

Article

Investigation on the Effect of Roasting and Leaching Parameters on Recovery of Gallium from Solid Waste Coal Fly Ash

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Abstract: Coal fly ash (CFA) provides important resources of gallium, which is regarded as an irreplaceable material in many technologies. A prospective roasting reagent assisted acid leaching process was proposed for the purpose of extracting gallium. The extraction efficiency of gallium by NaF (sodium fluoride) roasting followed by HNO₃ (nitric acid) leaching process was demonstrated. The effect of roasting temperature, roasting time, the NaF-CFA mass ratio, acid leaching temperature, acid leaching time, and acid concentration were investigated. The results revealed that under optimal conditions (roasting temperature of 800 °C, roasting time of 10 min, acid leaching in 2 mol/L HNO₃ for 1 h, and the NaF-CFA mass ratio of 0.75:1), 94% of gallium was extracted. Compared to previous studies, the process is a cost-effective method which can greatly shorten reaction time. It can reduce environmental pollution as it requires fewer acid reagents with low concentration and additives. It is expected to provide a method for the extraction of gallium from CFA.

Keywords: gallium; coal fly ash; solid waste; NaF; recovery; alkali roasting; acid leaching

1. Introduction

Gallium has been used in a large variety of solar technologies, telecommunications, and aerospace due to its lower melting point, higher boiling point, and the semiconducting properties of its compounds [1,2]. Because of the unique properties of gallium, it is irreplaceable compared with any other materials or metals in current technologies. However, gallium is a trace element and there are few Ga-bearing host minerals [3]. It mainly is extracted from bauxite or coal and is a by-product of zinc production [4]. Based on the fact that bauxite supply falls short of demand, recovery of this strategic element from coal and coal fly ash (CFA) has recently attracted attention [5].

Coal is the world's most abundant fossil fuel reserve. In fact, coal has widely been utilized as an energy resource for electricity generation and steel production in China [6]. Power plants and steel mills of the world produce about 780 million tons of CFA each year. Remarkably, coal contains many precious elements. In addition, the content of elements in CFA is much higher than in coal because these elements are retained in CFA during burning. The secondary utilization of CFA can reduce its detrimental effect on the environment including the amount of land required for its disposal. Moreover, the remaining waste may enable high economic benefit from the recovery of various elements [7]. Many coal fields with significant quantities of gallium have been discovered in the northwest of China. Compared with other coal fields across the world, coal from Inner Mongolia is particularly rich in gallium [8]. Therefore, CFA generated in Inner Mongolia was found to be an especially important source of gallium due to the relatively high content of gallium.

Over the past few decades extraction of gallium from coal and CFA has usually followed three main paths: Direct acid leaching [9,10] or alkali roasting followed by acid leaching [11–13] or alkali

leaching [14]. However, these methods have a number of disadvantages. The direct acid leaching process is an expensive and time-consuming method carried out in HCl (hydrochloric acid) or H₂SO₄ (sulphuric acid) for at least 24 h. It also requires a high ratio of liquid to solid, requiring more downstream treatment and greater consumption of acid. Na₂CO₃ (sodium carbonate) sintering followed by acid leaching is a relatively complex method with many steps. After the alkali sintering process, residues are immersed in hot water and then leached with high concentration HCl. This method, however, results in low gallium extractions. Alkali leaching can be conducted at a lower temperature, inevitably leading to longer time for extraction. It also does not leach much of the gallium.

In this article we describe a systematic study of the extraction of gallium from CFA collected from a power plant in Inner Mongolia, China was conducted using NaF (sodium fluoride) roasting followed by HNO₃ (nitric acid) leaching. The present work aims to develop an effective and low-cost process to extract gallium from CFA. This research compared the effect of alkali roasting followed by acid leaching and direct acid leaching methods to highlight the importance of the roasting stage. The effect of roasting time, roasting temperature, the NaF-CFA mass ratio, leaching temperature, acid concentration, and leaching time were also investigated. Compared with the previous study using a large amount of sintering additives and acid with high concentration, the process proposed in this paper requires fewer additives and acid with low concentration. It can reduce environmental pollution and cost.

2. Materials and Methods

2.1. Materials

The CFA sample used in this work was received from a power plant in Inner Mongolia, China. HNO₃ (65–68%) and HCl (36–38%) used in this study were analytical grade. All reagents were purchased from a Beijing chemical plant. Milli-Q water (18.2 MΩ·cm) from a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout for cleaning purposes, dilution of samples, and to generate reagents. X-ray fluorescence (XRF) analysis was performed using an AXIOS max Advanced XRF Spectrometer (PANalytical B. V, Almelo, The Netherlands) coupled with a 4.0 kW Rh X-ray tube and 8 analyzing crystals. The maximum voltage and current were 60 kV and 80 mA respectively. The phase analysis was carried out by X-ray diffraction (XRD, D8 Advance, Bruker, MA, USA). ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry, Optima 8000, PerkinElmer, Waltham, MA, USA) was used for the determination of gallium.

2.2. Methods

2.2.1. Alkali Roasting before Acid Leaching

CFA (1 g) and the additive, NaF, NaOH (sodium hydroxide), or Na₂CO₃ was uniformly mixed and then placed in a muffle furnace for heating. The temperature and reaction time for roasting varied from 250 °C to 900 °C and from 3 to 60 min, respectively. After the roasting stage, the residues were naturally cooled to room temperature and then subjected to grinding.

Acid leaching of the roasted product was conducted by heating on a hot plate using HNO₃ with varied concentrations at temperatures from 25 °C to 140 °C. After the leaching stage, the residues were filtered and the filtrate was diluted to 50 mL for ICP-OES analysis. The extraction of gallium in this study was the ratio of the content in the leach liquor to gallium concentration in the CFA—as determined using a published method [15].

2.2.2. Acid Leaching

For direct acid leaching, 1 g CFA was transferred into a PTFE beaker, then either HNO₃ (12 mL) or HCl (12 mL) was added. The mixture was heated on a hot plate at 120 °C for about 5 h, cooled, and then the residue was filtered and the filtrate diluted to 50 mL.

3. Results

3.1. Sample Characterization

The major chemical constituents in CFA were oxides as determined by XRF (Table 1). The results showed that Al_2O_3 (alumina) was the most abundant component followed by SiO_2 (silicon dioxide). The CFA sample was pretreated according to the previous study and gallium concentration was determined by ICP-OES [15]. The XRD pattern of CFA consisted of mainly glass phases, mullite, quartz, and some hematite (Figure 1).

Table 1. Content of major oxides and gallium and loss on ignition in CFA.

Sample	Al_2O_3 , %	SiO_2 , %	CaO , %	TiO_2 , %	Fe_2O_3 , %	Ga, %	Loss on Ignition, %
CFA	41.73	22.51	2.44	1.79	1.47	0.00671	9.19

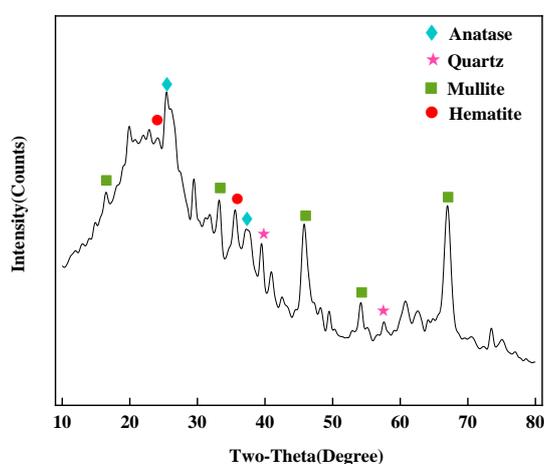


Figure 1. XRD pattern of the original CFA sample.

3.2. Comparison of Acid Leaching and Roasting before Acid Leaching

The comparison experiments between acid leaching using HNO_3 and HCl , and relative to roasting with three chemical additives followed by acid leaching were performed. The results for the extraction of gallium from CFA are given in Figure 2. This indicates that the recoveries from 1:1 NaOH and Na_2CO_3 sintering were low. In comparison Taggart et al. [12] reported that NaOH sintering was the most effective chemical method for extracting rare elements, though it extracted only 46% of gallium in this study. Clearly, the NaOH -based roasting method was not the most suitable to enable dissolution of gallium from CFA. Total gallium extracted by NaF sintering was higher than direct acid leaching methods, with increase from 48 to 62%. In addition, it can be seen from Figure 3 that intensities of the peaks corresponding to the mullite phase are high in acid leaching residues. Due to the fact that gallium is abundant with mullite [3], the acid leaching processes cannot totally extract gallium from CFA and required a relatively longer reaction time. Figure 4 shows that the XRD patterns of roasting residues. Though the characteristic peaks of mullite have appeared, some of the quartz and mullite can be transformed into nepheline, which is easily dissolved in the subsequent acid leaching stage [13].

Though the NaF roasting followed by HNO_3 leaching method extracted only $41.4 \mu\text{g}\cdot\text{g}^{-1}$ gallium, it had the best recovery efficiency. The variation in experimental conditions, as discussed in Sections 3.3 and 3.4, concentrated on improving the extraction.

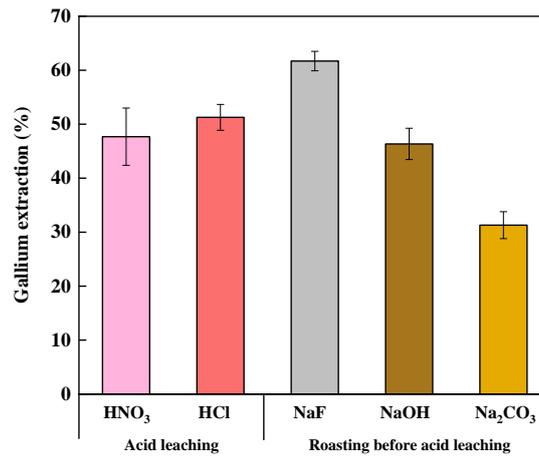


Figure 2. Gallium extraction from CFA through acid leaching or roasting before acid leaching (the reagent-CFA mass ratio of 1:1, roasting temperature of 800 °C, roasting time of 20 min, leaching temperature of 120 °C, leaching time of 1 h, and HNO₃ concentration of 2 mol/L).

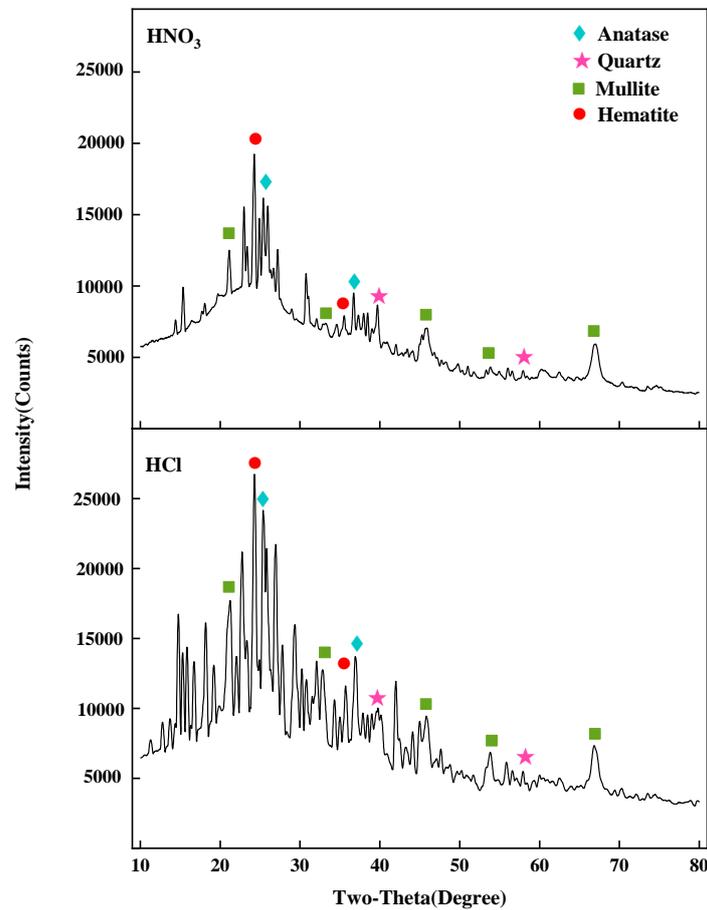


Figure 3. XRD patterns of the acid leaching residues.

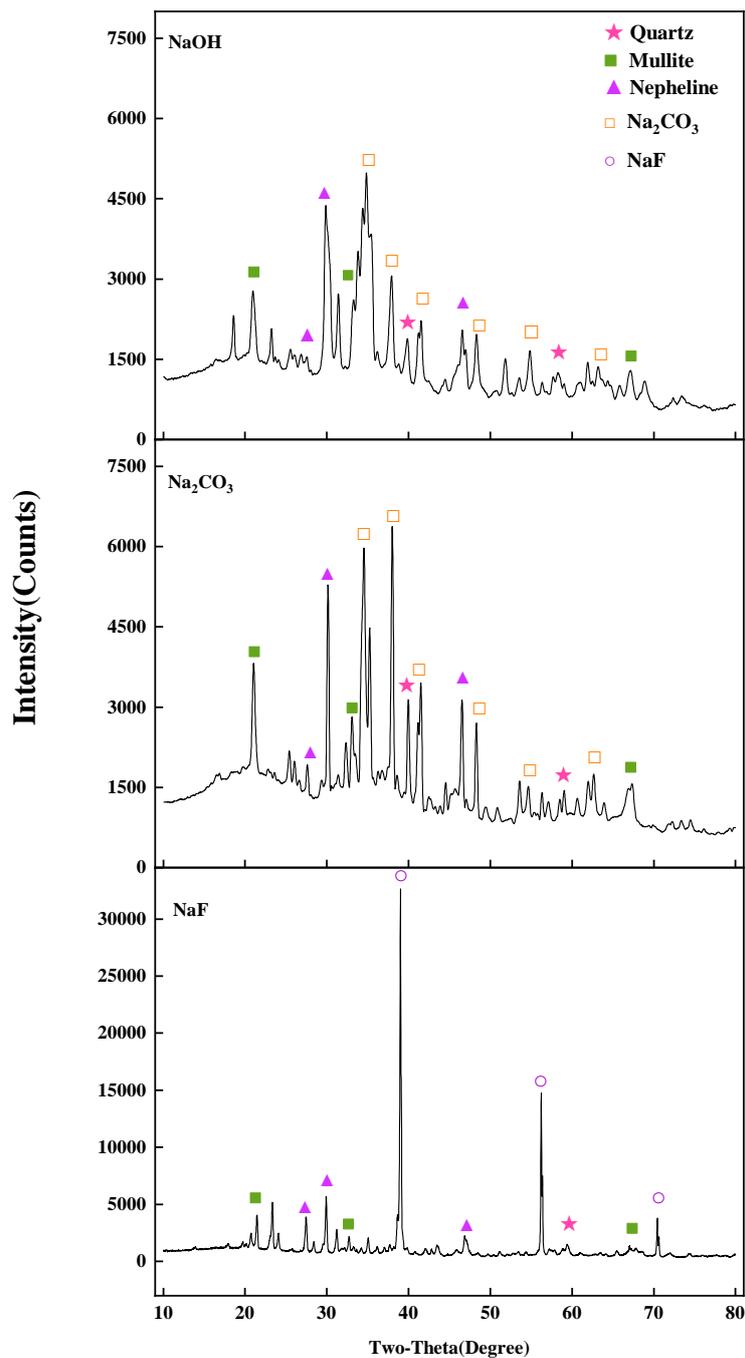


Figure 4. XRD patterns of the alkali roasting residues.

3.3. Influence of Roasting Stage

3.3.1. Effect of Roasting Temperature

The roasting temperature is a key factor to activate the inert materials in CFA, and has a direct influence on the subsequent acid leaching stage. It can be seen from Figure 5 that the extraction changed with temperature. As the roasting temperature increased from 250 °C to 800 °C, the recoveries increased 10%. Increasing temperature speeds up the reaction of CFA and NaF. The extraction rates of gallium after roasting at 700 °C to 800 °C were significantly higher than the rates after roasting at temperature of 250 °C to 600 °C. At a high temperature, part of the quartz and mullite phases can be transformed into nepheline, which can be easily dissolved by the next stage. Caking occurred at a

temperature of 900 °C, resulting in a much lower recovery. Therefore, 800 °C is selected as the optimal roasting temperature.

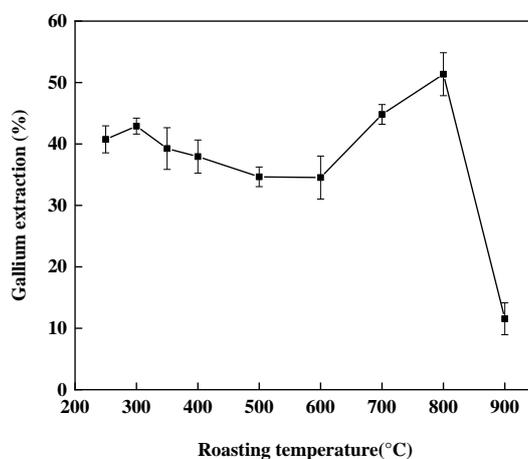


Figure 5. Influence of roasting temperature on gallium extraction (the NaF-CFA mass ratio of 1:1, roasting time of 30 min, leaching temperature of 120 °C, leaching time of 1 h, and HNO₃ concentration of 2 mol/L).

3.3.2. Effect of Roasting Time

Figure 6 shows the influence of roasting time on the percentage of gallium extraction for the purpose of estimating the shortest possible time required for maximum recovery. The gallium extraction rate was nearly 65% for 10 min roasting time. Moreover, the extraction efficiency of gallium decreased with roasting time. The activity of mullite is high, thus it can be preferentially reacted in the roasting process. The quartz also reacts with prolonged time, resulting in silicic acid during the acid leaching stage. The presence of silicic acid will adsorb aluminum ions. It is reported that gallium has similar chemical properties as aluminum, and gallium can replace aluminum into the mineral lattice by isomorphous substitution [16]. The adsorption of gallium ions could in part explain low extraction. Previous studies have used at least 30 min for the roasting stage [12]. From the current data, a roasting time of 10 min is regarded as sufficient.

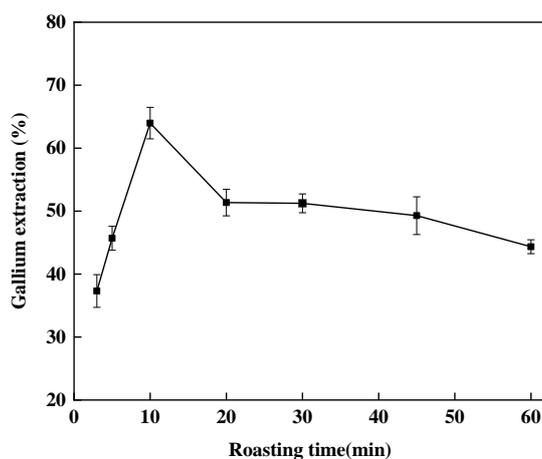


Figure 6. Influence of roasting time on gallium extraction (the NaF-CFA mass ratio of 1:1, roasting temperature of 800 °C, leaching temperature of 120 °C, leaching time of 2 h, and HNO₃ concentration of 2 mol/L).

3.3.3. Effect of the Mass Ratio of NaF to CFA

After optimizing the roasting temperature and roasting time, the maximum extraction of gallium was only about 65%, suggesting that these two conditions may not be the only key factors during the roasting stage. The extractions of gallium were greatly improved by adjusting the quality of the NaF sinter, proving that the mass ratio of NaF/CFA also plays an important role in gallium extraction from CFA (Figure 7). Decreasing the mass ratio of NaF/CFA from 5:1 to 1.25:1 gradually improved the gallium extraction, but the result for 2.5:1 NaF-CFA mass ratio seemed to be an anomaly. Also, the gallium extraction for mass ratios 1.25:1 and 0.75:1 did not differ significantly. Using a NaF-CFA mass ratio of 0.75:1 enabled 77% gallium extraction. Given the cost of using a higher ratio, a 0.75:1 mass ratio was chosen for subsequent experiments to test the extraction conditions. Conventional methods required at least 1 g additives, but this process only requires a smaller amount of NaF, which is less costly.

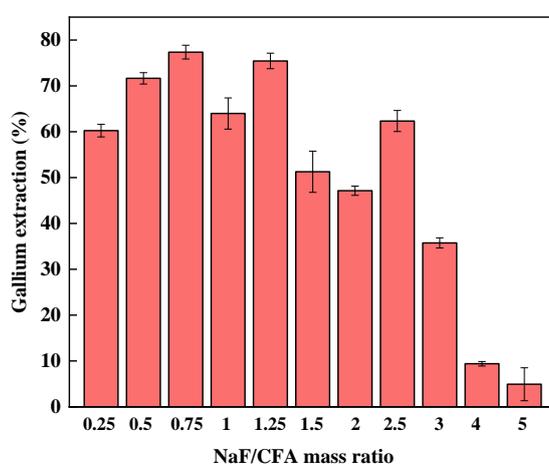


Figure 7. Influence of the NaF/CFA mass ratio on gallium extraction (roasting temperature of 800 °C, roasting time of 10 min, leaching temperature of 120 °C, leaching time of 2 h, and HNO₃ concentration of 2 mol/L).

3.4. Influence of Acid Leaching Stage

3.4.1. Effect of Acid Leaching Temperature

The influence of acid leaching temperature was investigated. As shown in Figure 8, the extraction of gallium was 23% at 25 °C, confirming that it is difficult to dissolve gallium from roasting residue at room temperature. Although roasting converts the aluminosilicates into acid-soluble phases, the HNO₃ is not able to dissolve these phases at a lower temperature on the time frame employed. Therefore, heating is required to increase extraction. It is shown from Figure 8 that the extraction of gallium improved gradually with the increase of leaching temperature. The extraction of gallium was 77% at 120 °C. These results confirm that the extraction of gallium requires the acid leaching process. This is in accordance with the observations of Taggart [12]. In addition, the boiling point of 68% HNO₃ is 120.5 °C. Going beyond 120 °C results in the decomposition or evaporation of HNO₃, which may explain why the extraction of gallium decreased sharply.

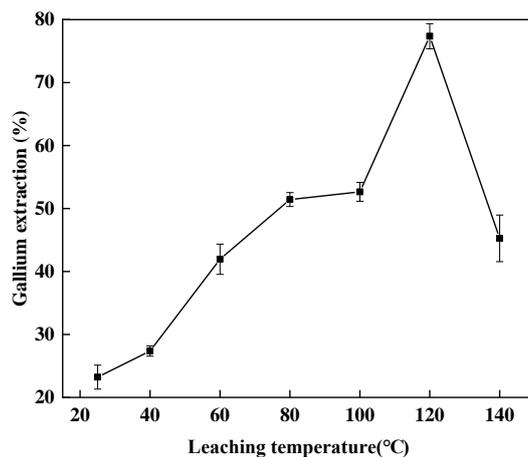


Figure 8. Influence of acid leaching temperature on gallium extraction (the NaF-CFA mass ratio of 0.75:1, roasting temperature of 800 °C, roasting time of 10 min, leaching time of 2 h, and HNO₃ concentration of 2 mol/L).

3.4.2. Effect of Acid Leaching Time and HNO₃ Concentration

Figure 9 revealed the variation in extraction of gallium with the increase in leaching time at various acid concentrations. It is clear that the effect of acid concentration is greater than that of leaching time since the acid concentration varied over a much wider range. When the leaching time was fixed at 1 h, the extraction increased by 34% as the acid concentration increased from 1 mol/L to 2 mol/L, but decreased as the acid concentration increased from 2 mol/L to 5 mol/L. The data indicate that a moderate concentration (2 mol/L) was optimal, such that even when the reaction time was 1 h, 94% of gallium was extracted. In contrast, the recoveries of gallium were the least at the high concentration (5 mol/L) in most situations, indicating that increasing acid concentration was not necessarily conducive to the leaching of gallium. As HNO₃ concentration increased the filtration of the leaching slurry became more difficult. At a high concentration of HNO₃, large amounts of silica gel form. This makes it difficult to filter the leaching slurry. Meanwhile, the loss of gallium increased due to the adsorption by silica gel [14]. A previous study noted that some rare elements were leached in 3 mol/L acid [13]. However, the best acid concentration obtained in this work was 2 mol/L. Thus, this process is considered to be a lower-cost method.

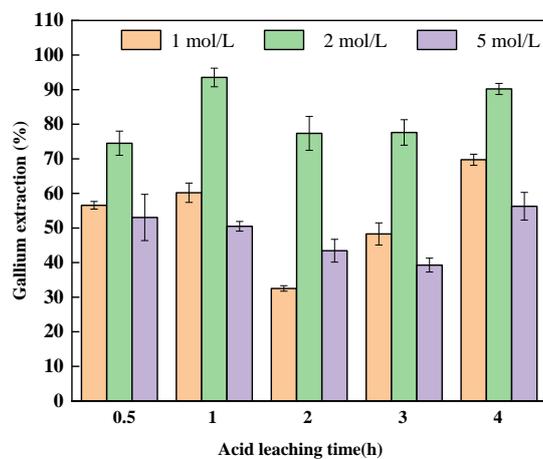


Figure 9. Influence of acid leaching time and acid concentration on gallium extraction (the NaF-CFA mass ratio of 0.75:1, roasting temperature of 800 °C, roasting time of 10 min, leaching temperature of 120 °C, leaching time of 1 h, and HNO₃ concentration of 2 mol/L).

Regardless of the acid concentration used, the results of the leaching time of 1 h and 4 h were higher than other leaching times. The results indicate that 30 min is not enough time to completely leach gallium. The gallium extraction decreased then increased with leaching time from 1h to 4 h. The reduction of gallium extraction may be due to evaporation of HNO₃. As the XRD pattern of the NaF roast residue shows (Figure 4) the characteristic peaks of NaF, this will have reacted with HNO₃ to form HF. HF may have improved gallium recovery at 4 h, as it can destroy the residual glassy phase and/or mullite, thus releasing gallium. Therefore, to save time, an hour of leaching time was deemed adequate for optimal extraction of gallium. Overall, these experiments demonstrate the importance of acid leaching concentration for extraction of gallium from CFA after the roasting stage.

4. Conclusions

A promising method was presented to leach gallium from CFA using NaF roasting followed by HNO₃ leaching. It can be concluded that the gallium extraction can be improved by the NaF roasting process. The XRD analysis of the NaF roasting residue indicates that mullite can be transformed into acid-soluble nepheline. The dosage of NaF and HNO₃ concentration influenced gallium extraction positively. In addition, under optimal parameters (roasting temperature of 800 °C, roasting time of 10 min, acid leaching temperature of 120 °C, leaching time of 1 h, and HNO₃ concentration of 2 mol/L), 94% of gallium was extracted from CFA. Gallium could be leached under more environmentally friendly and at a lower cost when compared to previous method.

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Conflicts of Interest: The authors declare no conflict of interest.

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