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Beneficiation of Ga from alunite concentrates by selective acid leaching and alkaline precipitation

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Abstract: In this study beneficiation of Ga from alunite ore was investigated. The effects of the calcination temperature, H₂SO₄ concentration, leaching temperature and liquid-solid ratio on the dissolution characteristic of Ga, K and Al were studied. The results showed that increasing the calcination temperature, H₂SO₄ concentration and leaching temperature can improve the solubility of K and Al. However, higher H₂SO₄ concentration and lower leaching temperature can improve the dissolution of Ga, which was beneficial to recovery of Ga. On the basis of the solubility difference in H₂SO₄, a two-stage process of selective acid leaching and alkali precipitation of Ga was proposed. The concentration of Ga was increased significantly from 54 g/t in alunite ore to 4100 g/t in alkali precipitation product. The major elements of Al and K in alunite were recovered as the alum crystal with a purity of 99.62%.

Keywords: gallium, selective leaching, precipitation, alunite concentrate

1. Introduction

Gallium (Ga) is an important component for semiconductors and chips applied in electronic equipment (FONT et al., 2007) such as mobile phones (NASUKAW, 2009), photovoltaic panels, optic-electronic devices (MAHAJAN, 1998) and computers (KIDA et al., 2009). At present, Ga is mainly produced by Bauxite, which was the by-product of Al₂O₃ production by Bayer method. Unfortunately, the concentration of Ga in commercial Bauxite minerals is very small. The largest mineral source of Ga is bauxite which contains 0.003 to 0.008% Ga (HART, 1989). The processes for the recovery of Ga are linked with other metal extraction or refining processes and effluent streams in metal production or power plants. Ga is usually extracted as a by-product in coal fly ash, zinc and aluminum industries (FRENZEL and KETRIS, 2016). With the increasing requirement of Ga in semi-conducting compounds, considerable attention has received in developing a more economic process to recover Ga from secondary sources. The alunite, a complex sulphate, is an important resource of Ga. Due to the similar chemical property of Ga and Al, the alunite contains 0.002 to 0.006% Ga (ZHOU and CHEN, 2008; ZHAI and LV, 2010). In China, the alunite reserve is 300 million ton. The comprehensive utilization technologies for alunite are classified into the acid method (ÖZDEMİR and ÇETİSLİ, 2005), the alkaline method (LUO et al, 2017) and the combination of acid-alkali method (WILIAM et al., 1938; NAZAROV et al., 2001). The alunite is widely used in the manufacturing of aluminium sulfate, potassium alum, alumina, potassium sulfate and sulfuric acid. Alumina can be obtained from alunite with sulfuric acid by following method. Firstly, the alunite is roasted at about 900 °C. The aluminium sulfate in the structure is decomposed to sulfur trioxide and alumina. In the calcination residues, potassium sulfate is the only soluble component which can be extracted by hot water leaching, and the

insoluble residue contains alumina and silica. Aluminium sulfate is extraction from the insoluble residue by leaching with sulfuric acid. Alumina is also obtained from the aluminium sulfate by calcination (ZHAO et al, 2015). The potassium sulfate can be obtained from alunite by roasting-water leaching-crystallization process (WANG, 2014). Ruan et al (RUAN et al., 2010) used pressurized alkali leaching process to recover alumina and potassium sulfate from alunite. Kuang (KUANG, 2016) proposed pressurized acid leaching process for the production of potassium alum and aluminum hydroxide products.

Although alunite has been considered as an alternative source of alumina and potassium, recovering Ga from the alunite during the extraction process are rarely studied (LIANG and WANG, 1999; HUANG et al., 2014). Therefore, a new method of selective leaching of alunite was investigated to recover gallium in the acid process. The effects of calcination temperature, leaching temperature, H₂SO₄ concentration, and solid-liquid ratio were investigated. The optimal parameters were determined. Finally, a hydrometallurgical process to recover efficiently gallium from alunite was proposed.

2. Materials and methods

2.1. Material

The alunite concentrate with an average particle size of 44 μm was obtained by flotation of copper tailings from Zijin Mountain in China's Fujian province. The chemical composition of the alunite concentrate is shown in Table 1. The concentration of Ga was 54 g/t. The content of Al and K (calculated in oxide form) are 30.72% and 7.16%, respectively. An analytical grade sulfuric acid (H₂SO₄, 98 wt.%) with a density of 1.84 g/mL was used in this study. The sodium hydroxide (NaOH) is also of analytical grade at 96%. Deionized water was used to prepare NaOH and H₂SO₄ solution.

Table 1. Multielement analysis results of alunite concentrate (wt%)

Ga (g/t)	SO ₃ ²⁻	Al ₂ O ₃	K ₂ O	S ²⁻	S ⁰	S ⁶⁺	S _(Total)	SiO ₂	Fe ₂ O ₃
54.2	27.02	30.72	7.16	1.03	0.01	10.68	11.72	19.6	0.89
Na ₂ O	TiO ₂	Cu	Pb	MgO	Zn	As	--	--	--
0.42	0.09	0.051	0.012	0.005	0.004	0.005	--	--	--

2.2. Methods

2.2.1 Calcination of alunite

In order to enhance the solubility of alunite in H₂SO₄ solution, dehydration of alunite was conducted by calcination. A 100 g of the alunite sample was placed in corundum crucible and calcined in a muffle furnace (KSS-1600, China) at temperatures from 300 to 650 °C in air atmosphere. After calcination for 2 h, the samples were taken out to cool down in air at room temperature. The calcined residues were characterized by X-ray diffraction (XRD, X'Pert PRO MPD, The Netherlands), Scanning electron microscopy (SEM, JSM-6700F, Japan) combined with energy dispersive spectrometry (EDS, Noran Systemsix, USA).

2.2.2 Selective leaching and beneficiation of Ga

In order to recover the valuable elements of Ga, a selective leaching process was carried out. At the first stage, a 20 g of the alunite sample after dehydration was leached in a 500 ml flask by dilute H₂SO₄ solution to remove K and Al in alunite. The leaching time was 2 h. The effects of the dehydration temperature, H₂SO₄ concentration, leaching temperature, and liquid-solid ratio (L/g) were investigated. The element Ga was enriched in the leaching residues, while K and Al were dissolved in acid solution. After solid-liquid separation by filter, the extraction of Ga, Al and K were determined by the metal concentrations in the leaching solution analyzed by an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-OES, SEIKO SPS 1500VR). The leaching solution was used for crystallizing the alum (KAl(SO₄)₂·12H₂O). At the second stage, a 20 g of the residues obtained by the first stage were leached in a 500 ml flask by concentrated H₂SO₄ solution. The leaching temperature

was 70 °C. The leaching time was 2h. The liquid-solid ratio was 5:1 (L/g). The effect of H₂SO₄ concentration was investigated. The element Ga was dissolved in acid solution, and the extraction of Ga was determined by ICP-OES analysis. After that, NaOH was added into the lixivium to precipitate Ga. The temperature was 80 °C with pH of 2.4-2.6. Finally, the precipitate was obtained. General flow sheet of this new process to treat alunite ores is shown in Fig. 1.

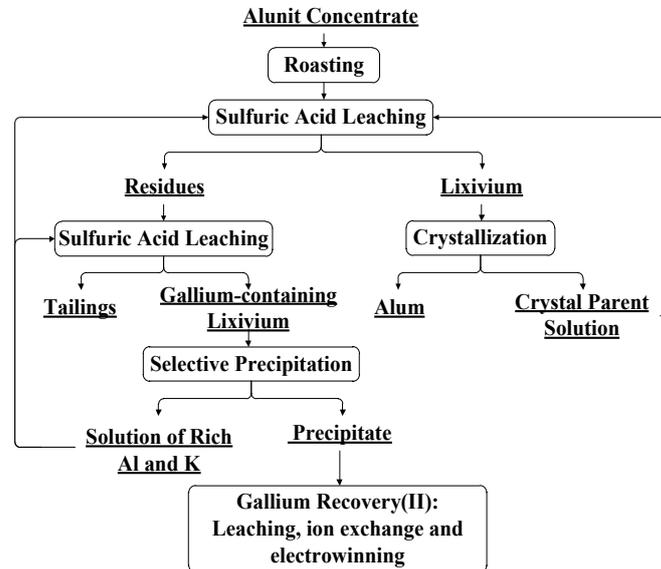


Fig.1 The flow sheet to enrich Ga from alunite by selective leaching and precipitation

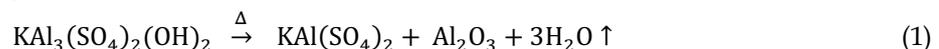
3. Results and discussion

3.1. Dissolution characteristic of Ga, K and Al in H₂SO₄

The purpose of the first stage leaching was to dissolve K and Al in H₂SO₄ solution, and to enrich Ga in the residues. It was necessary to investigate the effects of the calcination temperature, H₂SO₄ concentration, leaching temperature and liquid-solid ratio on the dissolution characteristic of Ga, K and Al.

3.1.1. Effect of the calcination temperature

In order to determine the characteristic of thermal decomposition, the alunite samples were analyzed by DSC-TGA (TGA/DSC 1, Switzerland), and the calcined products were analyzed by XRD. By comparing the phase compositions of calcined products at different temperatures, the calcination temperature before acid leaching was confirmed. According to the DSC-TGA results of alunite concentrate (Fig. 2), the temperature of endothermic reaction of alunite concentrate was from 520 to 630 °C, indicating the dehydration reaction of alunite (KUCUK and GULABOGLU, 2002; KUCUK and YILDIZ, 2006). X-ray diffraction analysis of alunite concentrate after calcination at different temperatures is shown in Fig. 3. At temperatures below 400 °C, the main phases of the calcined products were SiO₂ and KAl₃(SO₄)₂(OH)₆, indicating that the dehydration of alunite did not occur. However, At temperatures above 400 °C, most peaks of KAl₃(SO₄)₂(OH)₆ disappeared, while the phase of KAl(SO₄)₂ was clearly identified. It was indicated that KAl₃(SO₄)₂(OH)₆ decomposed to form KAl(SO₄)₂ due to the dehydration reaction (LI et al., 2014):



Previous studies suggested that KAl₃(SO₄)₂(OH)₆ was insoluble in acid or alkali unless dehydration (GUO, 1991; KUCUK and GULABOGLU, 2002; KUCUK and YILDIZ, 2006). The valuable elements in alunite were difficult to be recovered by direct leaching. However, the solubility of KAl(SO₄)₂ in H₂SO₄ was better than that of KAl₃(SO₄)₂(OH)₆. Therefore, translation of alunite into KAl(SO₄)₂ by dehydration was favorable to remove Al and K and thus enrich Ga by leaching.

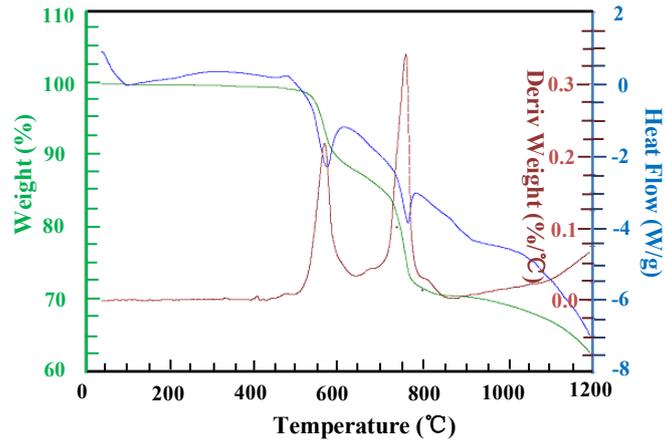


Fig. 2 DSC-TGA curves of the alunite sample

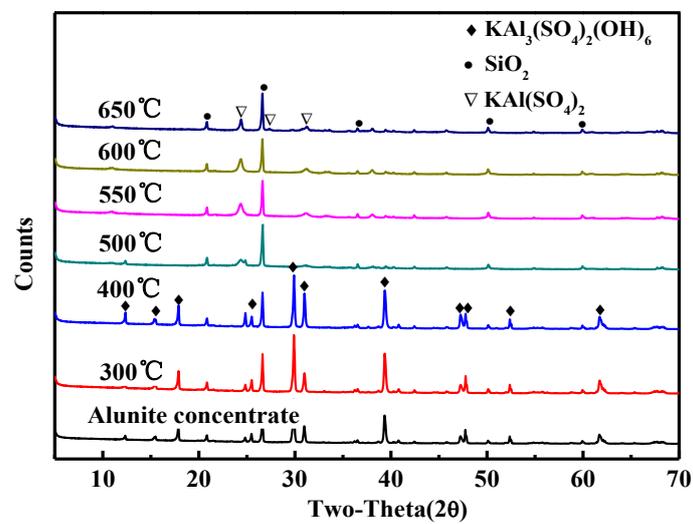
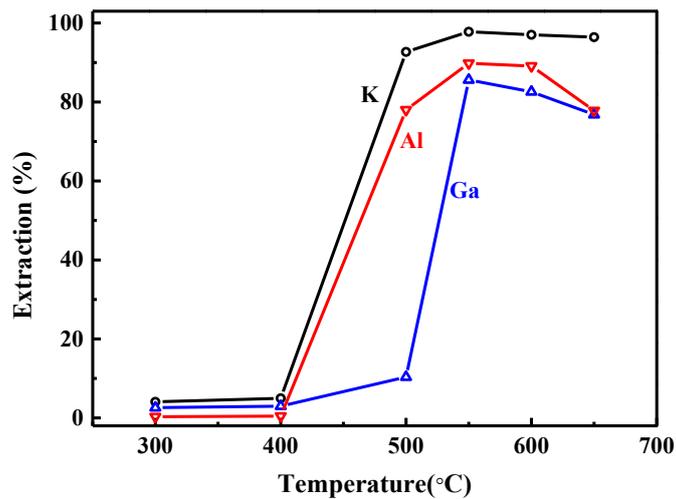


Fig.3 X-ray diffraction patterns of alunite after calcination at different temperatures

Fig. 4 The effect of the calcination temperature on the extraction of Ga, K and Al (leaching at 80 °C for 2 h, 100 g/L H₂SO₄, liquid-solid ratio 6:1)

The purpose of the calcination treatment was to improve the solubility of Ga, K and Al in alunite. To investigate the effect of calcination temperature on the extraction, the calcined products were

leached at 80 °C for 2 h. The concentration of H₂SO₄ was 100 g/L, and the liquid-solid ratio was 6:1. As shown in Fig.4, the extraction of Ga, K and Al were lower than 10%, when the calcination temperature of alunite was below 400 °C. It was because that the dehydration of alunite was incomplete when the alunite ore was calcined below 500 °C, and the crystal water still existed in alunite. The Al-O-S framework in alunite was not disintegrated completely (ZHONG et al, 2017), leading to a lower solubility in H₂SO₄. However, the extraction ratios of Ga, K and Al were increased significantly up to 80% when the alunite ore was calcined at 550 °C. According to the thermal analysis in Fig. 2, the dehydration of alunite had completed when the alunite ore was calcined at 550-600 °C. The crystal water was removed, and thus the solubility of the elements K and Al in H₂SO₄ increased (KUCUK and GULABOGLU, 2002; KUCUK and YILDIZ, 2006). In addition, when the dehydration temperature was above 600 °C, the extraction became to decrease. Aluminium sulfate KAl(SO₄)₂ was further decomposed into γ -alumina, and then γ -alumina began to transform into α -alumina at about 700 °C (GUO, 1991; KUCUK and GULABOGLU, 2002; KUCUK and YILDIZ, 2006). As a result, in order to obtain a higher extraction of K and Al, a dehydration temperature 500-600 °C was suggested.

3.1.2. Effect of H₂SO₄ concentration

The calcined product of alunite at 600 °C was used to acid leaching, and the element compositions are listed in Table 2. The effect of H₂SO₄ concentration on the extraction of Ga, K and Al was studied in the range from 30 to 100 g/L at 80 °C for 2 h. the liquid-solid ratio was 7:1. As shown in Fig. 5, the extraction of Al and K increase significantly from 5.21% to 82.23% and from 17.32% to 93.06%, respectively, when H₂SO₄ concentration increased from 30 g/L to 70 g/L. On the other hand, the extraction of Ga was close to 0 when the H₂SO₄ concentration increased from 30 to 70 g/L. The Ga content in leaching residues increased significantly from 51.2 g/t to 169.5 g/t with the increase of H₂SO₄ concentration from 30 g/L to 70 g/L. However, when H₂SO₄ concentration increased from 70 to 100 g/L, the extraction of Ga increased remarkably from 0.63% to 82%. This result showed that lower acid concentration was unfavorable to dissolution of Ga. The leaching of Ga needed higher acid concentration. In acid solution, Al³⁺ and K⁺ were soluble in H₂SO₄ and did not hydrolyze. As H₂SO₄ concentration increased, the activity of H⁺ increased, and thus the dissolution of Al³⁺ and K⁺ was improved. However, Ga³⁺ was very easy to hydrolysis. The precipitation of Ga₂O₃ and Ga(OH)₃ was sensitive to pH. The beginning pH for Ga precipitation is 2.1-2.2 at 80 °C, according to the E-pH diagram of Ga-H₂O system (POURBAIX, 1974). When H₂SO₄ concentration decreased, the pH of solution increased. As a result, the precipitation of Ga₂O₃ or Ga(OH)₃ generated, and the dissolution of Ga³⁺ was inhibited. Therefore, K and Al were removed from alunite by leaching with dilute H₂SO₄ (<70g/L), and Ga was enriched in the residues at the first stage leaching. Then the element Ga in the residues was leached by concentrated H₂SO₄ (>70g/L) at the second stage leaching.

Table 2. Multielement analysis results of the leaching residues at the first stage leaching (wt%)

Ga (g/t)	SO ₃	Al ₂ O ₃	K ₂ O	SiO ₂	Fe ₂ O ₃	Cu	Pb	MgO	Zn	Na ₂ O
62.5	30.18	34.34	8.63	22.44	1.46	0.068	0.14	0.021	0.003	0.52

3.1.3. Effect of leaching temperature

The effect of leaching temperature on the extraction of Ga, K and Al was studied with a H₂SO₄ concentration of 70 g/L for 2 h. The liquid-solid ratio was 7:1. As shown in Fig. 6, the extraction of K and Al increased from 16.24 to 86.92% and from 20.91 to 68.16%, respectively, when the temperature increased from 30 to 90 °C. For Ga, the extraction increased from 17.61% at 20 °C to 68.58% at 70 °C. However, the extraction of Ga decreased to 1.75% at temperatures above 70 °C. The Ga content in the leaching residues maintained at about 55 g/t in the temperature range from 20 to 70 °C, but increased significantly up to 156 g/t at 80 °C. It was indicated that higher temperature had an obstructive effect on dissolution of Ga. According to the E-pH diagram of Ga-H₂O system (POURBAIX, 1974), as temperature increased, the beginning pH for Ga precipitation decreased from 2.3-2.4 at 60 °C to 2.1-2.2 at 80 °C. As a result, the precipitation of Ga₂O₃ or Ga(OH)₃ was easier to generate at lower temperature. In order to obtain a higher recovery of Ga, lower temperatures were required.

Therefore, K and Al were removed from alunite by leaching at higher temperatures ($>70\text{ }^{\circ}\text{C}$), and thus Ga was enriched in the residues at the first stage leaching. Then the element Ga in the residues was leached at lower temperatures ($<70\text{ }^{\circ}\text{C}$) at the second stage leaching.

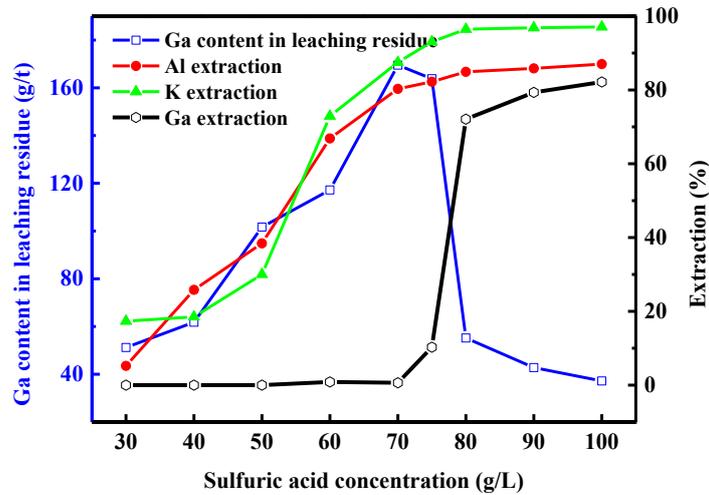


Fig. 5 The effect of H_2SO_4 concentration on the extraction of Ga, K and Al (leaching at $80\text{ }^{\circ}\text{C}$ for 2 h, liquid-solid ratio 7:1)

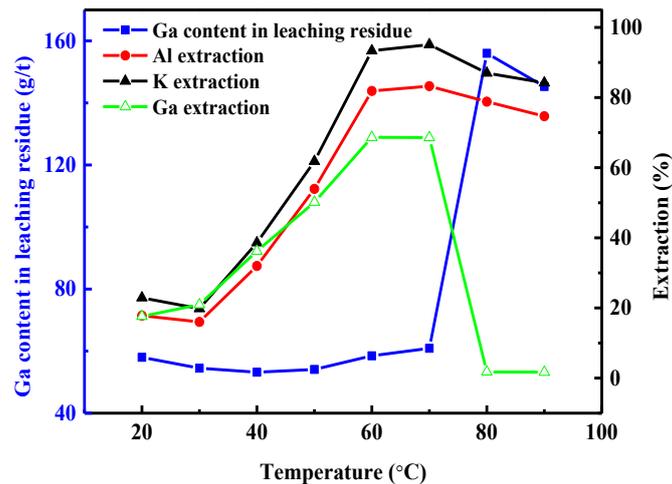


Fig. 6 The effect of leaching temperature on the extraction of Ga, K and Al (leaching in $70\text{ g/L H}_2\text{SO}_4$ for 2 h, liquid-solid ratio 7:1)

3.1. 4. Effect of liquid-solid ratio

The effect of liquid-solid ratio on the extraction of Ga, K and Al was studied with the liquid-solid ratio from 4:1 to 8:1 using 2 h leaching time. As discussed in 3.1.2 and 3.1.3, a higher recovery of Ga was obtained with H_2SO_4 concentration of 70 g/L and leaching temperature of $80\text{ }^{\circ}\text{C}$. Thus, the same H_2SO_4 concentration and leaching temperature were selected in this section. As shown in Fig.7, the leaching efficient is not proportional to the liquid-solid ratio. There appears to be a maximum in extraction efficiency of aluminum and potassium near the L/S ratio of 5. On the contrast, the maximum of Ga extraction appears near the L/S ratio of 6 which is the minimum of the leaching rate of aluminum and potassium. From the point of enrichment Ga in the leaching residues, the L/S ratio of 5 is the best, which the Ga content in leaching residues is 162.8 g/t .

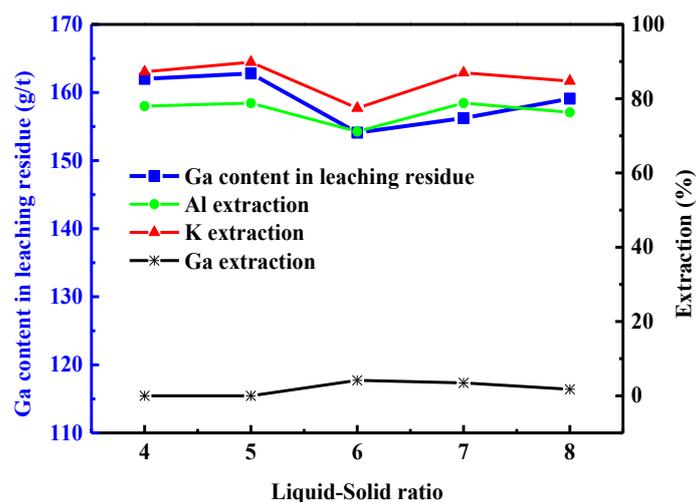


Fig. 7 The effect of liquid-solid ratio on the extraction of Ga, K and Al (leaching at 80 °C for 2 h, 70 g/L H₂SO₄)

3.2. Recovery of Ga from Ga-containing residues

As discussed in Section 3.1, the extraction of Ga was very low (1.75%), while the extraction of K and Al were over 80% when H₂SO₄ concentration was 70 g/L at 80 °C. The Ga content was 156.2 g/t in the leaching residues after filtration. Therefore, K and Al were removed at the first stage leaching, and Ga was enriched in the residues. In this section, recovery of Ga from the residues was investigated. The element compositions of the leaching residues at the first stage leaching are listed in Table 3.

Table 3. Multielement analysis results of the leaching residues at the first stage leaching (wt%)

Ga (g/t)	SO ₃	Al ₂ O ₃	K ₂ O	SiO ₂	Fe ₂ O ₃	Cu	Pb	MgO	Zn	As
156.2	14.73	20.08	4.19	43.52	3.04	0.074	0.27	0.006	0.004	0.005

3.2.1. Leaching by H₂SO₄

As discussed in Section 3.1, the dissolution of Ga was improved at temperatures below 70° C. Therefore, to recover Ga, the residues was leached by H₂SO₄ at 70 °C for 2h. The liquid-solid ratio was 5:1. Fig.8 shows the effect of H₂SO₄ concentration on the extraction. It was found that the extraction of Ga increased with increasing H₂SO₄ concentration. The extraction of Ga increased from 55% at 50 g/L to 85% at 80 g/L. However, when the H₂SO₄ concentration was higher than 80 g/L, the extraction of Ga decreased a little. High H₂SO₄ concentration may result in more consumption of acid and production cost. Therefore, in order to obtain a higher extraction of Ga, a H₂SO₄ concentration of 80 g/L was suggested.

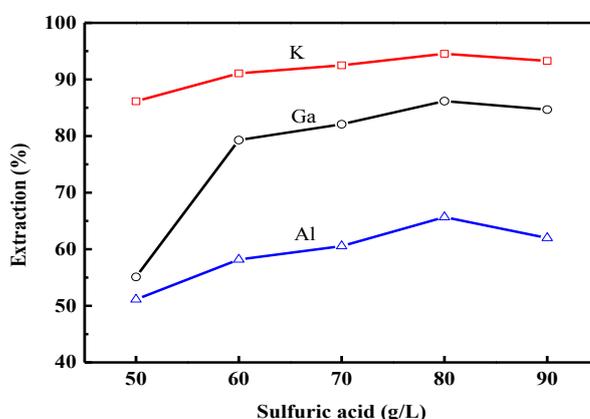


Fig. 8 The effect of H₂SO₄ concentration on the extraction of Ga from residues (leaching at 70° C for 2 h, liquid-solid ratio 5:1)

3.2.2. Precipitation of Ga by NaOH

After leaching and filtration, the element Ga was enriched in the lixivium. Then Ga precipitated from Ga-containing lixivium by adding NaOH at 80 °C with pH of 2.4-2.6 for 2 h. The precipitation reaction was as follows:



Table 4 shows the element composition of Ga-containing lixivium before and after precipitation. It was found that the concentrations of Ga in lixivium, before and after precipitation, were 25.6 mg/L and 0.36 mg/L, respectively. The recovery of Ga was about 98.6%. Because Al also was dissolved in H_2SO_4 , a few of Al was coprecipitated by NaOH. The recovery of Al was about 6.4%. Table 5 shows the chemical composition of the precipitate. The Ga content reached 4100 g/t. Therefore, most of the Ga was enriched in the precipitate.

Table 4 The element analysis of lixivium before and after precipitation (mg/L)

	Ga	Al	K	Fe	SO_4^{2-}
Ga-containing lixivium	25.6	18900	4040	680	108700
After precipitation	0.36	17680	4010	670	95360

Table 5 The element analysis of precipitate (%)

Element	Ga(g/t)	Al_2O_3	K_2O	Na_2O	Fe_2O_3	SO_3
Content	4100	28.23	7.05	1.64	1.08	33.25

3.3. Phase transformation during selective leaching

3.3.1. Characterization of the acid leaching residues

The XRD patterns of the acid leaching residues are shown in Fig. 9. It was observed that the main phases existed in the acid leaching residues was SiO_2 . The phase compositions of residues at the first stage leaching were nearly the same with those at the second stage leaching. Compared with the alunite calcined at 550 °C, the peaks of aluminium sulfate $\text{KAl}(\text{SO}_4)_2$ disappeared after leaching, however a small number of peaks of $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ still existed. This result suggested that the soluble K and Al salt in the calcined products was $\text{KAl}(\text{SO}_4)_2$, which was dissolved in H_2SO_4 after leaching. This result was in accord with that of the extraction (Figs. 4-6). After leaching and filtration, the lixivium was crystallized. In the crystal substance (Fig. 10), the main compositions were alum $\text{KAl}(\text{SO}_4)_2$. Element analysis showed that the alum content in the crystal substance was 99.62 wt% (Table 6). Therefore, the elements of Al and K in alunite were recovered as $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

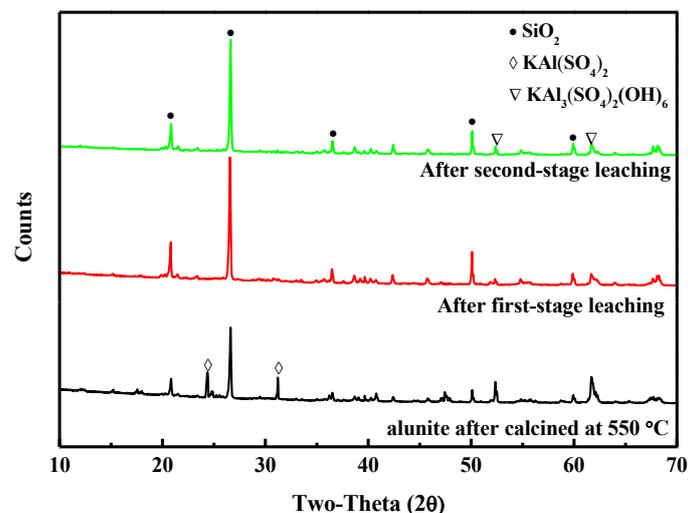


Fig. 9 X-ray diffraction patterns of the acid leaching residues

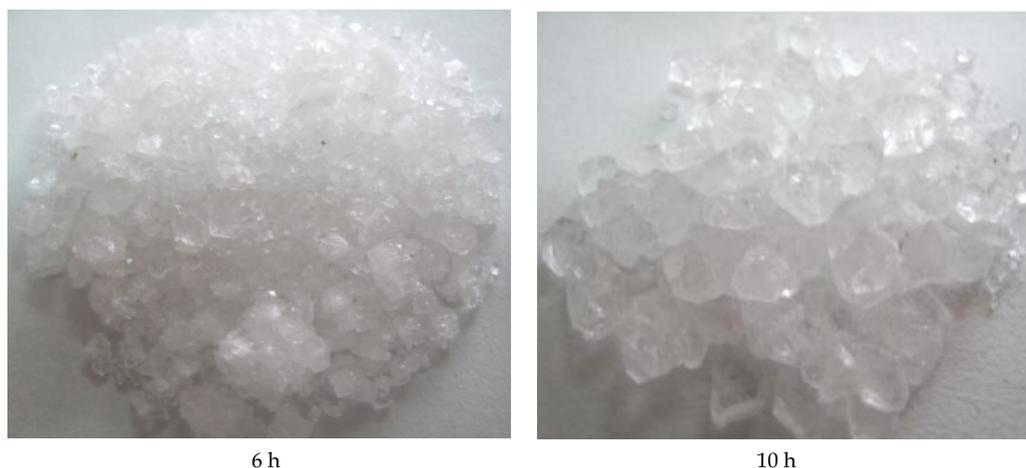


Fig. 10 The images of the alum products crystallized for 6 h and 10 h

Table 6 The element analysis of alum product (%)

KAl(SO ₄) ₂ ·12H ₂ O	As	Pb	Fe	water insoluble	water
99.62	<0.01	<0.01	<0.02	0.16	0.12

3.3.2. Characterization of Precipitate

The mineralogical compositions of the precipitates were identified by XRD analysis. As shown in Fig.11, the main phases of precipitate were $2\text{Al}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 8\text{H}_2\text{O}$ and $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$. It was possible that the Ga content of the precipitate was too low to be detected, or the element Ga may exist in the lattice sites in $2\text{Al}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 8\text{H}_2\text{O}$ or $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$. In order to remove the crystal water and obtain complete crystal, the precipitates were calcined at 600 °C for 2 h. XRD analysis (Fig. 12) showed that the element Ga was present in the form of $\text{KGa}(\text{SO}_4)_2$. It was attributed to the substitution of Al by Ga in $\text{KAl}(\text{SO}_4)_2$ due to the similar property. SEM images and EDS analysis (Fig. 13) showed that Ga was uniform distribution in the precipitate and was not enriched in a specific phase. Therefore, it was difficult to obtain Ga-compounds with a high purity by selective leaching and precipitation, but Ga can be enriched significantly. Comparing with the initial Ga content in alunite ore (54 g/t), the concentration in the precipitate was 4100 g/t. Ga was concentrated by 76 times. The precipitate would be further treated by leaching, ion exchange and electrowinning to produce the metal Ga.

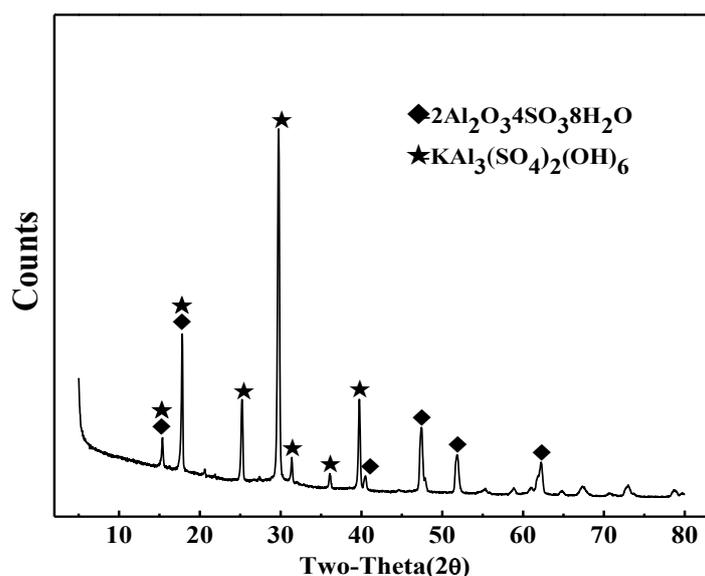


Fig. 11 X-ray diffraction patterns of the precipitate

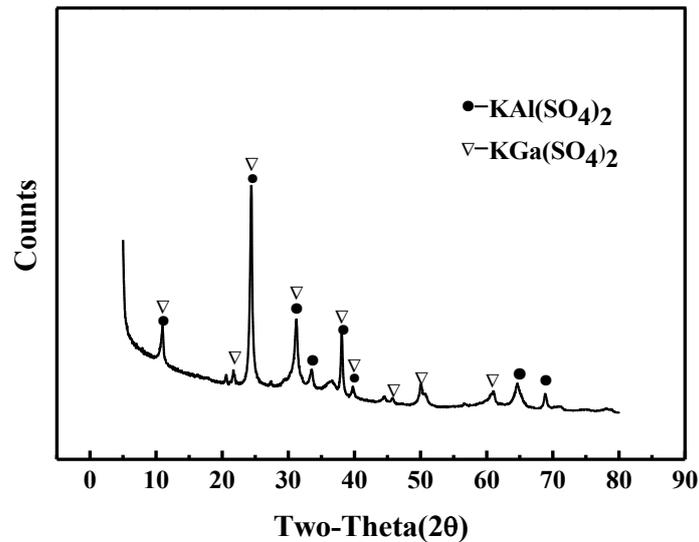


Fig. 12 X-ray diffraction patterns of precipitate after calcination

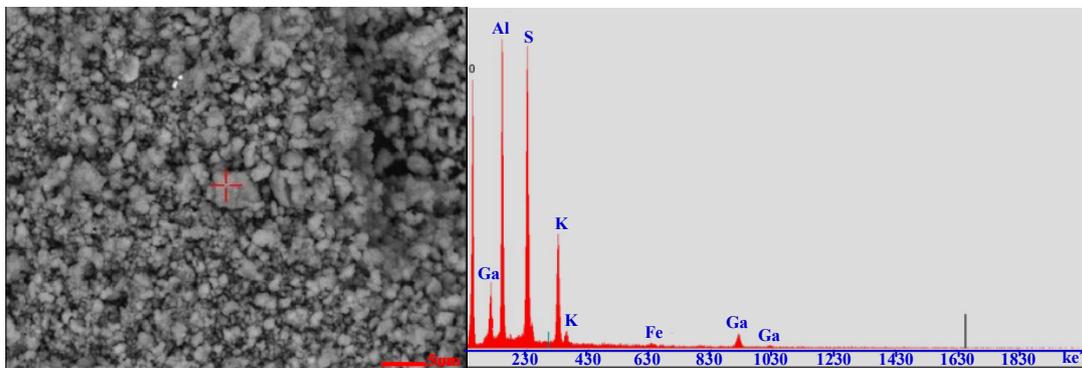


Fig. 13 SEM image and EDS analysis of precipitate

4. Conclusions

In this study, a new process for Ga recovery was proposed based on selective acid leaching and alkali precipitation. Before leaching the alunite was calcined at 550-600 °C to increase the solubility of Ga, K and Al. At the first stage leaching, the calcined products were leached in dilute H₂SO₄ solution <70 g/L using temperatures >70 °C to remove K and Al. The extraction of K, Al, and Ga were 82.23%, 93.06% and 0.63%, respectively. The element Ga was enriched in the leaching residues. After filtration, the lixivium was crystallized to generate alum (KAl(SO₄)₂·12H₂O) with the purity of 99.62%. At the second stage, the residues at the first stage were leached by concentrated H₂SO₄ solution >70 g/L at temperatures <70 °C. The extraction of Ga was 86.17%. Then NaOH was added into the lixivium to precipitate Ga with pH of 2.4-2.6. Finally, the precipitate was obtained with the Ga concentration of 4100g/t.

Acknowledgments

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