Gallium recovery from aluminum smelting slag via a novel combined process of bioleaching and chemical methods

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A B S T R A C T

Smelting slag generally contains a large number of heavy metals. In this study, the separation and selective recovery of gallium from aluminum smelting slag was studied deeply. Processes for bioleaching and recovering gallium from aluminum smelting slag have been executed. Under the condition of 2% pulp density, the Ga dissolution reached 505 mg/L, with a Ga bioleaching efficiency close to 100%. Ion exchange resin, fractionation precipitation, and milk of lime were assessed to test their efficiency in the separation and selective recovery of Ga from bioleachate. The results show ion exchange resin does not have selectivity to separate Ga from metals-based pregnant bioleachate. In addition, due to the similar properties between Ga and Al elements, coprecipitation reaction occurred, consequently resulting in the failure of chemical fractionation precipitation to separate and recover Ga. However, under the optimized experimental conditions, the milk of lime technique yielded the maximum recovery of 60.6%, proving that the method is superior to the first two methods. Therefore, a combined process development of bioleaching and milk of lime can be considered high-efficiency, economically and environmentally friendly for separating and selective recovery of Ga from aluminum smelting slag.

1. Introduction

Gallium is a rare metal with a low melting point that blends easily with most elements to form low-melting alloys (Moskalyk, 2003). Due to this property, gallium and gallium compounds are commonly used in the industry and medical fields (Gupta et al., 2007), for example, radioactive gallium (Ga) is used in nuclear medicine to detect and localize malignant tumor cells (Yu & Liao, 2011). Ga compounds including gallium nitride (GaN) are often used in electric devices like light emitting diodes (LEDs) due to its superior semiconductor properties which can convert electricity to light. The global market value of GaN power semiconductor soared from $2.5 million in 2011 to an estimated $12.6 million in 2012. The power GaN market report forecasts a $600 million market for GaN devices by 2020 (Jaskula, n.d.). Due to the rapid growth in consumption and importance for low-carbon technologies such as solid state lighting and photovoltaics, gallium and its compounds have been identified as crucially important materials (Løvik et al., 2015; Nancharaiah et al., 2016). The demand of gallium is estimated to increase 20-fold by the year 2030 due to the widespread use of gallium in electronics, atomics, lasers, the missile industry and the power sector which is driven by the development of technology

(Font et al., 2007; Chou et al., 2008; Gladyshev et al., 2015). However, the global primary production of gallium was estimated to drop 7% in 2012 from the previous year to 273 metric tons (Swain et al., 2015). The increasing demand for gallium promotes a search for new sources and extraction processes for this secondary metal resource.

Unlike other metals, Gallium does not exist in its pure metallic form in nature, and its compounds are not a primary source of extraction. The main sources of gallium are from waste streams derived from aluminum, zinc industries, coal fly ash, phosphorus flue dust (Xu, 2007), waste light-emitting diodes (Zhang et al., 2015) and scrap gallium arsenide (Lee & Nam, 1998), where it is recovered only as a by-product of other metals (mainly aluminum) (Wu et al., 2012).

As a conventional extractive metallurgy, smelting is used to separate a base metal from ore. However, during the process, it generates a huge quantity of smelting slag containing heavy metals (i.e., Ga, Al, Fe, Ca, and Mg). Currently the hydrometallurgical processes are the most broadly utilized processes to extract valuable metals from the smelting slag in which strong acids such as H_2SO_4, HNO_3, and HCl assisted with H_2O_2 serve as a working medium and always operate at a higher temperature of 60–90 °C (Lee & Nam, 1998; Wu et al., 2012; Li et al., 2010, 2011). Zhang et al. developed a combination process of pyrolysis,

physical disaggregation and vacuum metallurgy separation to recycle gallium from waste light-emitting diodes (Zhang et al., 2015). For the recovery of gallium, previous studies have essentially concentrated on the spent caustic solution, which is recycled in the Bayer process (Xue et al., 1989; Zhao et al., 2012), and these techniques have included fractional precipitation, electrochemical deposition, and solvent extraction (Ibragimov & Budon, 2010). Other methods, like acid leaching (Chen et al., 2012), organic solvent extraction (Ahmed et al., 2013), ion-exchange (Filik & Apak, 1998) and supercritical fluid extraction (Chou et al., 2008) have been carried out at the laboratory scale.

Among the above methods, some require a large amount of chemicals, leading to high operating costs. Moreover, the large consumption of various solvents and hazardous extraction substances increases the potential safe and environmental risks. In contrast, bioleaching can accomplish the release of metals from various solid matters under mild conditions with help of certain cells, which is relatively simple and eco-friendly and requires low energy and capital input (Lee & Pandey, 2012). So far, few studies have focused on the recovery of rare gallium metals from smelting slag by bioleaching (Wu et al., 2012; Zhao et al., 2012). In this work, bioleaching technology which uses cheap sulfur as sole energy source was first applied to the reclamation of aluminum smelting slag. Simultaneously, three different methods, i.e. ion exchange resin, fractionation precipitation and milk of lime, were tested to compare the performance of recycling Ga^{3+} in the bioleachate.

The objective of the current study is to accomplish the separation and recycling of gallium from waste smelting slag of aluminum. First, the bioleaching system was screened to determine the operational conditions for gallium leaching from dry Al-smelting slag and exploration of the leaching mechanisms involved. Second, this study mainly tested three different methods to compare the performance of recycling Ga^{3+} in the bioleachate: resin, chemical precipitation and milk of lime. Third, the optimum operating conditions of selectively recycling gallium from Al-smelting slag using the bioleaching-milk of lime was developed.

2. Materials and methods

2.1. Source and characteristics of Al-smelting slag

The Al-smelting slag was kindly provided by a professional smelter in Guizhou Province, southwest China. Prior to use, the smelting slag was dried at 105 °C for 2 h to a constant weight, and then ground and sieved to obtain a mesh size of < 150 μm. The fine slag material was used for characterization and bioleaching experiments. The smelting slag constituents were analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima 8300) after digestion using the HF–HNO$_3$–HCl digestion method (Xin et al., 2009). The detailed element contents of the slag sample were assayed as follows (%): Al, 7.5; Ga, 2.5; Fe, 0.5; Ca, 0.5; and Mg, 1.3. Other element contents, such as Zn, Mn, Co, Cd, Ni and Cr, were below the detectable limit (< 0.0001%). The slag contains 2.5% gallium.

2.2. Strain, media and culture condition

The bacterial strain used for bioleaching was isolated from a mine site in Shanxi Province, North China. The procedures regarding isolating the strain and growing the cells as an inoculum are available in our previous paper (Xin et al., 2009). The strain was identified using the 16S rDNA method. The upper and lower primers for PCR amplification were 27F and 1492R, respectively (Espejo et al., 1998). After analyzing the sequence, it was compared with the sequence in the GenBank database using the method of BLAST. Under accession number KJ719444 (XBP-1), the similarity between the 16S rDNA sequence of *Acidithiobacillus thiooxidans* ATCC19377 (accession number Y11596) was up to 99%, therefore, the strain was identified as *Acidithiobacillus thiooxidans*. It was cultured in inorganic salt media. The basal salts are listed

as follows (g/L): (NH$_4$)$_2$SO$_4$, 2.0 g; KH$_2$PO$_4$, 1.0 g; MgSO$_4$·7H$_2$O, 1.0 g; CaCl$_2$, 0.25 g; and FeSO$_4$·7H$_2$O, 0.18 g. Then, the media was adjusted to an initial pH of 3.0 with 6 mol/L H$_2$SO$_4$. To every 250-mL shake flask, 100 mL of basal salts media was added. All of the shake flasks with basal salts media were sterilized by a vertical heating pressure steam sterilizer (LDZX-75KBS, Shanghai, China) at 0.1 MPa (approximately 121 °C) for 20 min.

2.3. Bioleaching experiments

2.3.1. The growth of the strain under different energy substrates

At. thiooxidans grows as an obligate autotroph with various sulfur compounds, e.g., elemental sulfur, thiosulfate and tetrathionate (Schipper & Sand, 1999). In the first experiment, the inorganic salt media containing 10 g/L of sulfur, sodium thiosulfate and sodium sulfite as energy substrate were prepared and transferred into 250-mL flasks at 100 mL per flask, and then they were inoculated with the strain at a rate of 10% (V/V). The inoculated flasks were incubated in a shaker (30 °C, 120 rpm). The pH value and cell numbers in the slurry were monitored periodically during the process of cultivation. Sterile controls were obtained by inoculating the bioleaching media using sterile water instead of bioleaching cells. All of the experiments, including sterile controls, were performed in triplicate.

2.3.2. The growth of the strain under different concentrations of energy substrate

A certain amount of the selected best energy substrate from section 2.3.1 was divided to the final concentrations of 4.0, 8.0, 12.0, 16.0 and 20.0 g/L (w/v) in the flasks. The strain was inoculated into sanitized fresh media and incubated at 30 °C, at 120 rpm. In the process of cultivation, the concentrations of H$^+$ and the cell numbers were periodically monitored. The cell numbers and pH value reflected the growth of the strain, which affected the bioleaching efficiency. The pH value of media was measured using a pH meter (Hana HI2221, Italy), whereas the cell numbers were determined with a microscope (Olympus IX71, Japan). All of the experiments were conducted in triplicate.

2.3.3. Extraction behavior of metals from the Al-smelting slag by bioleaching

After 5 days of incubation, the pH value of the bioleaching system declined to ca. 1.0, and the cell density was controlled at 4.0×10^8 cells/mL. Then, different amounts of Al-smelting slag were added into the flasks containing media to a final pulp concentration of 1%, 2%, 4% and 8% (w/v), respectively. During bioleaching, the samples were collected periodically to determine the released concentrations of Ga, Al, Fe, Ca, and Mg using ICP-OES after an aliquot of bioleachate was filtered through a 0.45 μm nylon syringe filter (Corning Incorporated, Corning, Germany) to remove the cells and solid matter. All of the experiments were conducted in triplicate.

2.4. Three different methods for gallium recovery from bioleachate

2.4.1. Gallium purification through an ion exchange process

Two strong cation-exchange resins, D001 and D113 in hydrogen, were used for the recycling of gallium from bioleachate. Prior to use, the resins were washed with dilute hydrochloric acid and followed by multiple washings in a column system with deionized water (Kim et al., 2015). A 100 mL of bioleachate was added into 250 mL shaker flasks containing 4.0 g resin (30 °C, 120 rpm). During adsorption, the samples were collected periodically to determine the residual concentrations of Ga, Al, Fe, Ca, and Mg using ICP-OES. All of the experiments were conducted in triplicate.

2.4.2. Gallium purification through a metal hydroxide formed process

In the case, the aim was to improve the gallium purity through selective precipitation by addition of alkali. The solubility-product