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≫ 연구논문 ≪

Recovery of Gallium and Indium from Waste Light Emitting Diodes†

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Abstract

Recovery of gallium and indium from waste light emitting diodes has been emphasized gradually owing to high content of gallium and indium. This study was established the recovery of gallium (Ga^{3+}) and indium (In^{3+}) from waste gallium nitride was contained in waste light-emitting diodes. The procedure was divided into the following steps; characteristic analysis, alkaline roasting, and leaching. In characteristic analysis part, the results were used as a theoretical basis for the acid leaching part, and the chemical composition of waste light emitting diodes is 70.32% Ga, 5.31% Si, 2.27% Al and 2.07% In. Secondly, with reduction of non-metallic components by alkaline roasting, gallium nitride was reacted into sodium gallium oxide, in this section, the optimal condition of alkaline roasting is that the furnace was soaked at 900°C for 3 hours with mixing Na_2CO_3. Next, leaching of waste light emitting diodes was extremely important in the process of recovery of gallium and indium. The result of leaching efficiency was investigated on the optimal condition accounting for the acid agent, concentration of acid, the ratio of liquid and solid, and reaction time. The optimal condition of leaching procedures was carried out for 2.0M of HCl liquid-solid mass ratio of 30 ml/g in 32minutes at 25°C and about 96.88% Ga and 96.61% In were leached.

Key words : gallium nitride, recovery gallium and indium, alkaline roasting, leaching

1. General Introduction

With the expansion of light emitting diode (LED) markets, LED will contribute to a large stream of solid wastes along with abundant waste electric and electronic equipment (WEEE)[1], The demands for multiple LED lighting have rapidly increased during the previous decades[2], and so do the waste light emitting diodes. However, waste dust generated during manufacturing of LED contain significant amounts of gallium and indium, needs suitable treatment and can be an important resource for recovery.

According to the U.S. Geological Survey, the global gallium productions (4N) have raised 50 tons, moreover, the high purity gallium productions (9N) was 180 tons in 2017[3]. There are 70 percent of gallium was applicated in semiconductor including gallium nitride and gallium arsenide. Besides, U.S. Geological Survey also predicts the usage of gallium will increase 30% for the application of 5G in the future. However, gallium is one kind of critical raw materials. The recovery of gallium becomes important when the supply cannot meet the market demand. Also, the demand for indium worldwide exceeds 500 tons per year. Due to the abundant natural resources of indium, there is an urgent need for the development of indium-containing waste and waste liquid recovery technologies. Alternative sources of indium are focused on the disposal of waste materials containing indium, such as ITO waste,

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waste liquid crystal displays, etching waste and waste LEDs.

Gallium nitride (GaN) is a material that can be used in the production of semiconductor power devices as well as RF components and light emitting diodes (LEDs). There are a large amount of research and development in the industry of light emitting diodes[4]. It can be expected that recovery of gallium would be emphasized gradually because of its rarity and value. However, the chemical stability of gallium nitride is stable, and the acid and alkali resistance make gallium difficult to recover[5]. This research aims to conquer this tough problem and to recover gallium with high purity.

Presently, there are several methods have been proposed to recycle gallium and indium from waste light emitting diodes (LEDs). For instance, Cui et al. investigated that the gallium recovery from LEDs waste by oxalic acidic leaching, and they also have compared the difference between organic acid and inorganic[6]. Zhan et al. in 2015 figured out an efficient method to recycle gallium indium from waste LEDs by vacuum metallurgy[7]. To sum up, the treatment process of waste gallium nitride includes the following sequences: pre-treatment, enriching precious metal (concentration), and refining. Particularly, owing to the stable chemically properties of gallium nitride, leaching is the most vital to dominate the whole process[8]. In leaching process, the recovery of gallium and indium was studied by means of beneficiation-metallurgy combination process. Nevertheless, high energy consumption, equipment corrosion and serious environmental pollution limit the recovery efficiency with current methods although there are lots of research on separation of value metals. Besides, with the complex component of light emitting diodes and increasingly environmental protection awareness, it is essential to figure out an economical and eco-friendly approach to pretreat light emitting diodes, especially for the uncomplicated pretreatment[9].

Owing to the stable chemically properties of gallium nitride, the process would concentrate on bonding rupture firstly. In our current study, treatment of gallium nitride through oxidative roasting[10] followed by recovery of gallium through leaching from waste light emitting diodes. In this report would discuss the alkaline roasting with and Na_2CO_3 and query the optimize condition including roasting temperature, roasting time and solubilizer.

The leaching of waste light emitting diodes is an important method in hydrometallurgical processes[12]. Nowadays, there are few relevant reports to deal with waste light emitting diodes, and the leaching agent such as oxalic acid, sulfuric acid[11], nitrous acid, hydrochloric acid, and alkaline fusion-leaching are whole mentioned in this study. Compared with other reports, in this study, the research would focus on finding the most suitable acid concentration, reaction temperature, liquid-solid mass ratio and apposite oxidant added in the solution. The goal of this study was focus on the most suitable leaching condition on waste light emitting diodes.

2. Experiment

2.1. Materials

The sample of gallium nitride used in the experiment was provided from a technology materials company. The original waste light emitting diodes were crushed and were adsorbed by powdered activated carbon. The particle of waste dust was about 900nm shown in the Fig. 1. The content of waste light emitting diodes was shown in Table 1 by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian, Vista-MPX) with dissolving in aqua regia and hydrofluoric acid (3:1:1 HCl: HNO_3: HF ratio) at liquid- solid mass ratio of 1:100, 90°C for 3 hours. Besides, the whole chemical reagents of HCl, HNO_3 and H_2SO_4, NaOH, $C_2H_2O_4$, and Na_2CO_3 are of analytical grade.

2.2. Equipment

The materials were analyzed by energy-dispersive X-ray spectroscopy (EDS; XFlash6110, Bruker, Billerica, MA, USA), X-ray diffraction (XRD; DX-2700, Dangdong City, Liaoning, China), scanning electron microscopy

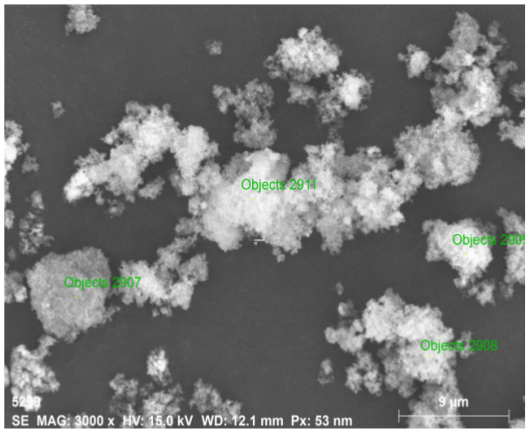

Fig. 1. (a) Microstructure analysis of waste light emitting diodes by scanning electron microscope (SEM).

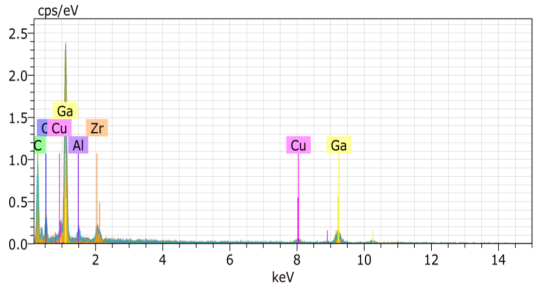

Fig. 1. (b) Characteristic analysis of waste gallium nitride by energy dispersive X-ray spectrometry (EDS).

Table 1. The content of waste light emitting diodes

Element	Ga	Si	Al	In
Wt.%	70.32	5.31	2.27	2.07

(SEM; S-3000N, Hitachi, Tokyo, Japan), X-ray fluorescence analyser (XRF, Spectro XEPOS), and inductively coupled plasma optical emission spectrometry (ICP-OES; Varian, Vista-MPX, PerkinElmer, Waltham, MA, USA).

2.3. Experiment procedures

2.3.1. Alkaline Roasting

The waste light emitting diodes were mixed with Na_2CO_3 at ratio of one to one. The temperature of alkaline roasting was set in the range of 800-1100°C, and the temperature of furnace was increased in linearly 10°C/min.

The entire alkaline roasting process was soaked for 3 hours. Hence, the whole process was carried out for about 6 hours.

Furthermore, the heater was turned off and the sample was cooled down to room temperature.

The chemical reaction equation was explained below, gallium nitride was converted into gallium oxide and then reacted with Na_2CO_3. Similarly, the pretreatment of waste light emitting diodes can be represented by Eqs. (1), (2), and (3).

$$4GaN + 3O_2 \rightarrow 2Ga_2O_3 + 2N_2 \quad (1)$$

$$Na_2CO_3 \rightarrow Na_2O + CO_2 \quad (2)$$

$$4GaN + 2Na_2CO_3 \rightarrow 2NaGaO_2 + CO_2 + N_2 \quad (3)$$

2.3.2. Leaching

Leaching procedures were carried out in standard laboratory leaching equipment. After the alkaline roasting, the waste light emitting diodes were leached by different kinds of chemical reagents such as nitric acid, sulfuric acid, hydrochloric acid, oxalic acid, and sodium oxidanide. Furthermore, the leaching parameters such as acid concentration, reaction temperature, reaction time and liquid-solid mass ratio were investigated. Leaching efficiency were calculated according to Eq. (4). Acidity was set from 0.25 to 8 M (mole/L) with liquid-solid ratio from 10 to 50 (ml/g). The effect of reaction time was set from 2 mins to 1024 mins to get optimal leaching condition of waste light emitting diodes.

$$X_A = \left(\frac{n_1}{n_2}\right) \times 100\% \quad (4)$$

Where X_A is leaching efficiency, n_1 is the actual quantity of metal leaching, n_2 is the metal quantity of raw material.

3. Results and discussion

3.1. Characteristic analysis

The raw material was analyzed by various instruments. As the Table 1 shown, the chemical composition of waste light emitting diodes were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian, Vista- MPX) with dissolving in aqua regia and hydrofluoric acid. In addition, the microstructure analysis by scanning electronic microscope (SEM) and the energy dispersive X-ray spectrometry (EDS) image of gallium nitride were shown in the Fig. 1. The particle of waste light emitting diodes was dispersal uniformly. Further, the crystal structure of waste light emitting diodes was detect by X-ray diffraction (XRD), shown in the Fig. 2.

3.2. Effect of Alkaline Roasting

In this section, we discussed the effect of alkaline roasting by Na_2CO_3. Owing to the chemically stability of gallium nitride, the gallium nitride was also difficult to be leached by acid and alkali without pretreatment. Hence, pretreatment of alkaline roasting become the most important process to decide the whole recovery method being successful or not. To acquire the optimal condition of alkaline roasting, the waste light emitting diodes samples were treated at 800, 900, 1000, 1100 and 1200°C for 3h/air with the ratio of waste LED dust over alkaline 1:1 and then characterized analysis by XRD. The XRD patterns of the waste light emitting diodes dust were shown in Fig. 2. The peaks of gallium nitride were observed and those peaks were remained until the reaction temperature was soaked on 900°C. As shown from Fig. 3 to Fig. 6, the peaks of gallium were all converted into sodium gallium oxide which was easily reacted with

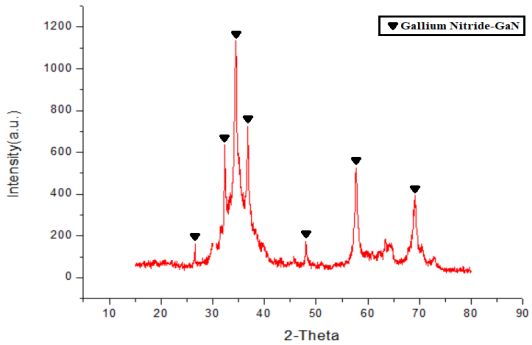

Fig. 2. XRD pattern of waste light emitting diodes.

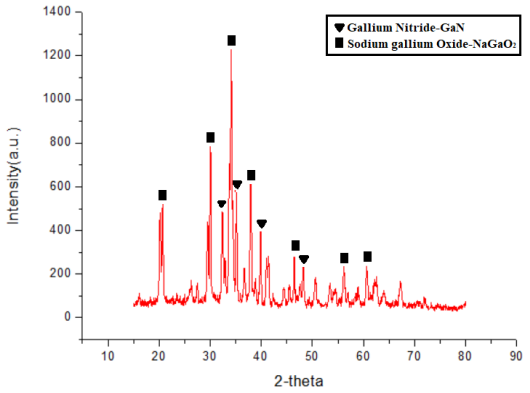

Fig. 3. XRD pattern of alkaline roasting at 800°C for 3 hours.

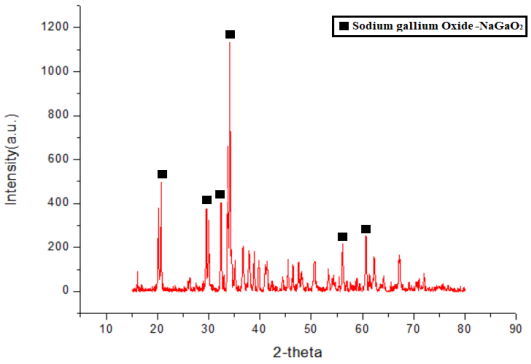

Fig. 4. XRD pattern of alkaline roasting at 900°C for 3 hours.

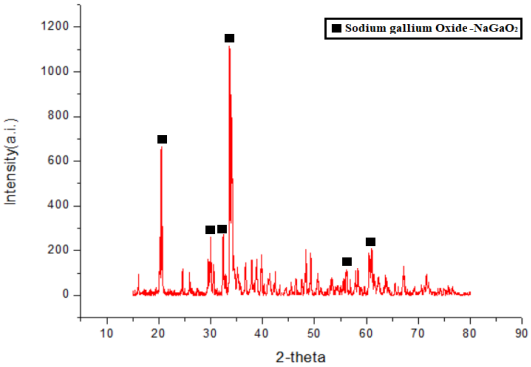

Fig. 5. XRD pattern of alkaline roasting at 1000°C for 3 hours.

acid and alkaline at room temperature. Besides, when the roasting temperature was raised to 1000°C and 1100°C, the peaks of sodium gallium oxide were almost remained. Consequently, the optimal roasting temperature was 900°C.

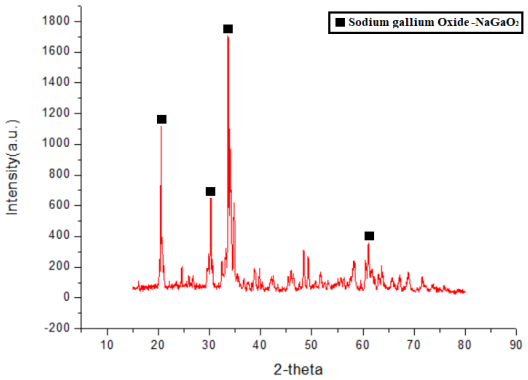

Fig. 6. XRD pattern of alkaline roasting at 1100°C for 3 hours.

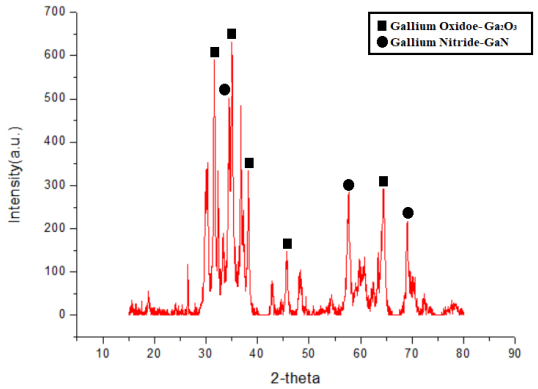

Fig. 7. XRD pattern of alkaline roasting at 900°C for 2 hours.

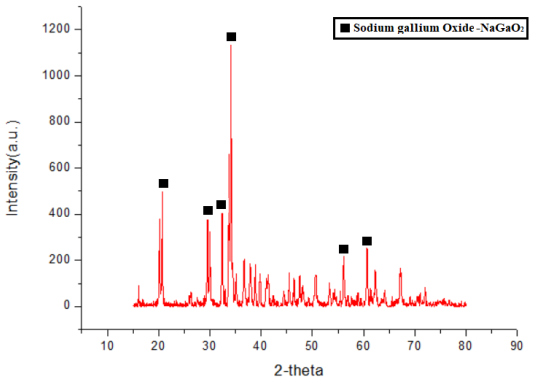

Fig. 8. XRD pattern of alkaline roasting at 900°C for 3 hours.

The optimal roasting temperature was investigated in the first part. And the next, to reduce the energy consumption and prevent equipment corrosion, the whole roasting time was also investigated in this section. Fig. 7 and Fig. 8 compared with the XRDs of raw and pretreated waste light emitting diodes samples at various alkaline roasting time. Fig. 7 indicated that there is no phase change observed in the raw waste light emitting diodes, nevertheless, the peaks of gallium nitride were almost disappeared shown in the Fig. 8. Hence, the optimal alkaline roasting time was carried out for 3 hours.

3.3. Leaching by H_2SO_4, HCl, HNO_3, $C_2H_2O_4$ and NaOH

This section discussed the leaching efficiency of pretreated LED dust by sulfuric acid, hydrochloric acid nitric acid, oxalic acid and sodium hydroxide respectively. The pretreated LED dust was reacted with 2 hours with concentration of 5M (mole/L) at liquid-solid ratio 50 (ml/g) at 25°C. Requiring the analysis of leaching efficiency in different kinds of reagents by ICP-OES.

As Table 2 shown, value metals, including gallium and indium, were all reacted with hydrochloric acid with high leaching efficiency. Therefore, hydrochloric acid was selected as our leaching reagent.

3.3.1. Concentration of HCl

As Fig. 9 shown, the leaching efficiency of gallium and indium in waste light emitting diodes were all apparently

Table 2. The leaching efficiency of pretreated LED dust by H_2SO_4, HCl, HNO_3, $C_2H_2O_4$ and NaOH with concentration of 5M at liquid-solid ratio 50 at 25°C

Value Metals	Gallium (Ga)	Indium (In)
Leaching efficiency by H_2SO_4, (%)	57.82	87.53
Leaching efficiency by HCl, (%)	95.58	96.64
Leaching efficiency by HNO_3, (%)	78.83	86.89
Leaching efficiency by $C_2H_2O_4$ (%)	73.62	79.61
Leaching efficiency by NaOH (%)	83.42	81.56

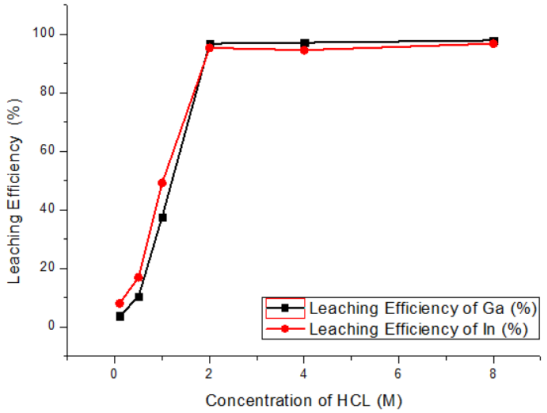

Fig. 9. Leaching efficiency by various concentration of HCl [HCl] = 2.0M, L/S=50 with 500 rpm for 2 hours at 25°C.

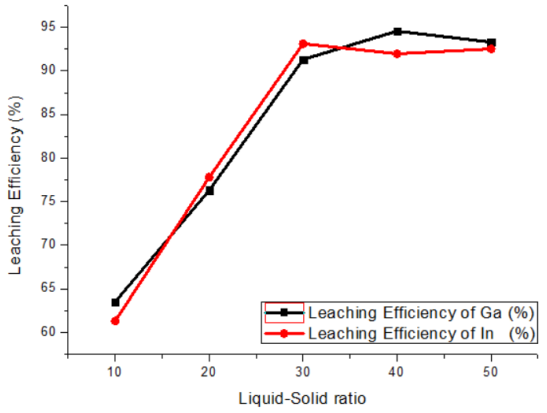

Fig. 10. Leaching efficiency by various liquid-solid ratio [HCl] = 2.0M, with 500 rpm for 2 hours at 25°C.

elevated when the concentration of HCl was significantly increased from 1M to 2M with liquid-solid mass ratio of 50 ml/g and 500 rpm for two hours at 25°C. However, it tended to slowly increase and then keeping constant when the concentration was higher than 2.0M. Hence, to acquire better leaching efficiency and avoid the unnecessary waste, the concentration of HCl was selected as 2.0M, and all further experiments were carried out at this concentration.

3.3.2. liquid-solid (L/S) ratio

Liquid-solid ratio (L/S) plays an important role in the stage of leaching of waste LED dust. The effect of L/S was therefore investigated by using 2.0 M HCl with 500 rpm for two hours at 25°C, and the results are conveyed in Fig. 10. It indicated that both the leaching efficiency of gallium and indium gradually elevated when the L/S was raised to 30 mL/g. Another key thing to remember, as the L/S was elevated over 30 mL/g, leaching efficiency of Ga and In kept constant and being sluggish. Consequently, the optimal Liquid-solid ratio (L/S) was considered as 30 mL/g.

3.3.3. Leaching time

Fig. 11 shows the effect of leaching efficiency with reaction time which utilize 2.0M HCl with liquid-solid

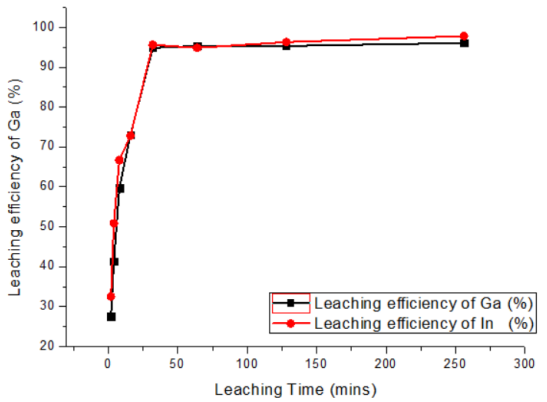

Fig. 11. Leaching efficiency by various leaching time [HCl] = 2.0M, L/S=30 with 500 rpm at 25°C.

ratio 30 (ml/g) at 25°C. The leaching efficiency of waste light emitting diodes was elevated dramatically when the reaction time was raised to 32 minutes from 16 minutes. With the increase of leaching time, several surface of unreacted particle core would be reacted with HCl. The leaching efficiency of waste light emitting diodes was in balance and stopped increasing when the reaction time was over 32 minutes. Therefore, the optimal leaching time was carried out for 32 minutes.

4. Conclusion

This study proposed an operative method to leach

gallium and indium effectively, and it was based on conducive to environmental technology and issues. Besides, the content of waste light emitting diodes was analyzed 70.32% Ga, 5.31% Si, 2.27% Al and 2.07% In by characteristic analysis.

Based on the previous references, confirming that although the chemical property of gallium nitride was stable so that they could not reacted with any acid or alkaline. Hence, pretreatment of recovery gallium and nitride became extremely important. Alkaline roasting was applicated and the optimal condition of alkaline roasting was that the furnace was soaked at 900°C for 3 hours with mixing Na_2CO_3. Moreover, the results also indicated that the pretreated LED dust could easily dissolved with HCl. The optimal condition of leaching procedures was carried out for 2.0M of HCl liquid-solid mass ratio of 30 ml/g in 32minutes at 25°C and about 96.88% Ga and 96.61% In were leached. The pretreatment of alkaline roasting was competitive with each other, and it had the potential to be applicated in the industrial leaching procedures in the future.

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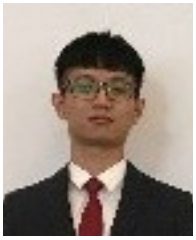

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요 약‡

발광다이오드는 많은 양의 갈륨과 인듐을 함유하고 있어, 폐발광다이오드로부터 이들 원소의 회수는 최근 많은 관심을 받은 연구 분야이다. 본 연구에서는 폐발광다이오드에 포함된 질화갈륨으로부터 갈륨과 인듐을 회수하고자 시도하였다. 전체 공정은 물성분석, 알칼리배소, 침출의 세 단계로 구성되었다. 화학성분 분석결과 폐발광다이오드의 경우, 70.32% 갈륨, 5.31% 규소, 2.27% 알루미늄 및 2.07% 인듐이 함유됨을 확인하였다. 두 번째 단계인 알칼리배소 공정은 탄산나트륨과 함께, 900°C하에서 3시간의 반응이 최적 조건인 것으로 확인되었고, 이 공정을 통해 질화갈륨이 질화산화물로 변화되었다. 마지막은 침출 단계로서, 산의 종류 및 농도, 고액비, 반응시간에 따른 변화를 조사하여, 최적조건을 확립하였다. 최적조건은 반응온도 25°C 및 2.0 M의 염산 환경에서 30 ml/g의 고액비와 반응시간 32분으로 나타났으며, 그 때의 침출 효율은 갈륨 96.88%와 인듐 96.61%로 나타났다.

주제어 : 질화갈륨, 갈륨 및 인듐 회수, 알칼리배소, 침출

‡상기 국문초록은 저자가 작성한 영문초록의 내용을 편집위원회에서 번역, 작성하였습니다.