherically. As environmental awareness and regulation increased, sulfur dioxide emissions were sequestered and converted into sulfuric acid, although this process was not always deemed advantageous — in fact, the feasibility of sulfur removal and/or sequestration hinges on process economics. As early as the 1960s,

new methods were being investigated to treat sulfidic ores that involved a mix of hydrometallurgical and pyrometallurgical processes (Bolton, 1981). Zinc residues were a natural candidate for sulfur removal via oxidative leach as zinc concentrates have a high zinc content and relatively low gangue constituents. As such, the leach residues consist mostly of elemental sulfur. Other concentrates such as those based on copper or nickel do not fare so well. Peacey et al. (2004) indicate that wastes derived from copper concentrates are up to five times more voluminous than those of zinc per unit of metal produced. In terms of precious and platinum group metals (PGMs), Milbourne et al. (2003) argue that if leach conditions favor the production of elemental sulfur, it is highly desirable to produce a low mass, highly concentrated PGM residue as a product. The leach residue from partial sulfide oxidation leach processes could be subjected to flotation, assuming that the sulfur can be floated and that the PGMs are not removed with the sulfur. The CESL Process (Jones, 2002), used to treat copper–gold concentrates, can involve an elemental sulfur removal step using a hot perchloroethylene leach, followed by the oxidation of the remaining sulfides to release refractory gold. Milbourne notes that although tested on copper concentrates at a demonstration plant scale, it has yet to be used for a copper–nickel system. He further suggests that the total oxidation of sulfides to sulfates (225 °C, 700 kPa O_2, 3400 kPa total pressure) is presently the best alternative for the subsequent capture of PGMs, although such a process has high operating costs in terms of oxygen consumption and maintenance requirements.

Generally, elemental sulfur exists as a light yellow or beige solid in its most stable allotrope, α-S_8. Individual molecules of sulfur form into clusters of $(S_8)_n$ which will also incorporate S_6, S_7, and other

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allotropes if present. In addition, the actual crystallization of α-S_8 can be hindered due to the fact that α-S_8 crystals require a unit cell consisting of no less than 16 molecules of specific orientation and therefore formation of β-S_8, whose unit cell consists of six molecules, can be favored (Steudel, 1996). In the case of copper sulfides, Filmer et al. (1979) proposed that the conversion of metal sulfides to elemental sulfur proceeds via a solid state reaction rather than via reactions with dissolved sulfide ion. The thermal properties of various allotropes of sulfur has also been studied with S_8 and S_{12} being the most stable as both allotropes share near identical average bond distances (Steudel et al., 1984).
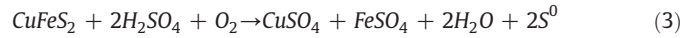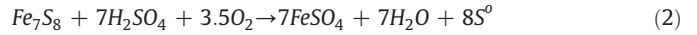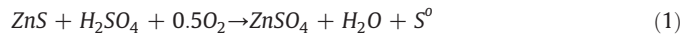
The first half of this paper covers the most widely used commercial process for the removal of sulfur from hydrometallurgical residues, namely that developed by Sherritt International. Concentrate and residue constituency as well as sulfur micropellet particle size play critical roles in the efficiency of commercial sulfur removal. Although research has been conducted by industry involving the removal of elemental sulfur in residue by quantitative conversion to sulfuric acid (Marsden et al., 2002), only those processes involving the isolation of elemental sulfur as a product will be discussed. The second half of the paper reviews some of the research that has been conducted but not yet commercialized including the use gangue dispersants, electrochemical impurity removal, polysulfides and supercritical fluids.

2. Sherritt sulfur removal

2.1. Sherritt Zinc Pressure Leach Process

The Sherritt Zinc Pressure Leach Process was first commercialized at the Trail, British Colombia, zinc refinery of Cominco Limited (now Teck Resources) in early 1981. The process has been used commercially in other firms including Falconbridge, Hudson Bay Mining, and Ruhr Zink GmbH. The chemistry is quite straight forward in that zinc sulfide (ZnS), pyrrhotite ($Fe_{(1-x)}S_x$), sphalerite ((Zn,Fe),S), galena (PbS) and chalcopyrite ($CuFeS_2$) react with sulfuric acid and oxygen – with dissolved iron serving to facilitate

oxygen transfer – to yield metal sulfates and elemental sulfur (Chalkley et al., 1993).

$$ZnS + H_2SO_4 + 0.5O_2 \rightarrow ZnSO_4 + H_2O + S^o \tag{1}$$

$$Fe_7S_8 + 7H_2SO_4 + 3.5O_2 \rightarrow 7FeSO_4 + 7H_2O + 8S^o \tag{2}$$

$$CuFeS_2 + 2H_2SO_4 + O_2 \rightarrow CuSO_4 + FeSO_4 + 2H_2O + 2S^0 \tag{3}$$

Pyrite, an important constituent in the concentrates of massive sulfide deposits, is generally converted to sulfate with very little or no elemental sulfur production.

$$FeS_2 + H_2O + 3.5O_2 \rightarrow FeSO_4 + H_2SO_4 \tag{4}$$
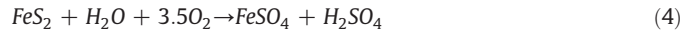
Additionally, up to 5% of the non-pyritic sulfide sulfur in the concentrate is oxidized to sulfate sulfur during the pressure leach (Chalkley et al., 1993). As mentioned earlier, the variation on concentrate constituents plays a critical role in flow sheet design. As old mines go offline and new feed stocks are introduced, fundamental changes in process flow configurations occur. Fig. 1 represents the flow sheet of the Teck Zinc Pressure Leach process as the traditional Sullivan feed stock was replaced by a newer feed stock from the Red Dog mine (D'Odorico, 2004).

2.2. Pressure leaching

Zinc pressure leaching is conducted in a horizontal multicompartment autoclave and is operated in a continuous mode. The zinc concentrate slurry is ground and milled to a specific particle size having been combined with water to form a slurry of 70% solids. The slurry is then injected into the autoclave together with acid containing recycled spent electrolyte and pressurized oxygen at elevated temperature. Temperature plays a key role in leaching efficiency — too low and retention times must increase reducing throughput, too high and elemental sulfur viscosity increases exponentially inhibiting further leaching. Even at optimal temperatures, 140 °C–150 °C, the
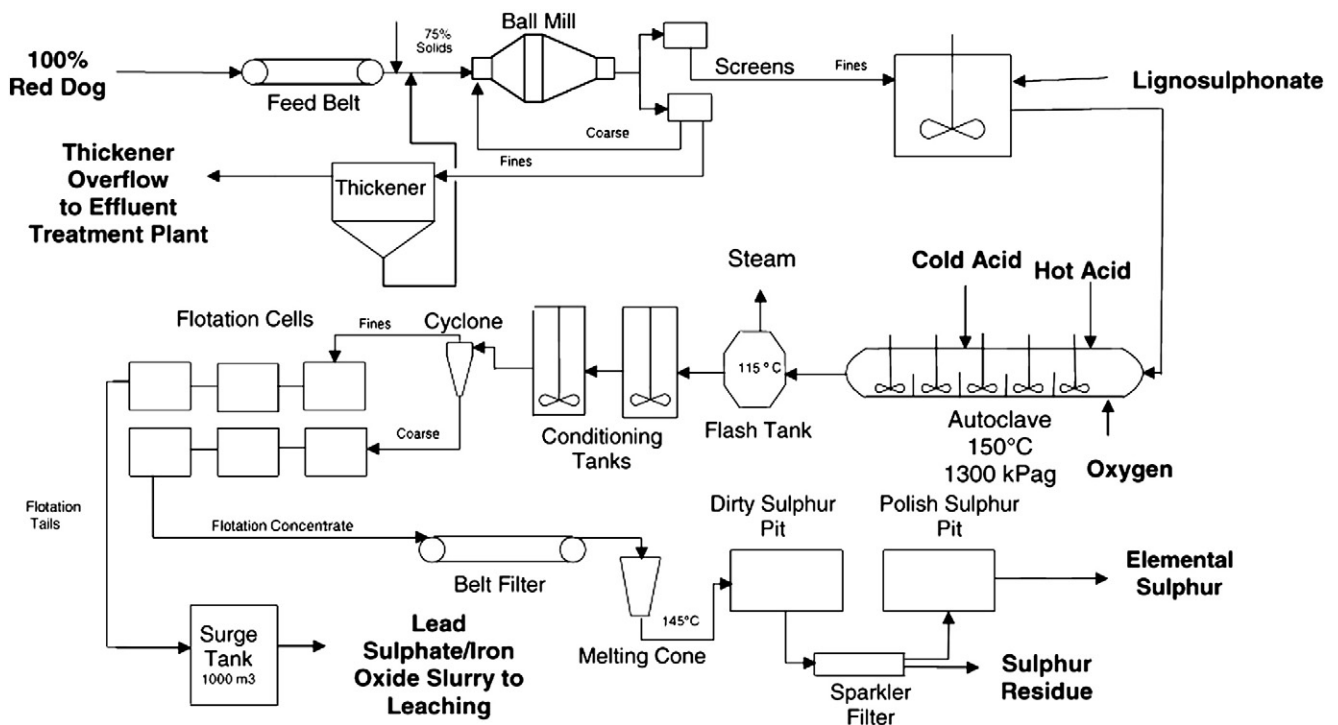

Fig. 1. Teck Zinc Pressure Leach Process Flow Sheet (D'Odorico, 2004). Autoclave pressure denoted in kilopascal-gage.