FLUID BED ROASTING OF METAL ORES AND CONCENTRATES FOR ARSENIC REMOVAL

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ABSTRACT

The main features of fluid bed roasters are described. The key process requirements for arsenic removal from metal concentrates (copper and nickel) and ores (gold) by roasting are summarized from open literature. A simple flow diagram is presented for a hypothetical copper concentrate. A pros and cons analysis is provided for the fluid bed arsenic roasting, versus other industrial options (rotary kiln and multi-hearth).

INTRODUCTION

During the past decade the quality ore feeds with low contamination (including arsenic) content are being depleted and more attention is being directed to processing arsenic bearing ores. Arsenic is a toxic impurity primarily found in copper, iron, nickel, and gold ore deposits. Strict environmental regulations on the emission of arsenic to the environment require the arsenic to be removed efficiently and in a controlled process. Removing arsenic before smelting the ore is important as it contaminates the slag and metallic phases and can cause environmental and safety problems during the smelting and refining operations.

In pyrometallurgy, arsenic can be removed by roasting the concentrate upstream of the smelters, which volatizes the arsenic, while leaving the valuable metals in the calcine. This practice has been used for decades, though early roasters, such as that at Giant Mine in Yellowknife, were conducted in open vessels, causing high arsenic emissions to the environment (Diekmeyer, 2011).

Advancements in roaster and off-gas treatment technology have significantly improved the removal efficiency and recovery of arsenic as a stable solid trioxide. Existing commercial roaster designs include the multi-hearth and the fluid bed roaster, both bubbling and circulating fluid beds. However, in the late 20th century, there was a significant decrease in the market for arsenic trioxide (used mainly for wood preservation), affecting the economics of roasting technologies, making the hydrometallurgical route of pressure oxidation more popular while the number of new roaster installations decreased.

In recent years with the decrease in ore grades and increase in required throughputs, there has been renewed interest in roasting, particularly in fluid bed technology due to its advantages over the multi-hearth and rotary kiln. This paper describes the arsenic removal process by roasting and compares the fluid bed roaster to other technologies based on open literature.

ARSENIC REMOVAL BY ROASTING

As-O-S Stability Diagram

Enargite (Cu-As-S), arsenopyrites (Fe-As-S), and gersdorffite (Ni-As-S) are examples of common minerals of the ores mined for copper, iron, nickel and gold production. By exploiting the fact that the arsenic in these minerals volatilizes under the proper process conditions, the arsenic can be removed from the calcine during the roasting step.

Much literature has been published on the chemistry of arsenic volatilization, including from Fan (1996) for Chilean copper concentrates, Luganov (2002) for arsenic bearing gold ores, and Jorgensen (2005) for Western Australian nickel concentrates. Although there are differences in the optimum conditions for each concentrate, the gas phase for each is well represented by the As-O-S stability diagram.

In summary, at temperatures ranging from 550 – 700 °C, arsenic decomposes to arsenic sulphides or oxides, depending on the atmospheric conditions. The arsenic oxide is acidic and can quickly react with the alkaline gangue present in the ore/concentrate, resulting in recapture in the calcine. The arsenic sulphide is volatile and less reactive, and therefore, can be more easily removed through the roaster off-gas.

According to the phase stability diagram for As-O-S at 700 °C (Figure 1), solid arsenic oxides are dominant under oxidizing conditions, while at low oxygen (less than 10^{-15} atm) and high S_2 partial pressure, gaseous species of arsenic sulphide and oxide are formed. Therefore, if the roast is carried out under oxidizing conditions, the arsenic will be fixed in the calcine in the form of alkaline neutralized As_2O_5. However, by maintaining inert or reducing conditions in the roasting step, arsenic can be removed as a gas from the calcine, then safely and separately oxidized in the off-gas system to form stable arsenic oxides for sale or disposal.
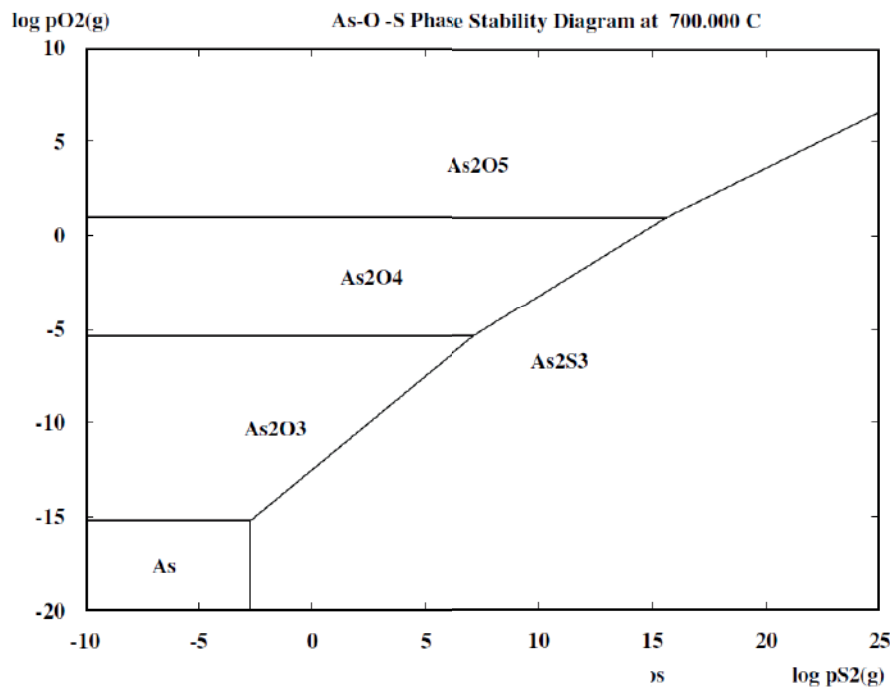
Figure 1 – As-O-S system at 700 °C

Process Requirements for Different Minerals

The roasting conditions for arsenic removal are different depending on the minerals contained in each ore or concentrate. Care must also be taken to avoid sintering of metals. Lab scale test work is required to determine the roasting temperature, residence time and atmospheric condition required for maximum arsenic removal and optimum calcine quality.

For example, Barrick's El Indio plant in Chile roasted its copper concentrate in a 14-hearth Nichols-Herreshoff roaster at temperatures ranging from 500 °C in the first hearth up to 720 °C at the discharge, while maintaining less than 0.5% oxygen in the gas. The roaster processed about 8.5 t/h concentrate, reducing the arsenic content from 8.5 – 10% in the flotation concentrate to less than 0.5% in the calcine (Smith, 1986).

The Boliden Metall Ronnskar smelter in Sweden operated a Dorr-Oliver fluid bed roaster at 700 °C, reportedly reducing the arsenic content from up to 3% in the concentrate to 0.1 – 0.2% in the calcine (Lindkvist, 1985; Peacey, 2010).

In gold roasting, where an oxidative roast is required to convert pyrite (FeS_2) to sufficient hematite (Fe_2O_3) for downstream leaching; roasting of ores containing arsenopyrite can be carried out in two stages. The first stage maintains a neutral or low oxidizing atmosphere to eliminate arsenic, while the second stage can be carried out in a highly oxidizing atmosphere and relatively higher temperature to complete the pyrite conversion. This process was used by Kennecott Copper, which operated a two stage Dorr-Oliver fluid bed roaster at 675 – 680 °C, with a retention time of approximately 1 – 2 hours (Gupta, 1998). Barrick's Kanowa Belle roaster in Kalgoorie, Australia also operated a Dorr-Oliver fluid bed roaster to remove arsenic from its refractory ore (Environmental Protection Authority, 1993).

Some concentrates require additional sulphur, usually in the form of elemental sulphur or pyrite, to be added to the roaster, in order to achieve the high S_2 potential required for arsenic volatization. Pyrite was added to the speiss concentrate fed to the Capper Pass fluid bed roaster to achieve high arsenic

removal (from 30 – 35% in the feed to 0.5% in the calcine). Roasting temperatures were reported to be 730 – 750 °C, with retention times of 1 – 3 hrs (Litten, 1987).

Similarly, test work done by CSIRO on Western Australian nickel sulphide concentrates (Jorgensen, 2005) and testwork by Outokumpu for complex concentrates of Ni, Cu and Cu-Co (Tuovinen, 1982), both reported benefits of adding sulphur to the roaster feed to improve arsenic removal. Jorgensen (2005) also found that adding a chloride to the roast had similar benefits to adding sulphur.

Process Description

A simple block diagram for roasting a hypothetical copper concentrate is proposed in Figure 2 to illustrate a typical ore roasting process to remove arsenic. The roaster shown in the figure is the bubbling fluid bed roaster, although other technologies such as circulating fluid bed, multi-hearth roaster, and rotary kiln have also been used. The concentrate is pneumatically fed as dry powder, through several injectors into the fluid bed roaster, which is maintained at its roasting temperature by using preheated air from a direct fired air preheater.

The gas atmosphere is maintained by controlling the concentrate-to-air ratio in the fluid bed. An adequate amount of oxygen is supplied to the roaster, in order to burn a minimum amount of sulfur in the concentrate (for the required energy release), while maintaining most of the sulfur content for the downstream smelter.

The roaster off-gas contains concentrate dust and arsenic sulphide vapour. It is first passed through two cyclones placed in series for high recovery efficiency of the concentrate. The large amount of fines captured in the first cyclone is recycled to the fluid bed, while the remaining fines captured in the second cyclone is fed forward with the calcine to product cooling. The roaster off-gas is then oxidized in a post combustion chamber or afterburner to convert the arsenic sulphide to arsenic trioxide.

Next, the gas is cooled using a spray tower to allow the arsenic trioxide to sublimate. The arsenic trioxide is collected in an electrostatic precipitator (ESP) before the gas is forwarded to an acid-plant. This process can also use a wet venturi scrubber for the final gas cleaning, instead of the ESP. With wet scrubbing, the effluent will contain arsenic which needs to be treated properly.
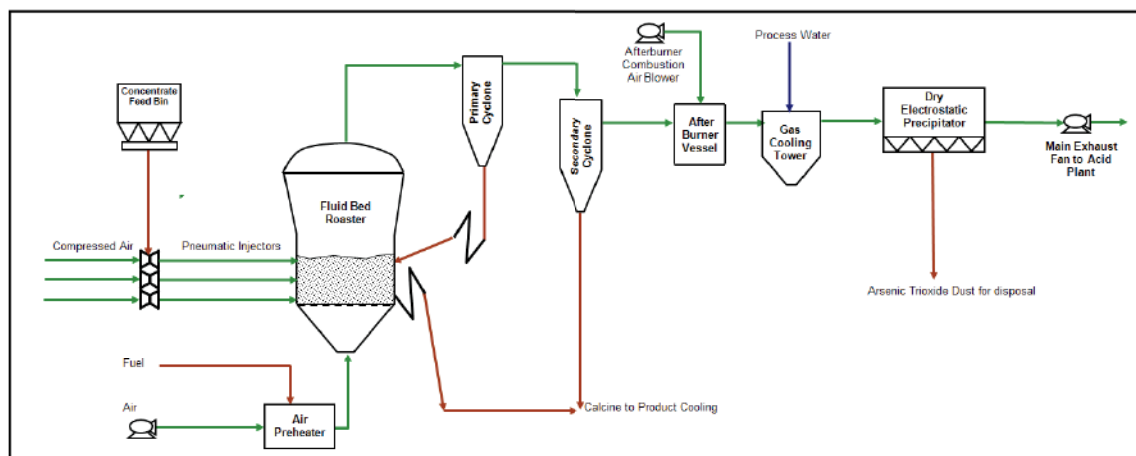

Figure 2 – Simple flow diagram for arsenic roasting of copper concentrate

FLUID BED ROASTERS

The majority of the fluid bed roasters discussed in this paper operate in the so called 'bubbling regime' Figure 3. Bubbling fluidization occurs when the hot gas velocity through the bed of solids is more than the minimum to suspend it, with most of the excess gas moving through the suspended solids in bubble-like pockets (Kunii and Levenspiel, 1991). Bubbling beds normally operate at 3 to 30 times the minimum fluidization velocity, which increases with the particle size and decreases with temperature Figure 4.
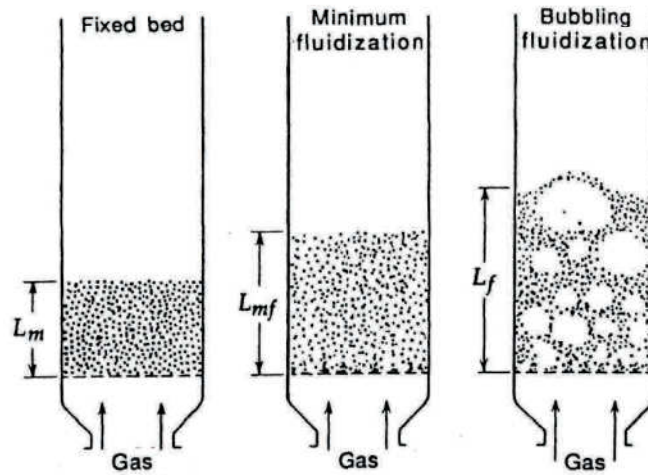

Figure 3 – Solids behaviour in uplift contact with a fluidizing hot gas flow (Kunii and Levenspiel, 1991)

Under bubbling conditions, most of the solids remain in a dense and distinct 'bed' phase, with only a fraction of the fines reporting to the off-gas discharge. As a solid phase reactor, the bubbling bed is similar to a well mixed single stage unit where, depending on the bed inventory, an average residence time from several minutes up to many hours can be achieved.
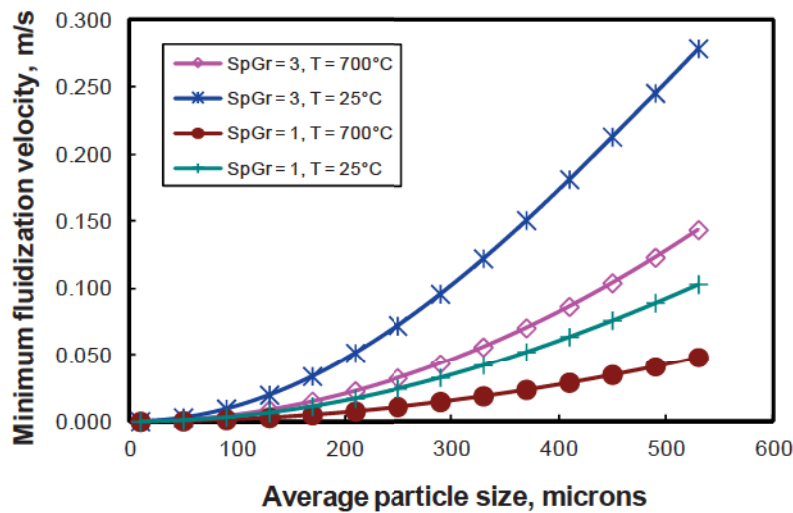

Figure 4 – Minimum fluidization velocity for spherical particles

Some roasters are circulating fluid beds. In contrast to the bubbling fluid bed, there is almost no distinct 'bed' in the circulating fluid beds. The circulating fluid bed works at higher gas velocities, where

all the solid particles can be carried in the gas stream. The reported advantages of circulating fluid beds are smaller diameter units, better heat and mass transfer and more intense reaction. Circulating fluid bed limitations can be more abrasion and lower (less than 0.5 hr) residence time unless a large recirculation from the cyclone is utilized. The velocity required for carrying solid particles is called the terminal velocity, with typical values provided in Figure 5.
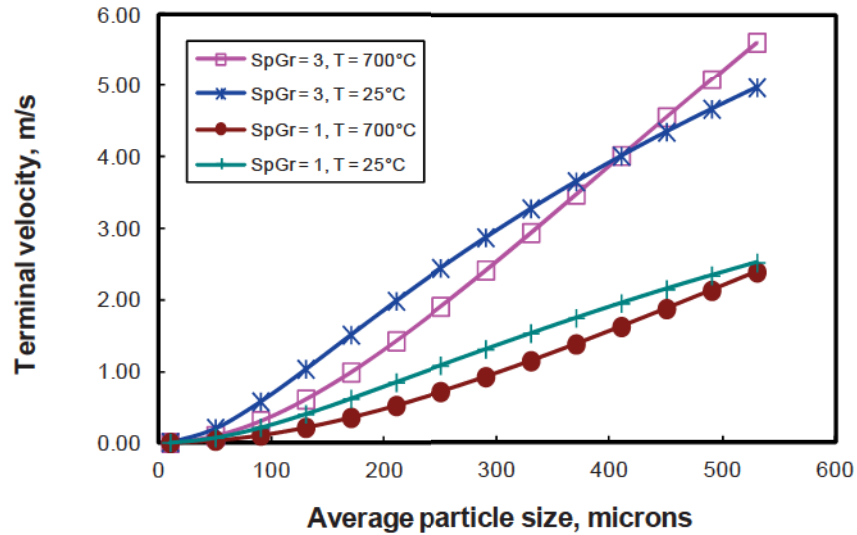

Figure 5 – Terminal velocity calculated for spherical particles in air
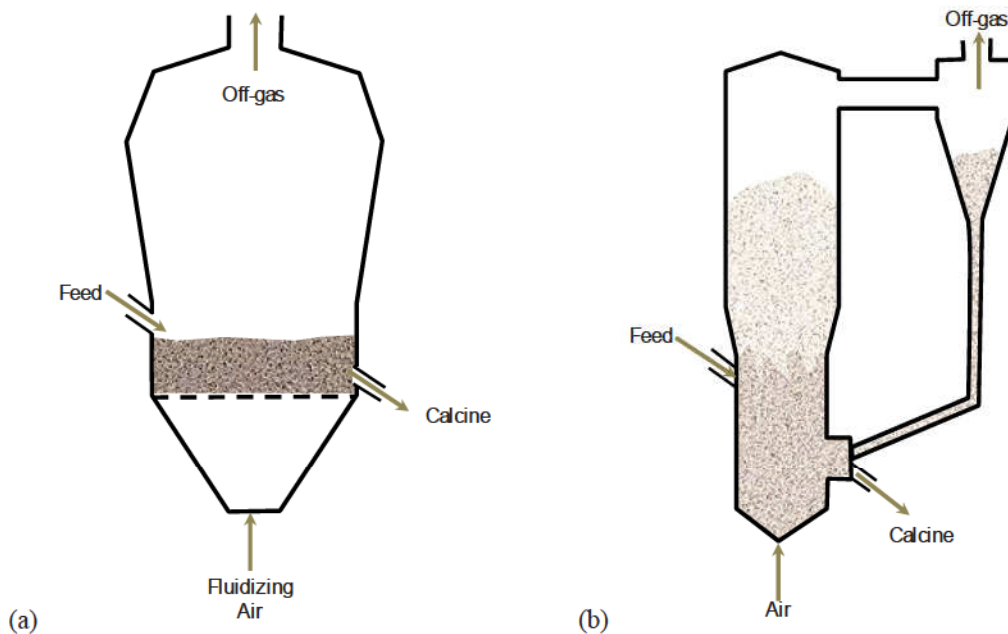

Figure 6 – Sketch of bubbling (a) and circulating (b) fluid beds

Fluid beds are popular reactors because the action of the fluidizing gas creates a well-mixed reaction zone with uniform temperature and chemistry. This allows for simple temperature control and efficient reaction kinetics. As well, fluid beds have no moving parts, making their mechanical design simpler than the rotary kiln and multi-hearth roaster, which are the main alternative technologies.

Rotary kilns are usually selected over a fluid bed when the particle size distribution is wide, with a large fraction of coarse (> 10 mm) material. Since the fluidizing velocity is dependent on the particle size, fluid beds are limited to processing a relatively narrow range of particle sizes to avoid operating at high velocity to fluidize the coarse fraction, while causing a high rate of attrition and erosion. The main drawback of the rotary kiln for roasting is poor temperature control and the temperature gradient along the length of the kiln.

Multi-hearth roasters are rarely being chosen over fluid beds today due to the complexity of the equipment with its rotating centre shaft that has to be cooled and the multiple hot gas injection points. However the multi-hearth can provide longer residence times than the fluid bed and can easily accommodate a multi-stage roasting process.

Compared to the multi-hearth and rotary kiln, another limitation of the fluid bed is the high pressure of the gas required to fluidize the material. However, a benefit of the bubbling fluid bed over the multi-hearth and rotary kiln is its ability to process a wide range of throughputs without significant impact on the solids residence time and hence product quality. This can be achieved in the bubbling fluid bed by adjusting the height of the bed.

Roasting of arsenic bearing copper, iron, nickel, and gold materials in fluid beds has proven to be successful in lab and pilot scale, though commercial bubbling and circulating fluid bed roasters exist mainly for pyrite concentrates and whole-ore or gold concentrates to remove arsenic and sulphur. Commercial bubbling fluid bed roasters include dearsenifying roasters at Boliden and Lepanto and the gold roasters at Kennecott Copper and Kanowna Belle. Circulating fluid bed roasters have been used at Cortez for gold ores containing arsenopyrites. Recently, Codelco announced installation of a two-stage fluid bed roasting plant to remove 90% of the arsenic contained in the copper concentrate from Codelco's Mina Ministro Hales mine in Chile (Knuutila, 2011).

CONCLUSION

By roasting ores and concentrates at high temperature under the right process conditions, arsenic volatizes and can be efficiently separated from the metal. To volatize arsenic, the roasting temperature generally ranges between $500 - 700$ °C in an inert or reducing atmosphere, with residence times ranging from 0.5 to 3 hrs. However, each body of ore needs to be thoroughly tested to determine the optimum roasting conditions for the calcine product quality and required arsenic removal.

With more stringent environmental limits on arsenic emissions and the increase in demand to process high arsenic bearing metal ores at high throughput, roasting has re-emerged as an attractive treatment method. While the multi-hearth and rotary kiln can be considered for this application, the fluid bed roaster can offer higher throughput with simpler equipment, and seems to be the front-runner in recent studies and projects.

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