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, HNO_3, H_2SO_4) were investigated for the extraction process in addition to a low molecular weight organic acid ($H_2C_2O_4$). 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, HNO_3, H_2SO_4) were investigated for the extraction process in addition to a low molecular weight organic acid ($H_2C_2O_4$). 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 HNO_3 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 HNO_3 solution. This 1M HNO_3 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 mortal. The samples were then leached with equivalent normality acids (1 M H_2SO_4, 2 M HNO_3, 2 M HCl, 1 M $H_2C_2O_4$; 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 $H_2C_2O_4$ 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.

Minitab 17 software was used for development and analysis of experimental designs using the response surface methodology. A quadratic model was fitted to the maximal extractable Ga which was recovered by extraction with $H_2C_2O_4$ under varied parameters. The effects of four factors were considered i.e. $H_2C_2O_4$ concentration, contact time, temperature and slurry concentration. The levels for the factors were selected based on the leaching experiments. They were 0.05 and 3 M, 1 and 24 h, 50 °C and 80 °C, and 10 and 200 g/L for $H_2C_2O_4$ concentration, contact time, temperature and slurry concentration, respectively. The proposed parameters for extraction of the maximal concertation were tested afterwards experimentally.

3. Results and Discussion

In this study, an extensive inventory of critical strategically important metals in bauxite residue was created including rare earth elements using microwave assisted aqua regia digestion with subsequent ICP-OES analysis. From these elements, Ga and Sc had the highest economic value (i.e. concentration x market value). The following amounts were measured from the observed elements: Ga ~ 106.8 ± 7.3 mg/kg (42.7 US $/t); Sc ~ 51.4 ± 5.4 mg/kg (17.5 US $/t). Among these Ga (42.7 US $/t) contributed most to the total economic value [16]. Similar Ga contents were described, for instance, 89 mg/kg in Australian bauxite residue [17], as well as 91 mg/kg in Indian bauxite residue [18]. Based on this, further comparative extraction studies focused on Ga.

Three mineral acids were used for the extraction process (HCl, HNO_3, H_2SO_4). Experiments were also conducted with $H_2C_2O_4$, a small molecular weight organic acid, since Ujaczki et al. [13] reported that extraction with $H_2C_2O_4$ (1 M; 24h; 60 °C; 100 g/L slurry concentration) resulted in the most efficient extraction of Ga from Hungarian bauxite residue.

In the present study, the most efficient extraction was achieved by $H_2C_2O_4$ (42.0%) followed by acids in the order HCl > H_2SO_4 > HNO_3 (Table 1). Therefore, $H_2C_2O_4$ was chosen for further investigation of leaching parameters.

Table 1. Extraction efficiencies for leaching bauxite residue with HCl, H_2SO_4, HNO_3 and $H_2C_2O_4$ under the following conditions: normality = 2, 24h, 60 °C, 100 g/L slurry concentration, 250 rpm).

Acid	pH	Ga extraction efficiency* [%]
HCl	0.1	34.8 ± 2.5
HNO_3	0.2	27.9 ± 2.0
H_2SO_4	0.8	28.6 ± 1.0
$H_2C_2O_4$	1.1	42.0 ± 2.1

*Based on aqua regia accessible content.

The effect of acid concentration, temperature, contact time and slurry concentration on the extraction of Ga from bauxite residue were studied (Figure 1). Increasing the $H_2C_2O_4$ concentration from 0.05 to 3 M increased extraction efficiencies of Ga from 3% to 48% at 24h, 60 °C, 100 g/L slurry concentration and 250 rpm. 41% of Ga extraction efficiency was already achieved with using 1 M $H_2C_2O_4$, therefore, 1 M $H_2C_2O_4$ was chosen for the following leaching experiments (Figure 1).

Similarly, increasing contact time from 1h to 24 h increased extraction efficiencies of Ga from 13% to 41% using 1 M $H_2C_2O_4$, 60 °C, 100 g/L slurry concentration and 250 rpm. Also, elevating temperature from 22 to 80 °C led to considerably increased extraction efficiencies of

Ga from 18% to 40% using 1 M $H_2C_2O_4$, 24h, 100 g/L slurry concentration and 250 rpm (Figure 1).

Slurry concentration had a strong effect on extraction efficiencies like acid concentration. Here, decreasing slurry concentration from 200 g/L to 10 g/L resulted an increase in extraction efficiencies of Ga from 4% to 54% at 1 M $H_2C_2O_4$, 24 h, 60 °C and 250 rpm (Figure 1).
Other studies described similar trends regarding leaching parameters e.g. REE and Ga leaching with HCl from Hungarian bauxite residue by Ujaczki et al. [13] or REE leaching with HCl from Greek bauxite residue by Borra et al. [19].

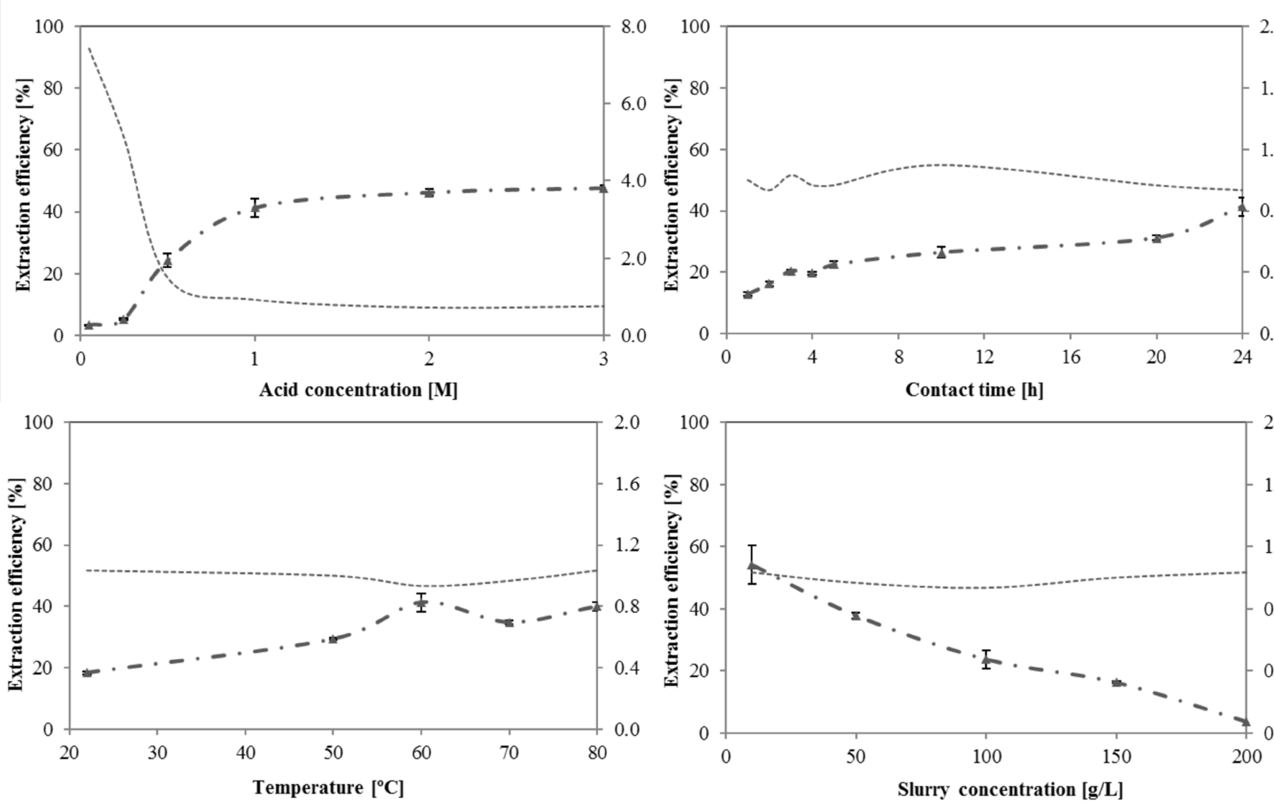

Figure 1. Effect of leaching parameters ($H_2C_2O_4$ concentration, contact time, temperature, slurry concentration) on extraction efficiency (primary Y-axis) and pH (secondary Y-axis) of Ga (squares). Single parameters were varied whereas all other parameters were kept constant at (1M $H_2C_2O_4$, 24h, 60°C, 100 g/L slurry concentration).

A design of experiment approach was used to optimize Ga extraction and to obtain an empirical model describing the data within the experimental conditions (0.05–3 M $H_2C_2O_4$, 1–24 hours, 50–80 °C, slurry concentration 10–200 g/L). The response surface reduced quadratic model considered both linear effects and interaction effects between $H_2C_2O_4$ concentration, contact time, temperature, and slurry concentration.

Optimal conditions predicted by the model regarding extraction of maximal extractable Ga from bauxite residue were 2.5 M $H_2C_2O_4$, 21.7 h contact time, 80.0 °C temperature and 10.0 g/L slurry concentration. The model predicted maximal extractable Ga of 81.2 mg/kg and the corresponding leaching experiment at these conditions confirmed the accuracy of this prediction, yielding a maximal extractable Ga of 85.8 mg/kg (Table 2). Since the experimentally determined and predicted maximal extractable Ga did not differ significantly (prediction was 95% of obtained), the model was considered accurate.

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, HNO_3, H_2SO_4) and one organic acid ($H_2C_2O_4$) were evaluated regarding their efficiency to extract Ga from bauxite residue. The highest extraction efficiency for Ga was reached using $H_2C_2O_4$ 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 $H_2C_2O_4$, 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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