

Bauxite Residue as a Source of Gallium – An Extraction Study

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Abstract



The world economy is confronted with an increasing supply risk of 'critical' strategically important metals such as gallium (Ga). These are defined as materials with high supply risk and above average economic importance compared to other raw materials. In the search for alternative sources, bauxite residue may offer potential. Bauxite residue or red mud is a major by-product of the aluminium industry, with an annual global production of 150 million tonnes and a total inventory of more than 2.7 billion tonnes. Depending on the source, bauxite residue can contain considerable amounts of valuable elements including Ga and its extraction may be economically feasible. This research, therefore, discusses the possibility of recovering Ga from bauxite residue. An extensive inventory of economically interesting elements in bauxite residue was created using microwave-assisted aqua regia digestion with subsequent inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. Furthermore, the extraction of Ga from bauxite residue by selective acid leaching was explored. A number of mineral acids (HCl, HNO₃, H₂SO₄) were investigated for the extraction process in addition to a low molecular weight organic acid (H₂C₂O₄). Consequently, an experimental design approach was used to determine optimal conditions for Ga extraction.

Keywords: Bauxite residue, recovery, critical raw materials, acid leaching, design of experiment.

1. Introduction

Recent studies in the EU, USA, Japan and UK have identified the most 'critical' metals and minerals [1–4]. These are defined as materials with a high supply risk and an above average economic importance compared to other raw materials [5]. According to a recent EC study, the following are considered the most 'critical' strategically important metals: antimony (Sb), beryllium (Be), cobalt (Co), gallium (Ga), germanium (Ge), indium (In), lithium (Li), niobium (Nb), platinum group metals, rare earths, rhenium (Re), tantalum (Ta) and tungsten (W) [1].

Ga appears in trace amounts (<50 ppm) as a salt in bauxite and zinc ores [6]. Most are extracted from crude aluminum hydroxide solution generated while refining bauxite into alumina [6]. However, currently the best process can only extract 10% of the Ga from bauxite ore and only 15% of refiners can actually recover Ga [6]. The increase in Ga price could lead to process improvements aimed at increasing extraction rates, the installation of Ga recovers circuits or development of recycling technologies from alternative sources [6]. Competing technology demand for Ga are semiconductor applications, multi-featured cell and "smart" phones, blue-ray

video disk players, high-concentration PV collectors, biomedical applications, fuel cells and ultra-violet activated phosphorus powders [6].

The supply risk can be reduced if previously untapped sources (primary, secondary) can be exploited in the future. Due to its content of strategically important metals, bauxite residue has been recently discussed as an upcoming source for critical raw materials including Ga [7–9].

Bauxite residue or red mud is the residue generated from alumina production where bauxite is digested in hot sodium hydroxide solution by the Bayer process. The annual production of smelter grade and chemical grade alumina in 2015 was over 115 million tonnes [10]. The global average bauxite residue generated per tonne of alumina is between 1 and 1.5 tonnes. It is estimated that over 150 million tonnes of bauxite residue are produced annually [11], while more than 2.7 billion tonnes were already stockpiled by 2011 [12]. Alternative uses for bauxite residue to date has not been successful on an industrial scale, with the exception of some limited use in cement and ceramic production [12]. Bauxite residue can contain considerable amounts of strategically important metals with high relative economic importance. Recovery of such metals from bauxite residue can be economically feasible [5].

This study evaluated the efficiency of Ga extraction from bauxite residue. First, an extensive inventory of economically interesting elements in bauxite residue was created. Then the extraction of Ga from bauxite residue by selective acid leaching was explored. A number of mineral acids (HCl, HNO₃, H₂SO₄) were investigated for the extraction process in addition to a low molecular weight organic acid (H₂C₂O₄). Consequently, an experimental design approach was used to determine optimal conditions for Ga extraction.

2. Materials and Methods

Chemical analysis of Ga was performed after aqua regia digestion with 100 g/L slurry concentration in a Multiwave 3000 (Rotor 8XF100) type microwave digestion system at 200 °C 1.25 MPa. The solutions after digestion were filtered with 0.45 µm PVDF syringe filter and diluted in 1 M HNO₃ before analysis [13].

An Agilent Technologies 5100 inductively coupled plasma optical emission spectrometer (ICP-OES) was used for metal analysis. Samples were prepared with a 1M HNO₃ solution. This 1M HNO₃ solution was also used for the dilutions of the standard solutions and as a calibration blank. The calibration curve was constructed by fitting through the origin using standard solutions of 100, 50, 10, 5, 1 g/L multi element standard. The following analytical line (in nm) was used for calculations: Ga 294.363 [14, 15].

The leaching tests were developed according to Ujaczki et al. [13]. Bauxite residue samples (from Hungary) were dried at room temperature and crushed in mortar. The samples were then leached with equivalent normality acids (1 M H₂SO₄, 2 M HNO₃, 2 M HCl, 1 M H₂C₂O₄; at 60 °C; 24h; 100 g/L slurry concentration) in triplicate. All tests were carried out in 100 ml conical flasks. These were shaken on an IKA KS 4000 i control incubation shaker at 250 rpm. The leaching of Ga with H₂C₂O₄ was performed varying several parameters, i.e. acid concentration (0.05 M, 0.25 M, 0.5 M, 1 M, 2 M, 3 M), contact time (1h, 2h, 3h, 4h, 5h, 10h, 20h, 24h) temperature (22 °C, 50 °C, 60 °C, 70 °C, 80 °C) and slurry concentration (10 g/L, 50 g/L, 100 g/L, 150 g/L, 200 g/L). The contact time was extended to 24 h for every extraction step to ensure that the leaching was complete. The extraction efficiencies were determined by the ratio of metal extracted to the aqua regia accessible metal content. The pH was measured with an Aqualytic AL15 multimeter.

Using these optimal conditions, 80% of the aqua regia accessible Ga content was extracted in bauxite residue.

Table 2. Conducted experiment to test prediction of the reduced quadratic model regarding maximal extractable Ga.

Acid conc.	Contact time	Temperature	Slurry concentration	Maximal extractable Ga	
M	h	°C	g/L		
2.5	21.7	80.0	10.0	Experimentally determined	85.8 mg/kg
				Predicted	81.2 mg/kg
				Accuracy	95%

4. Conclusion

The extraction of Ga from bauxite residue by selective acid leaching was explored in this study. Three mineral acids (HCl, HNO₃, H₂SO₄) and one organic acid (H₂C₂O₄) were evaluated regarding their efficiency to extract Ga from bauxite residue. The highest extraction efficiency for Ga was reached using H₂C₂O₄ when compared on a molar base to the other acids investigated. Further parameters affected by acid leaching were also studied for instance contact time, temperature and slurry concentration. Finally, an experimental design approach was used to determine optimal conditions for maximal Ga extraction. Optimal conditions predicted by the model regarding recovery of maximal extractable Ga were 2.5 M H₂C₂O₄, 21.7 h, 80.0 °C and 10.0 g/L, acid concentration, contact time, temperature and slurry concentration, respectively. These conditions allowed to extract 80% of the of the aqua regia accessible Ga content from bauxite residue. The result of this study clearly indicates that bauxite residue can be considered as a secondary source of Ga in future, thereby reducing the supply risk of critical strategically important metals such as Ga.

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