



Recovery of gallium from Bayer red mud through acidic-leaching-ion-exchange process under normal atmospheric pressure

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ARTICLE INFO

Keywords:

Bayer red mud (BRM)

Gallium

Acidic-leaching-ion-exchange process (ALIEP)

Recovery

ABSTRACT

The Bayer red mud (BRM), generally containing 0.002 wt%–0.008 wt% of gallium (Ga), is an overlooked resource of Ga. In this work, an efficient method, called acidic-leaching-ion-exchange process (ALIEP), was developed to extract Ga from BRM. The ALIEP method involved three main steps: the BRM sample was firstly dissolved by mineral acid and the obtained leaching solution was further purified to remove the Fe^{3+} . Consequently, the purified solution, pre-concentrated by re-circulation process, was efficiently treated by ion-exchange process for the Ga recovery. The main influencing factors of the acidic-leaching process were systematically investigated. The optimal Ga leaching conditions were determined as HCl 159 g/L, liquid-to-solid ratio of 8 mL/g, 55 °C, and 5 h, attaining Ga leaching rate of 94.77% and the corresponding Ga^{3+} concentration of 3.91 mg/L in leachate. A nearly complete iron removal from the leachate was achieved by employing LSD-396 resin under conditions of 45 ± 2 °C, resin dosage of 0.6 g/mL and 2 h. Subsequently, the recovery efficiency of Ga from re-circulation leaching solution using the ion-exchange technology was evaluated. The results indicated that an adsorption rate of 59.84% and desorption rate of 95.32% for Ga were obtained. The concentrated solution contained 97.54 mg/L of Ga, which was enriched 24.95 and 4.75 times compared to the initial leaching solution of 3.91 mg/L and re-circulation solution of 20.52 mg/L, respectively.

1. Introduction

The Bayer red mud (BRM), a highly alkaline solid residue, is produced during the Bayer process for extraction of alumina from bauxite ores (Zhu et al., 2012). Approximately 0.6–2.5 t of BRM is generated per ton of alumina from the process, depending on the original properties of bauxite and operating conditions (Li et al., 2016). With the increasing alumina demand worldwide, the accumulated red mud was estimated to be 4 billion tons in 2015 (Zhu et al., 2015).

The disposal of BRM poses a serious environmental problem due to the corresponding highly pH nature (10–12.5) and complex chemical composition. Currently, most of raw red mud is directly stored in high-sized holding ponds without treatment (Sahu et al., 2010; Gomes et al., 2016). In contrast, the residue is regarded as a “polymetallic raw material” or an “artificial ore” because it is enriched in alumina, soda, silica, iron, calcium oxide and rare metals (Qu et al., 2013, 2015; Liu and Naidu, 2014). To alleviate the storage pressure increase of BRM, extensive research efforts have been devoted to the development of

processes for utilization of the waste in the past several decades. Particularly, the extraction of valuable elements from the residue has received much interest (Balomenos et al., 2011; Lindsay, 2011; Samouhous et al., 2013; Gladyshev et al., 2015). The recovery techniques of the base metals from the residue, such as alumina, soda, ferric and titanium oxides, have been studied by many researchers (Agatzini-Leonardou et al., 2008; Bruckard et al., 2013; Ghosh et al., 2011; Zhang et al., 2011; Liu et al., 2012a,b; Huang et al., 2016); however, only a few techniques have been applied in commercial scale production (Balomenos et al., 2011). Also, certain special metals have been recycled as secondary raw materials, including boron dioxide (Cengelglu et al., 2007), scandium (Tsakanika et al., 2004; Wang et al., 2013), and other rare-earth elements (Borra et al., 2015; Borra et al., 2016). Apart from the aforementioned valuable metals, Ga has also been discovered in BRM with its content ranging from 0.002 wt% to 0.008 wt% (Liu and Li, 2015). In the Bayer process, approximately 70% of Ga occurring as Ga_2O_3 in bauxite is dissolved out and accumulates in the Bayer liquor, which produces approximately 90% of the worldwide Ga quantities.

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The remaining 30% of undissolved Ga in bauxite is left in the BRM (Figueiredo et al., 2002). Ga metal is extensively employed in high-tech industries as it provides the benefits of low energy consumption and high computational speeds (Swain et al., 2015). Accordingly, Ga production has been continuously increasing and is estimated to increase 20-fold by the year 2030 compared to the 273 metric tons during 2012 (Alonso et al., 2012; Frenzel et al., 2016). It is worth mentioning that the Ga-bearing host minerals are quite scarce, consequently a large amount of research has been done on the potential Ga resources. Unfortunately, few efficient investigations have been conducted to extract Ga from the BRM, except a recent report from Abdulvaliyev et al. (2015). The researchers treated red mud by using Bayer-hydrogarnet process. In this process, the red mud sample contained 0.0025 wt% Ga was leached using a 240 g/L Na₂O solution in the presence of lime for 1.5 h at 240 °C under 20 atm with a liquid-to-solid ratio of 6 (abbreviated as L/S ratio hereafter). The leaching efficiency of Ga by this method was approximately 58%. The leaching solution was then treated by precipitation, followed by carbonation process to generate a concentrate (0.32 wt% Ga), which needed further treatment to recover Ga. In this work, an efficient method, called acidic-leaching-ion-exchange process (ALIEP), was developed by our group to recover Ga from the residue. The method mainly consisted of three steps: the BRM sample was firstly dissolved by a mineral acid under normal atmospheric pressure and the Ga was transformed into the liquid phase, followed by the removal of iron from the filtered leached solution. Subsequently, the purified solution, pre-enriched by circulation process, was efficiently treated by the ion-exchange process to concentrate Ga. The main benefits of this process are high extraction efficiency, simple procedure, and excellent Ga selectivity of resin. The aim of this work was to evaluate the Ga recovery from the BRM using the ALIEP method. The main factors influencing acidic-leaching of Ga from the BRM were investigated in detail. Also, Ga concentrations from the leaching solution by the ion-exchange method were performed.

2. Experimental

2.1. Materials and analysis

2.1.1. Major chemical compositions of BRM sample

The BRM utilized in this study was collected from a local alumina refinery in Guizhou Province of China. The sample was first dried in an oven at 105 °C for 48 h, then crushed into a fine powder and stored in a desiccator. From the inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500a, US) analysis, the Ga of 0.0033 wt% was detected in the sample. The results are presented in Table 1.

2.1.2. Morphological characteristics and particle size distribution of BRM sample

The morphological characteristics of the BRM sample were observed by a scanning electron microscope (SEM, JSM-6700F, Japan) (Fig. 1), and the corresponding particle size distribution was analyzed by a laser particle size distribution analyzer (SEISHIN LMS-30, Japan) (Table 2). As presented in Fig. 1 and Table 2, the fines appeared as crystalline aggregates and some large-sized crystals of various shapes and sizes; the particle sizes of the sample ranged from 0.315 μm to 1.991 μm. The mean particle size was only 0.889 μm. The fine particles contribute to the increase in leaching efficiency increase for all metals.

Table 1
Major chemical compositions of BRM sample (wt%).

Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	Na ₂ O	TiO ₂	Ga	V	LOI
20.73	17.19	20.74	15.85	6.39	5.29	0.0033	0.03387	10.74

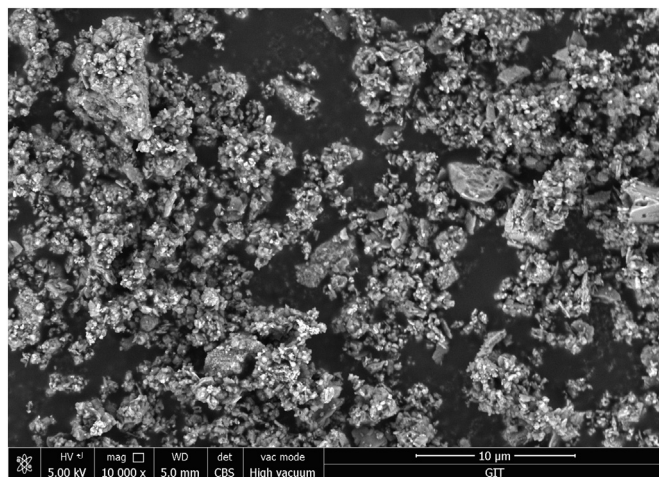


Fig. 1. SEM image of raw BRM.

2.1.3. X-ray diffraction measurement of BRM sample

The X-ray diffraction (XRD) pattern of the BRM sample was determined using a diffractometer (XRD, XRD-6100, Japan) and the result is presented in Fig. 2. The residue mainly consisted of hematite (Fe₂O₃, PDF #89-0596), katoite (Ca₃(Fe_{0.87}Al_{0.13})₂(SiO₄)_{1.65}(OH)_{5.4}, PDF #87-1971), cancrinite [Na₈(Si₆Al₆O₂₄)(H_{0.88}(CO₃)_{1.44})(H₂O)₂], PDF #77-1145) and kaolinite (Al₂Si₂O₅(OH)₄, PDF #72-2300). Aluminosilicates were found to be the primary phases in the sample. The Ga-bearing mineral was not observed, likely because it was below the detection limit.

2.2. Methods and procedure

2.2.1. Leaching experiments

The acid leaching experiments were performed in a 1000 mL glass reactor equipped with a mechanical stirrer. The stirrer was equipped with a digital controller unit and a thermostat for controlling the reaction temperature with an accuracy of ± 0.5 °C. In addition, the reactor was installed with a reflux cooler to prevent the mass from evaporation. A specific amount of acid was initially slowly added into distilled water in the reactor according to a predetermined L/S ratio. When the dilute acid solution was heated up to the required temperature, a 50 g BRM sample (dry weight, precision 0.1 mg) was introduced into the reactor and the mixture was agitated well at 300 r/min for a specific duration. The leaching slurry was filtered, and the produced leached residue and solution were chemically analyzed. The extracted amounts of Ga and Al were calculated from chemical analysis of the leached residue.

The effects of acid concentration, leaching temperature, leaching duration and L/S ratio on the leaching efficiency of Ga were studied to determine the optimum conditions for Ga extraction. The leaching behavior of Al was also analyzed due to the geochemical affinity between the two elements (Zhao et al., 2012). From this analysis, the percentage extraction of Ga (or Al) was calculated by Eq. (1) as follows:

$$\eta(\%) = 1 - \frac{(\text{Me})_{\text{RE}} \times M_{\text{RE}}}{(\text{Me})_{\text{RM}} \times M_{\text{RM}}} \times 100\% \quad (1)$$

where, η (%) is the leaching rate, $(\text{Me})_{\text{RE}}$ and $(\text{Me})_{\text{RM}}$ are the contents of metal in the leached residue and the BRM sample (wt%); M_{RE} and M_{RM} are the masses of the dried final leached residue and the BRM sample (g), respectively.

2.2.2. Iron removal experiments

For eliminating the interference of Fe³⁺ with Ga extraction by resin adsorption, the leaching solution was treated to remove iron prior to Ga recovery. LSD-396 is a chlorinated polystyrene macroporous resin,

Table 2
The particle size distribution analysis of BRM sample (μm).

Mean	Median	0.315	0.401	0.554	1.526	1.991
0.889	D50 = 0.554	< 10 wt%	< 25 wt%	< 50 wt%	< 75 wt%	< 90 wt%

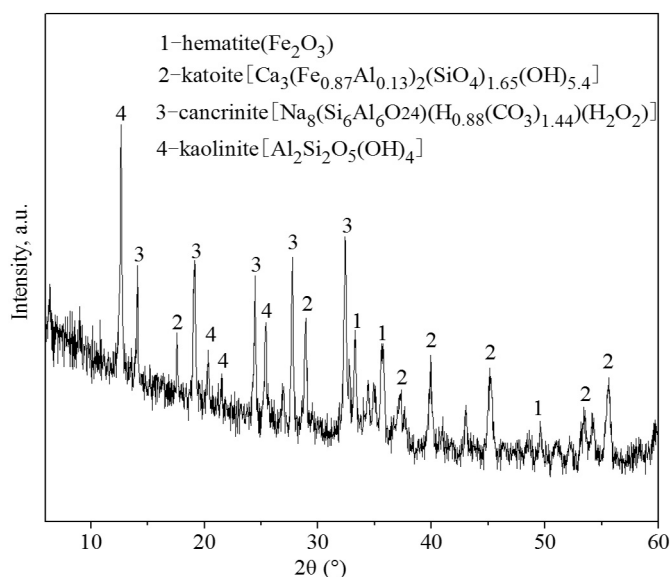


Fig. 2. XRD patterns of BRM sample.

which was specially developed for Fe^{3+} removal in strong hydrochloric acid media by the Xi'an Sunresin Technology Co., Ltd. (Xi'an, China). The resin displayed an excellent selectivity for Fe^{3+} due to its strong affinity for Fe^{3+} in hydrochloric acid media (Qi and Wang, 2016). Adsorption of Fe^{3+} onto LSD396 involves an ion exchange with Cl^- , and the reaction can be described by the following chemical Eq. (2):



where R represents the chemistry of the resin not involved in ion exchange:

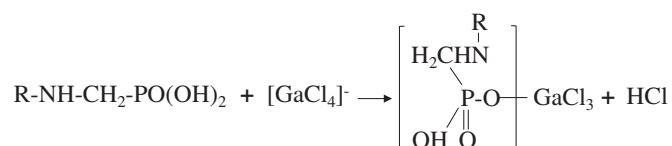
In iron removal experiment, 50 mL of leaching solution and a certain amount of resin were added into a 250 mL conical flask with a rubber stopper, and vibrated using a constant temperature water bath shaker at certain temperature. When the adsorption process was completed, the resin and solution were separated immediately by filtration. Then the concentrations of major elements in the processed solution were analyzed, and the removal efficiency was calculated using formula Eq. (4).

2.2.3. Ga recovery experiments

The leachate was recycled for a continuous leach fresh sample acquisition for the efficiency improvement of the mineral acid and the Ga concentration under the optimal conditions. It is worth noting that a similar mineral acid concentration in the solution was required to maintain for yielding maximum Ga extraction rates in each extraction step. Each filtration solution was treated by resin of LSD-396 to remove iron.

LSC-500S resin, containing reactive groups of $[-\text{NH}-\text{CH}_2-\text{P}(\text{O})(\text{OH})_2]$, was adopted as the adsorption agent of Ga. The resin displays excellent selective adsorption property for Ga in a strong acidic solution due to the formation of stable complexes through reactive groups binding with metal ions (Shu et al., 2006). According to literature review (Xiong et al., 2002; Zhao et al., 2015), the O of P-OH might be the main binding motif toward Ga^{3+} in hydrochloric acid media, Ga^{3+} is usually present as $[\text{GaCl}_4]^-$ in the strong hydrochloric acid media (Zheng and Gesser, 1996). When the O atom bonds with Ga, the

released H^+ will take one Cl^- from $[\text{GaCl}_4]^-$ to form HCl. The adsorption mechanism of Ga^{3+} onto LSC500s might be described by the below chemical Eq. (3).



During Ga recovery experiments, the LSC-500S resin was pretreated by soaking it in a hydrochloric acid solution of 2 mol/L for 24 h and washing with distilled water until the pH was neutral. Consequently, the resin was oven-dried at 75 °C until it reached a constant weight prior to the adsorption experiments. A proper pretreated resin dosage and 500 mL pre-concentrated solution were placed in a 1000 mL conical flask with a rubber stopper. The flask was sealed and placed in the reactor with a thermostatic oscillator (CHA-SA, Feipu enterprise of Changzhou, China) with the temperature of 40 ± 0.5 °C and the duration of 16 h. When the adsorption process finished at the pre-set duration, the resin and the solution were separated immediately through filtration. In an elution experiment, the loaded resin was washed with deionized water to pH = 7 and placed in a 250 mL conical flask with a rubber stopper. It was subsequently desorbed with 60 mL of 0.5 mol/L hydrochloric acid (rinse solution) in the thermostatic oscillator at room temperature for 4 h. The adsorption and desorption rates were evaluated from Eqs. (4)–(5):

$$\varepsilon_{\text{AD}} (\%) = \left(\frac{C_0 - C}{C_0} \right) \times 100\% \quad (4)$$

$$\varepsilon_{\text{DE}} (\%) = \left[\frac{V_{\text{DE}} \times C_{\text{DE}}}{V_0 \times (C_0 - C)} \right] \times 100\% \quad (5)$$

where, ε_{AD} (%) is the resin adsorption rate, C_0 and C are the initial and final metal concentration (mg/L) in the adsorption experiment, respectively; V_0 is the volume of the initial solution (mL), ε_{DE} (%) represents the desorption rate of the resin, V_{DE} and C_{DE} are the volume (mL) and metal concentration (mg/L) of the desorbed solution for Eq. (5), respectively.

In the present study, elemental concentrations of the liquid phase were measured using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500a, US). Chemical compositions of samples and residues were analyzed by Sequential X-ray Fluorescence Spectrometer (XRF, Shimadzu XRF-1800, Japan). The chelating ion-exchange resins, LSD 396 and LSC-500S, were purchased from the Xi'an Sunresin Technology Co., Ltd. of China. The chemical reagents utilized in this work were of analytical grade and the statistical analysis was conducted using ORIGINPRO v9.0 software. The ALIEP process flowsheet for the Ga extraction from the BRM is presented in Fig. 3.

3. Results and discussion

3.1. BRM characterization

The thermal stability of BRM was investigated by thermogravimetry (TG) and derivative thermogravimetry (DTG) analysis under air atmosphere (Fig. 4). As observed from Fig. 4, a total weight loss of approximately 10.74% occurred and it was possible that three defined regions of weight loss were observed. The first weight loss region, at a

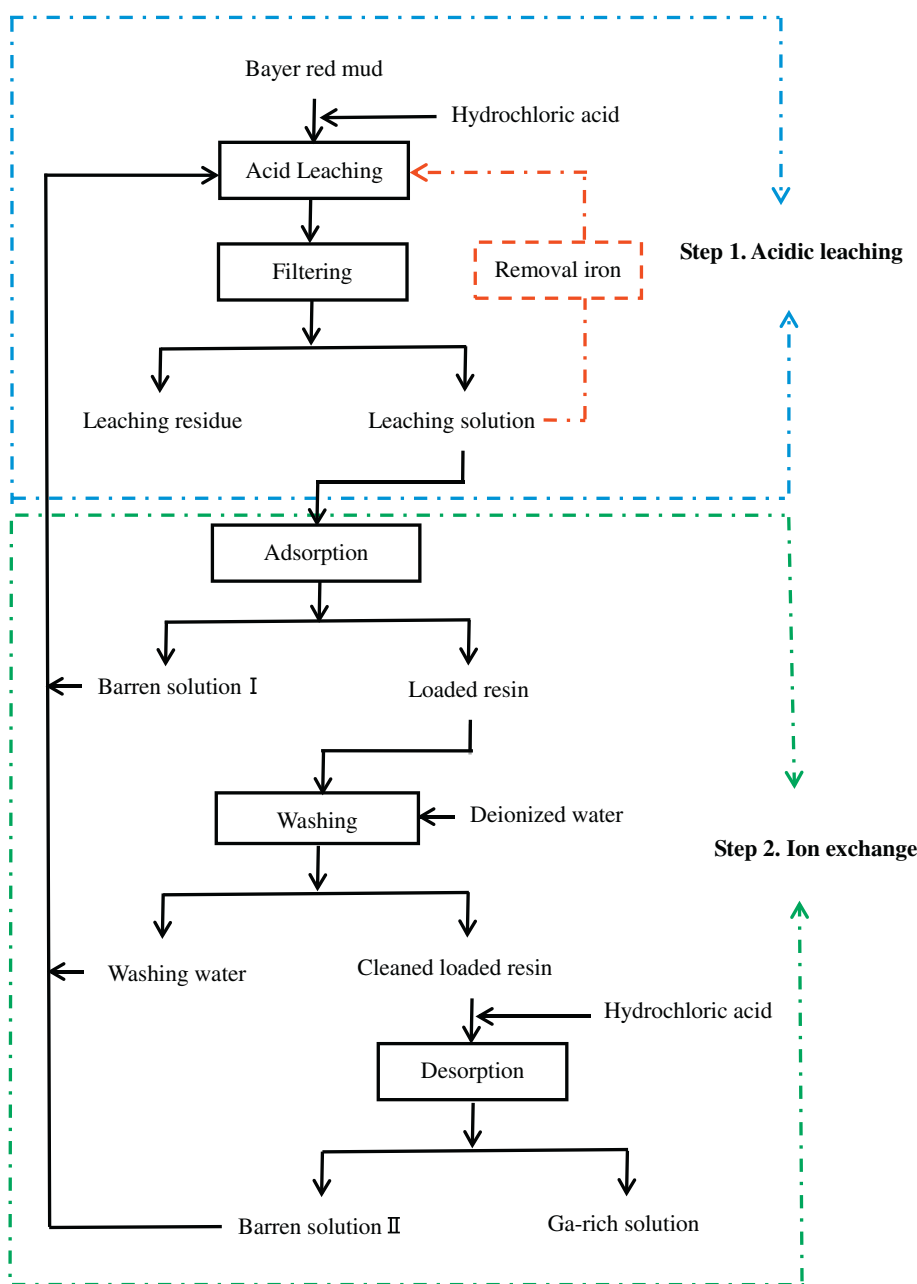


Fig. 3. Conceptual flowsheet of ALIEP for recovering Ga from BRM.

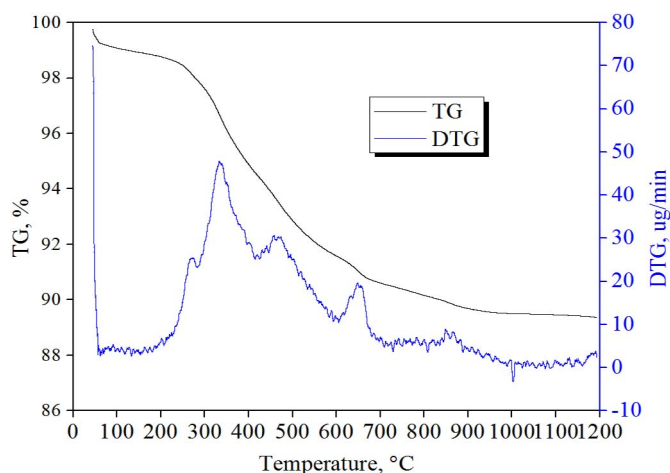


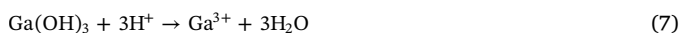
Fig. 4. TG analyses and DTG profiles of BRM under air atmosphere.

temperature lower than 100 °C, could be attributed to free water evaporation (Bento et al., 2016). In the second region, in the range of 100–320 °C, the weightlessness became fast and was apparently observed for the BRM by the DTG peak at 320 °C approximately, which was mainly caused by the evaporation and release of the crystallized water in the sample (Dodoo-Arhin et al., 2013). Then, the weight loss rate began to slow down from 320 °C to 650 °C, during which time the crystallized water and certain amounts of combined water were overflowed (Liu et al., 2012a,b), especially from 600 °C to 650 °C. A tremendous amount of carbonate minerals started to decompose, which could be explained by the existing peak at approximately 650 °C of the DTG. The results obtained were similar to the findings by Zhu et al. In the last region from 650 °C to 1200 °C, the weight loss rate became significantly slow and remained at almost the same value.

3.2. Leaching experiments of Ga and Al

3.2.1. Effects of different mineral acids on the Ga leaching rate

Leaching experiments were executed to select a good extraction performance reagent from hydrochloric (HCl, 36.5 wt%), sulfuric (H₂SO₄, 98 wt%) and nitric (HNO₃, 66 wt%) acids based on the leaching rate of Ga under the same conditions. The main reactions are stated below (6, 7). Also, the stoichiometric consumptions of mineral acids were calculated according to the major components of 100 g BRM as 105.92 g of HCl, 143.94 g of H₂SO₄, and 174.10 g of HNO₃, respectively.



The experimental conditions were: temperature 100 °C, leaching duration 4 h, L/S ratio 8 mL/g, and the mineral acid additions were increased to 1.2 times of stoichiometric consumption because certain minor constituents of the sample were not accurately estimated for the acid consumption. This was equivalent to 159 g/L of HCl, 219.51 g/L of H₂SO₄ and 261.15 g/L of HNO₃, respectively. The leaching rates of Ga by using these mineral acids were $\eta_{\text{HCl}} = 97.73\%$, $\eta_{\text{H}_2\text{SO}_4} = 90.92\%$ and $\eta_{\text{HNO}_3} = 78.33\%$, respectively. This indicated that the leaching efficiency of Ga treated with HCl was higher by 6.81% and by 19.4% than that treated with H₂SO₄ and HNO₃, respectively. Al(Ga) recovery is usually influenced to some degree by the amount of H⁺ available in the reaction system. Generally, sulfuric acid, being a diprotic acid, performs better than mono-protic acids (hydrochloric and nitric acids) under the same reaction conditions (Pepper et al., 2016). However, the highest recovery of Ga in this study was with hydrochloric acid followed by sulfuric acid, and then nitric acid. The reason for this leaching behavior is not known, but it could potentially be a result of the presence of sulfate/nitrate species, which reduces the amount of Ga³⁺ in the solution by precipitation or adsorption.

Based on the discussion above, the hydrochloric acid was preferentially selected as the extracting reagent in all following leaching experiments. Leaching rates of major elements in BRM under the conditions were presented in Table 3. The results showed that most of Ca, Na, V as well as Fe were dissolved into the leachant in addition to Ga and Al, whereas only moderate amount of Ti and trace quantity of Si were extracted.

3.2.2. Effect of hydrochloric acid concentration

The acid concentration is an important parameter affecting the leaching process. In the present study, the effect of hydrochloric acid concentration on the Ga leaching from the sample was studied in the range of 132 g/L to 238 g/L following the experimental conditions of temperature 100 °C, leaching duration 4 h, and L/S ratio 8 mL/g. The leaching rates of Ga and Al as a function of the hydrochloric acid concentration are presented in Fig. 5. According to the results presented in Fig. 5, the leaching rate of Ga significantly increased from 81.00% to 94.82% as the acid concentration increased from 132 g/L to 159 g/L. This might be attributed to the fact that a higher amount of acid was available for the reaction, which could attack the soluble Ga in a better manner (Sancho et al., 2009). When the addition amount of acid increased further from 159 g/L to 211 g/L, the leaching rates of Ga and Al showed a slight improvement; however, both Al and Ga leaching efficiencies increased sharply at 238 g/L, especially for Al, which increased

Table 3
Leaching rates of major elements in BRM (%).

Al	Si	Fe	Ca	Na	Ti	Ga	V
95.49	0.44	69.94	87.03	86.18	49.60	97.73	77.86

Notes: leaching conditions: 159 g/L HCl; 100 °C; 4 h; L/S: 8 g/mL.

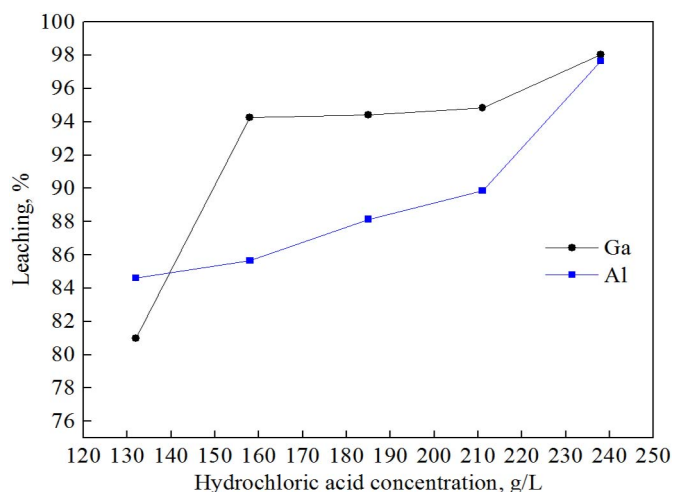


Fig. 5. Effect of hydrochloric acid concentration on leaching rates of Ga and Al (100 °C; 4 h; L/S: 8 g/mL).

remarkably from 89.86% to 97.66%. This may be due to the initial leaching of only the most easily digested Al (Ga) phases in the sample, such as kaolinite, at lower acid concentrations (from 159 g/L to 211 g/L) (Yang and Steefel, 2008; Liang et al., 2014). When the acid concentration was increased to 238 g/L, the higher extraction for Al(Ga) was likely due to an less saturation of BRM. Under these conditions, the reaction system contains a large amount of acid compared to the substance that is being leached (Cornell and Schwertmann, 2003), which may have caused partial dissolution of some of the more stable aluminosilicate phases that were present. However, the Ga dissolution was < 4% when the acid concentration increased from 159 g/L to 238 g/L. Furthermore, exceed concentration would increase the hydrochloric acid volatilization and reduce the acid utilization rate. Consequently, the concentration of the acid was fixed at 159 g/L according to the experimental results.

3.2.3. Effect of leaching temperature

Temperature plays a crucial role in the BRM dissolution, and the leaching of aluminosilicate phases in red mud has been shown to increase with rising reaction temperatures (Davris et al., 2016; Pepper et al., 2016). The experiments were performed in the temperature range of 40 to 100 °C, with 15 °C intervals, under the conditions of leaching duration 4 h, L/S ratio 8 mL/g, and hydrochloric acid concentration 159 g/L, and the experimental results are presented in Fig. 6. As illustrated in Fig. 6, it could be clearly observed that the leach ratios of Ga

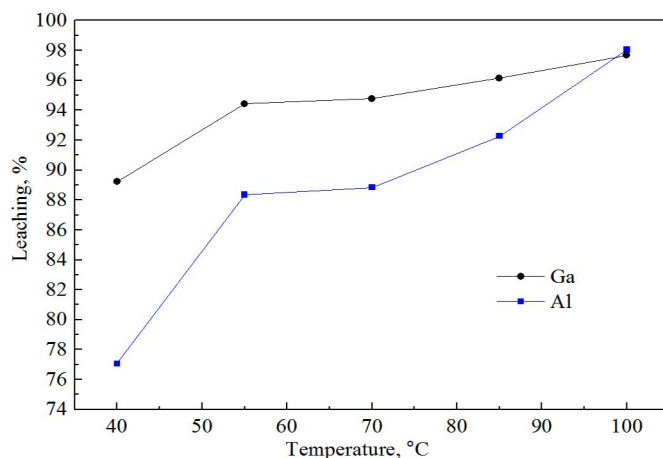


Fig. 6. Effect of temperature on leaching rates of Ga and Al (159 g/L HCl; 4 h; L/S: 8 g/mL).

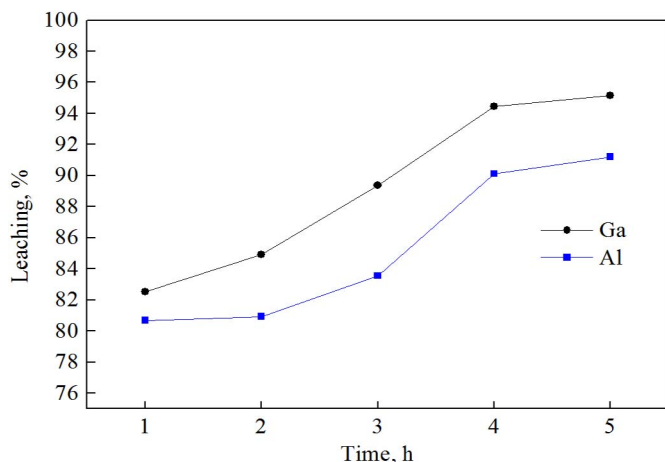


Fig. 7. Effect of time on leaching rates of Ga and Al (159 g/L HCl; 55 °C; L/S: 8 g/mL).

and Al increased rapidly from 89.22% and 77.06% to 94.44% and 88.36%, respectively, as the temperature increased from 40 to 55 °C. When the temperature was further raised from 55 to 100 °C, the leach rates of Ga and Al increased slowly from 94.44% and 88.36% to 97.73% and 95.49% only, respectively. This trend could be explained by the enhanced dissolution of Al(Ga)-bearing phases (i.e. katoite, cancrinite and kaolinite) at higher temperatures, since these phases were dissolved quite readily as the reaction temperatures increased, which was in accordance with the observed trends in the Al leaching from the red mud reported by Pepper et al. (2016). In contrast, excessively high temperature will result in high energy consumption of the process. According to the results presented in Fig. 6, the subsequent experiments were executed at 55 °C.

3.2.4. Effect of leaching duration

Five experiments were carried out at different leaching durations varying from 1 to 5 h, with 1 h intervals, at 55 °C with hydrochloric acid concentration 159 g/L and using L/S ratio 8 mL/g. The experimental results are shown in Fig. 7. As given in Fig. 7, the leach rates of Ga and Al increased continuously from 82.53% and 80.68% to 95.14% and 91.21%, respectively. This occurred as the reaction duration increased from 1 h to 5 h. Whereas the Ga and Al dissolution did not exceed 1.5% from 4 h to 5 h, where the leach rates increased from 94.44% and 90.13% to 95.14% and 91.21% only, respectively. Accordingly, the leaching duration should be maintained at approximately 4 h. The reason might be that the H^+ concentration was higher during the initial stage of the reaction system, where the reaction mainly occurred at the surface of the BRM particles and formed loose solid surfaces, which was favorable for the Ga^{3+} and Al^{3+} diffusion from the solid phase to the liquid phase. As the duration increased, the H^+ concentration quickly decreased in the solution and the reaction rate slowed down until it was remained almost constant.

3.2.5. Effect of L/S ratio

The L/S ratio effect was evaluated at 55 °C, with leaching duration 4 h, and hydrochloric acid concentration 159 g/L. The results are presented in Fig. 8. According to experimental results in Fig. 8, when the L/S ratio changed from 4 to 12 mL/g, the leach rates of Ga and Al increased from 89.49% and 86.23% to 95.78% and 89.73%, respectively. This indicated that there was no significant improvement in the extraction efficiency, especially for Al. Moreover, it was found that the leached slurry filtration was quite difficult when the L/S ratio was below 8 mL/g, which could be attributed to a high concentration of formed silica gels (silica occurs as SiO_3^{2+}) in the leaching slurry as the L/S ratio decreased (Zheng and Gesser, 1996; Liu et al., 2016). In contrast, a high L/S ratio indicates that a higher volume of liquid phase

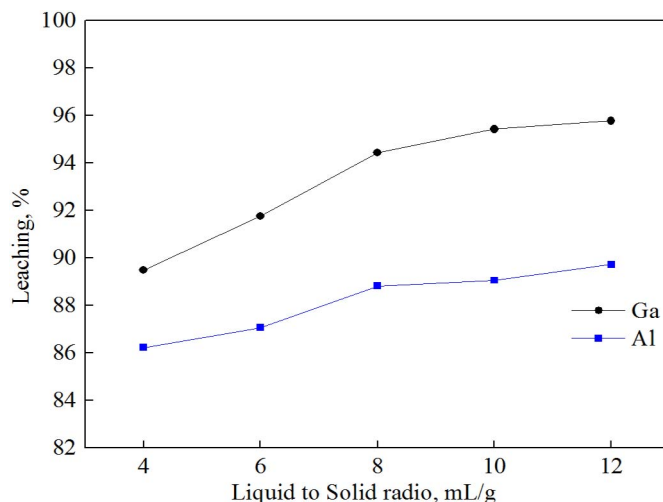


Fig. 8. Effect of L/S ratio on leaching rates of Ga and Al (159 g/L HCl; 55 °C; 4 h).

is produced and the concentrations of Ga and Al in the leaching solution are diluted, which will increase the processing costs of the subsequent treatment. As a result, the L/S ratio of 8 mL/g was selected in this work.

Based on the above experimental results, the optimum leaching conditions of Ga from the BRM were determined to be: hydrochloric acid concentration 159 g/L, temperature 55 °C, leaching duration 4 h, and L/S ratio 8 mL/g.

3.2.6. Verification experiments

In order to verify the reproducibility of the experimental results, three parallel experiments of Ga extraction from the BRM were performed under the optimum leaching conditions (i.e. 159 g/L hydrochloric acid concentration, 55 °C, 4 h and L/S ratio 8 mL/g). The results are tabulated in Table 4 and the leach residue SEM image is presented in Fig. 9. As revealed in Table 4, the average leaching rates of Ga and Al were 94.77% and 88.34%, respectively, which indicated a good reproducibility of the leaching experiments under the optimum leaching conditions. Also, approximately 69% of iron was dissolved in the liquid that contained about 12,462 mg/L of Fe^{3+} . The chemical analysis of leached residue given in Table 5 presents that the leach residue became a SiO_2 rich material (31.97 wt%), and most of CaO , Na_2O and Fe_2O_3 were extracted. Also, low amounts of TiO_2 (4.98 wt%), Al_2O_3 (7.51 wt%) and V (0.0140 wt%) existed. The Ga content was only 0.000540 wt%. As presented in Fig. 9, the morphology of the leached residue showed significant changes compared to the raw BRM (Fig. 1). The fines of the raw BRM particles disappeared within the leached residue, which further indicated that most of Al, Fe, Na and Ca were dissolved out. Moreover, the crystalline particles that were extruded from the red mud surfaces increased in size, which was likely due to the formation of additional phases, such as NaCl (Liang et al., 2014).

3.3. Iron removal experiments

Iron removal experiments were carried out at $45 \pm 2^\circ C$ with resin dosage of 0.6 g/mL for 2 h. The experimental results are presented in Table 6. As observed from the chemical analyses, the concentrations of major element in solution before and after treatment with LSD-396 resin showed almost no change, except Fe and Si. It is noteworthy that Si was decreased by 15.10%, which might be due to the attachment of Si to LSD-396 resin (Zheng and Gesser, 1996). Fe was not detected in the purified solution, or perhaps its concentration was below the limit of detection (1 mg/L), indicating that a highly efficient iron removal was achieved, while the loss of Ga was 1.29%.

Table 4
The results of parallel tests under optimum conditions.

No.	Leaching residue				Filter solution (mg/L)			η_{Ga} (%)	η_{Al} (%)	η_{Fe} (%)
	Mass (g)	Ga (ppm)	Al (wt%)	Fe (wt%)	Ga	Al	Fe			
1	16.65	5.60	4.14	14.07	3.89	11,993.24	12,192.37	94.35	87.43	67.72
2	15.92	5.20	3.78	13.98	3.92	12,211.49	12,591.31	94.98	89.03	69.34
3	15.61	5.30	4.02	14.21	3.92	12,143.32	12,602.41	94.99	88.56	69.44
Average	16.06	5.37	3.98	14.09	3.91	12,116.02	12,462.03	94.77	88.34	68.84

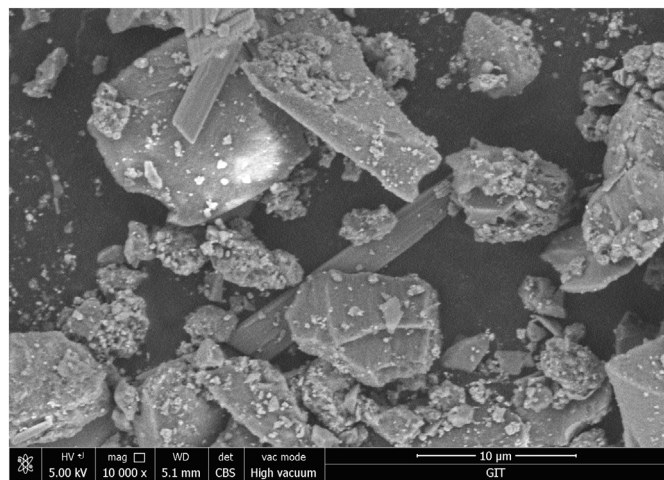


Fig. 9. SEM image of leached residue (159 g/L HCl; 55 °C; 4 h; L/S: 8 g/mL).

Table 5
Major chemical compositions of leached residue (wt%).

Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	Na ₂ O	TiO ₂	Ga	V	LOI
7.51	31.97	20.10	3.84	1.65	4.98	0.00054	0.0140	20.47

Notes: leaching conditions: 159 g/L HCl; 55 °C; 4 h; L/S: 8 g/mL.

3.4. Pre-enrichment experiment of Ga in leachate

Re-circulation process was employed to pre-enrich Ga by the leachate produced in the first Ga extraction cycle under the optimum leaching conditions. Also, the Fe³⁺ in each leachate was treated by employing the LSD-396 resin. According to the experimental results presented in Fig. 10, the Ga and Al concentrations could reach up to 20.52 mg/L and 60,791.74 mg/L after 6 cycles, respectively. The leaching rates were 77–94% for Ga and 68–88% for Al. From the seventh to the tenth re-circulation cycle, however, the two element concentrations had a slight improvement, which ranged from 21.81 to 23.68 mg/L for Ga and from 63,821.32 to 68,343.48 mg/L for Al, respectively. This indicated that the leaching efficiencies of Ga and Al decreased significantly (only 13.58% and 8.24% at the tenth re-circulation step, respectively). This might be explained by the fact that the concentration of the formed silica gels in the leaching slurry increased along with the number of re-circulation steps, so some amounts of the extracted Ga and Al were adsorbed by silica gel (Zheng and Gesser, 1996). Furthermore, the leaching slurry exhibited a poor filtration

Table 6
Concentrations of major element in solution before and after iron removal (mg/L).

Elements	Al	Fe	Ca	Na	Ti	Si	Ga	V
Raw solution	12,110.32	12,491.27	11,201.30	54,817.70	2603.45	38.40	3.91	22.20
Purified solution	12,093.03	ND	11,197.80	54,798.40	2600.76	32.60	3.86	21.10

Notes: ND: not determined.

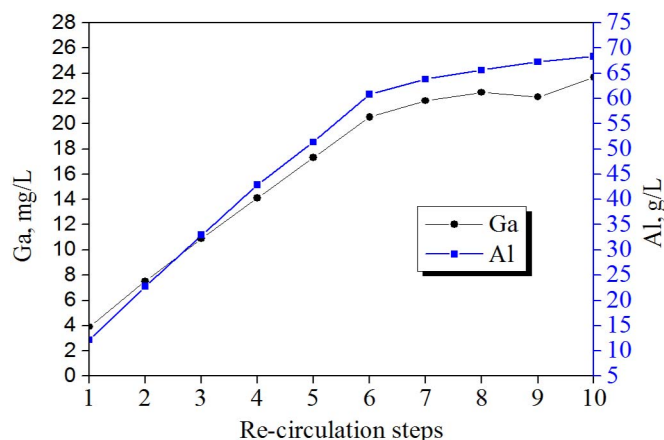


Fig. 10. Ga and Al concentrations in the leachate during the re-circulation process.

performance after seven steps. Accordingly, the 6 cycles process was selected to pre-concentrate Ga in the leaching process, and the final leachate contained 20.52 mg/L of Ga and 60,791.74 mg/L of Al, respectively. Moreover the Fe content was found to be merely 130.42 mg/L due to the iron removal treatment (Table 7).

3.5. Exploratory experiments of Ga recovery from leaching solution

During the Ga recovery experiments, three parallel adsorption experiments of Ga enrichment through LSD-500S resin were performed under these conditions: resin dosage 8 g/L, temperature 45 ± 0.5 °C, and duration 24 h. Also, the corresponding desorption of loaded resin was carried out under the conditions of duration 4 h with 60 mL of 0.5 mol/L hydrochloric acid (rinse solution) at room temperature. Concentrations of major elements in the 6th re-circulation leaching solution before and after LSD-500S adsorption are showed in Table 7, and the results of adsorption and desorption experiments are presented Table 8.

Generally, Al³⁺ and Fe³⁺, due to their ionic radii being similar to that of Ga³⁺, can interfere with the extraction of Ga through a chelating ion-exchange process. As seen from Table 7, the concentrations of Al, Ca, Na, and Ti in solution nearly remained constant before and after the adsorption process, indicating that these elements had almost no effect on Ga adsorption and LSD-500S exhibited an excellent selectivity for Ga. 18.27% of anionic Si was lost in the process, likely due to its attachment to the resin (Zheng and Gesser, 1996). Furthermore, 20.70% of V and 8.40% of Fe were reduced during the treatment, respectively. This indicated that V and Fe co-extraction took place

Table 7

Concentrations of major element in solution before and after LSD-500S treatment (mg/L).

Elements	Al	Fe	Ca	Na	Ti	Si	Ga	V
Before adsorption	60,791.74	130.42	43,163.80	24,813.90	11,273.31	93.60	20.52	79.85
After adsorption	60,782.61	119.47	43,158.40	24,808.50	11,269.86	76.50	8.23	63.32

Table 8

Resin adsorption and desorption experiments.

No.	Dosage of resin (g)	Re-circulation solution (mL)	Resin adsorption rate (%)	Acid consumption (mL)	Desorption rate (%)	Desorption solution concentration (mg/L)
1	4	500	61.28	60	96.01	100.61
2	4	500	59.37	60	94.51	95.95
3	4	500	58.86	60	95.45	96.07
Average	–	–	59.84	–	95.32	97.54

simultaneously (Zhao et al., 2015; Bautista, 2003). Fortunately, the average adsorption rate of Ga was 59.84% and its corresponding average desorption rate was 95.32% (Table 8), respectively, indicating that the co-extraction of V and Fe had a slight effect on the Ga ion-exchange process. The average concentration of Ga in the desorption solution was as high as 97.54 mg/L, which was enriched by 24.95 and 4.75 times in comparison with the initial leaching solution of 3.91 mg/L and the sixth re-circulation solution of 20.52 mg/L, respectively.

4. Conclusions and outlook

In summary, the ALIEP method employed to recover Ga from the Bayer red mud was demonstrated to be a facile and effective method. The main results of this work are summarized as follows:

- (1). The main parameters affecting the acidic-leaching process, including acid concentration, leaching temperature, leaching duration and L/S ratio, were examined in detail. The optimum conditions were found to be: hydrochloric acid concentration 159 g/L, leaching temperature 55 °C, leaching duration 4 h and L/S ratio 8 mL/g. The average leaching rates of Ga and Al were 94.77% and 88.34%, while the concentrations of Ga^{3+} and Al^{3+} were 3.91 mg/L and 12,116.02 mg/L, respectively.
- (2). The re-circulation process was employed to pre-enrich the Ga concentration and reduce the hydrochloric acid consumption prior to the ion-exchange treatment. The results demonstrated that the Ga concentration increased from 3.91 to 20.52 mg/L in the leachates after six cycles, whereas the Fe content was decreased significantly by the iron removal process.
- (3). The sixth re-circulation leaching solution obtained under the optimum conditions of leaching was used to study the recovery efficiency of Ga through the ion-exchange method. The results indicated that the average efficiencies of Ga adsorption and desorption were 59.84% and 95.32%, respectively. The desorption solution contained 97.54 mg/L, compared to the initial leaching solution and the sixth re-circulation solution. Enrichment coefficients of 24.95 and 4.75 times were obtained respectively.
- (4). Significant efforts would be further devoted to the following studies: a) Further enhancement of Ga concentration in the desorption solution (≥ 0.45 g/L) to meet the requirements of Ga electrolysis (Gladyshev et al., 2015); b) Aluminium extraction (as $AlCl_3$) from leaching solution and ferric recovery (as $FeCl_3$) from the elution solution produced by washing the Fe loaded resin with hot deionized water; c) Reasonable utilization of leached residue.

Acknowledgements

The fund supports are from the National Natural Science Foundation

of China (51664010, 51664009, 51664008 and 51764006) and the Guizhou Provincial Natural Science Foundation of China (2014-2083, 2016-7095). The anonymous referees for helpful comments and suggestion are also appreciated.

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