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Separation of gallium and copper from hydrochloric acid by D_2EHPA

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ABSTRACT

Solvent extraction offers a better option for gallium recovery among many techniques. The liquid–liquid extraction of gallium(III)–copper(II) solution from hydrochloric acid medium using di-2-ethyl-hexylphosphoric acid (D_2EHPA) in kerosene was studied. The effect of the reagent concentration and other parameters on the extraction of gallium(III)–copper(II) was also studied. The stoichiometry of the extracted species of gallium(III) was determined based on the slope analysis method. The maximum extraction efficiency of gallium was 99.9%. The gallium that contained organic phase could be stripped completely by 1 M HCl.

Keywords: Gallium(III); Liquid–liquid extraction; Copper(II); Strip; D_2EHPA

1. Introduction

The gallium metal is scarce in nature, only 0.0015%. Most of gallium is commonly associated with aluminium, zinc and germanium [1,2]. In recent years, the gallium metal has been extensively used in both solar and electronic industries. The solar power generation technology is divided into crystalline silicon and thin film solar cells according to the process. The thin film solar cell is regarded as the most potential in the solar energy technology, along with crystalline silicon solar cell, given its advantages of lightweight, thinness, low cost, flexibility and diversified design. The types include CIGS solar cell and cadmium telluride solar cell. The CIGS is direct band gap material, which has higher absorptivity than amorphous silicon, and its light absorption frequency range is 1.02–1.68 eV. The copper-gallium alloy sputtering target is applied to solar cell CIGS process as the light energy conversion absorption layer. The development and application of gallium will lead to producing a lot of process waste as the demand increases in the future. Therefore, the recovery of gallium metal has attracted much attention. Many separation techniques are used to recover gallium metal, including chemical precipitation, ion exchange resin and solvent extraction [3–5]. The solvent extraction can recover low-concentration

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metal selectively and change different parameters to reach high distribution coefficient. The solvent extraction will provide an effective method to recover metals [2,5,6].

Liu et al. used TBP to extract gallium from high acidity solution [7]. The organic phase was 30% TBP, the water phase was HCl solution and the O/A ratio was 1:1. The experimental result showed the percentage extraction was 97%, and the stripping could be completed by 1 M NaCl water solution. Lee et al. used di-2-ethyl-hexylphosphoric acid (D_2EHPA) to separate indium and gallium metals from sulphuric acid solution [8]. The organic phase was 0.05 M D_2EHPA in kerosene solution, and the water phase was indium and gallium metals dissolved in sulphuric acid solution. The experiment showed the distribution coefficient of indium and gallium increased with the pH value and D_2EHPA concentration. The single extraction recovery ratio of indium was 99.9%, and that of gallium was 26%. The indium and gallium could be separated completely by a second-stage extraction. Gupta et al. discussed the extraction effect of gallium-containing electronic scrap in HCl, nitric acid, sulphuric acid media and 0.5 M Cyanex 923 solution in toluene [2]. The experiment showed the percentage extraction was 90% under the conditions of HCl solution, O/A = 1:1, temperature 25℃ and 5 min oscillation.

This study used solvent extraction to recover valuable gallium metal from solar energy waste copper-gallium sputtering target. It was used in HCl system, and the D_2EHPA was used as extractant and kerosene as diluent, so as to discuss the optimal separation parameters of copper-gallium metal.

2. Materials and methods

2.1. Solvent extraction

The copper gallium solution was extracted and stripped. The experimental parameters include initial solution pH value, O/A ratio (extractant/aqueous phase volume ratio, oil phase/aqueous phase volume ratio), shake frequency, shake time and D_2EHPA concentration, as shown in Fig. 1.

2.2. Material source and methods

The extraction sample was prepared by copper chloride and gallium chloride in distilled water. The initial concentration of copper in the solution was about 300 mg/L, and that of gallium was about 150 mg/L. The concentrations of ions distributed between the two phases were determined by atomic absorption spectrometer. The percentage of extraction was also calculated to determine the conditions of optimal extraction effect. To evaluate the reproducibility of the results, all experiments were prepared and measured in triplicate samples.

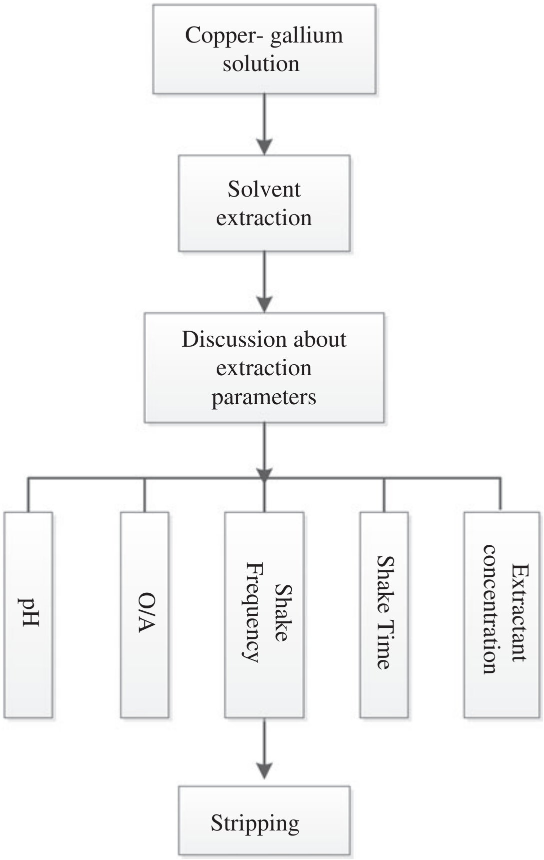

Fig. 1. Flow chart of experimental procedures.

3. Results and discussion

3.1. Effect of initial solution pH value on extraction efficiency

The initial solution pH value was changed within 0.1–3.5 in the conditions of fixed O/A = 1/1, 0.005 M D_2EHPA, shake frequency of 500 min^{-1} and shake time of 30 min. Fig. 2 shows the effect of aqueous phase pH value on extraction percentage. The optimal pH was observed. The result showed that the extraction percentage of gallium increased with an increase in aqueous phase pH value. The D_2EHPA is an acidic extractant. In the solvent extraction of metal ions, the hydrogen ions are released for coordination with metal ions, expressed as follows [8]:

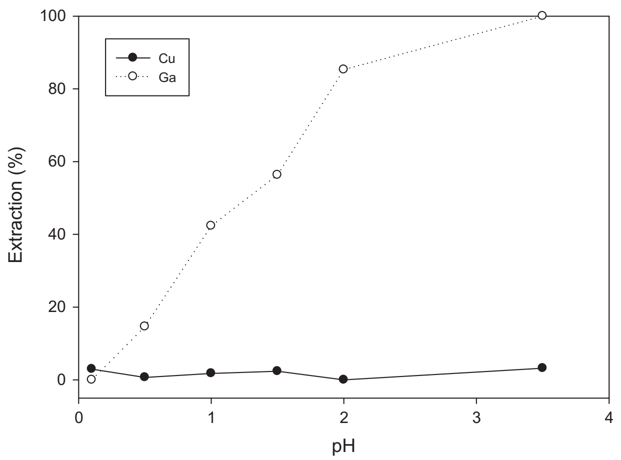

Fig. 2. Effect of aqueous phase pH value on extraction efficiency (0.005 M D_2EHPA; O/A = 1/1; Shake frequency: 500 min^{-1}; Shake time: 30 min).

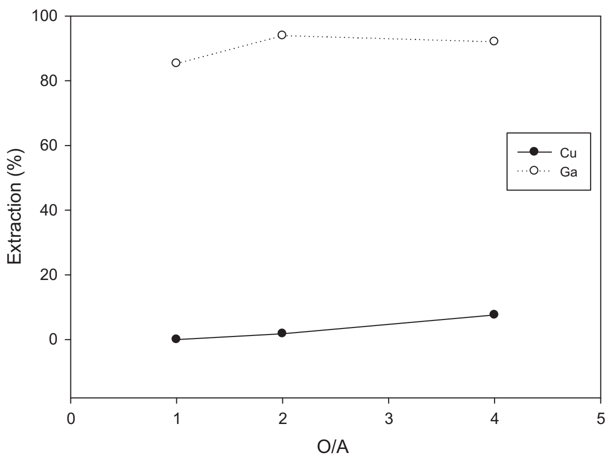

Fig. 3. Effect of oil-aqueous volume ratio on extraction efficiency (Aqueous phase: pH 2; 0.005 M D_2EHPA; Shake frequency: 500 min^{-1}; Shake time: 30 min).

$$M^{3+}_{aq} + \frac{3}{2}(HA)_{2,O} = MA_{3,O} + 3H^{+}_{aq} \qquad (1)$$

HA: Extractant D_2EHPA; M^{3+}: Trivalent metal ion; aq: aqueous phase; O: organic phase.

Therefore, higher acidity of aqueous phase is disadvantage to the release of hydrogen ion from D_2EHPA. Fig. 2 shows the copper is not extracted to organic phase at all. Because the D_2EHPA exchanges hydrogen ion with trivalent gallium ion selectively, the copper ions mostly exist in water phase in monovalent and bivalent forms under acidic condition. The copper and gallium of extract phase can be separated.

3.2. Effect of oil-aqueous volume ratio on extraction efficiency

The effect of O/A ratio was examined, and the results are shown in Fig. 3. There is emulsion in the case of O/A ratio = 1/20, ¼, and 1/2. The result showed that no significant change in the extraction percentage of gallium. The O/A ratio = 1/1 was fixed for subsequent experiments.

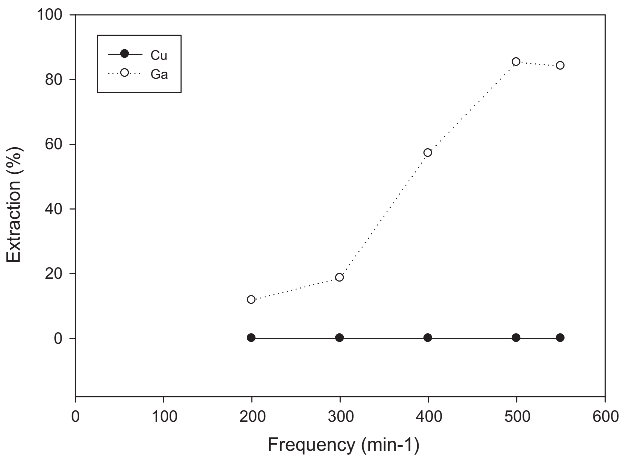

Fig. 4. Effect of shake frequency on extraction efficiency (Aqueous phase: pH 2; 0.005 M D_2EHPA; O/A = 1/1; Shake time: 30 min).

3.3. Effect of shake frequency on extraction efficiency

Under the conditions of fixed solution pH value = 2.0, O/A = 1/1, 0.005 M D2EHPA and shake time of 30 min, the shake frequency was changed to 200, 300, 400, 500 and 550 min^{-1}, and the relationship is shown in Fig. 4. The results showed that the extraction efficiency changes slightly when the shake frequency was 200–300 min^{-1}. When the shake frequency was up to 300 min^{-1}, the extraction percentage increased with the shake frequency. There was better contact effect between two phases, so that the extraction percentage of gallium increased. When the shake frequency was 500 min^{-1}, the extraction percentage of gallium was 85%. The effect of shake frequency is not apparent if the frequency is over 500 min^{-1}.

3.4. Effect of shake time on extraction efficiency

Under the conditions of fixed solution pH value = 2.0, O/A = 1/1, 0.005 M D_2EHPA and shake frequency of 500 min^{-1}, the shake time was changed to 5, 15, 30 and 60 min, respectively. The relationship is shown in Fig. 5. The results showed that the extraction percentage of gallium increased with an increase in shake time, and the extraction percentage of gallium was 95% at 60 min.

3.5. Effect of extractant concentration on extraction efficiency

Under the conditions of fixed solution pH 2, O/A = 1/1, shake frequency of 500 min^{-1} and shake time of 30 min, the D_2EHPA concentration was changed to 0.001, 0.005, 0.01, 0.1, 0.2, 0.5, 1 and 2 M. The effect of D_2EHPA concentration on the extraction efficiency was also observed. As shown in Fig. 6, the extraction percentage of gallium increased with an increase of concentration up to 0.1 M. The extraction percentage was 99.98% when the D_2EHPA concentration was 0.1 M. The extraction percentage of gallium did not increase significantly when the concentration was higher than 0.1 M. It was because there is excessive solvent when the D_2EHPA concentration is higher than 0.1 M

3.6. Stripping experiment

From the extraction experiments, it was observed that D_2EHPA could extract gallium selectively from the Cu-Ga mixed solutions. The gallium of organic phase was extracted to water phase by different stripping reagents. Six solutions were prepared as stripping reagents. The results of stripping studied at O/A = 2/1, temperature was 25℃, and shake frequency was 500 min^{-1} are shown in Table 1. The results indicated that 1 M HCl solution can efficiently strip the gallium from organic phase, so as to facilitate subsequent electrolytic refining.

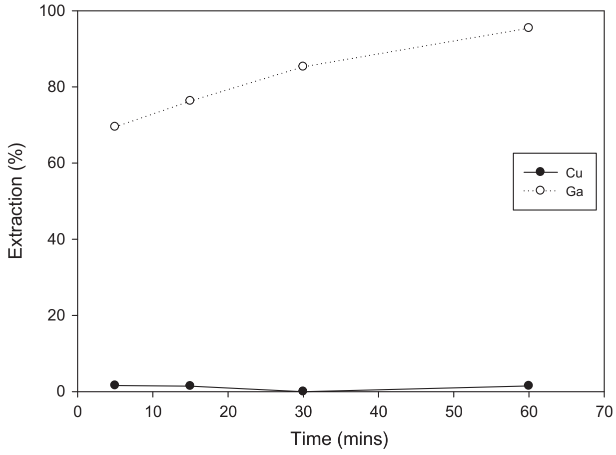

Fig. 5. Effect of shake time on extraction efficiency (Aqueous phase: pH 2; 0.005 M D_2EHPA; O/A = 1/1; Shake frequency: 500 min^{-1}).

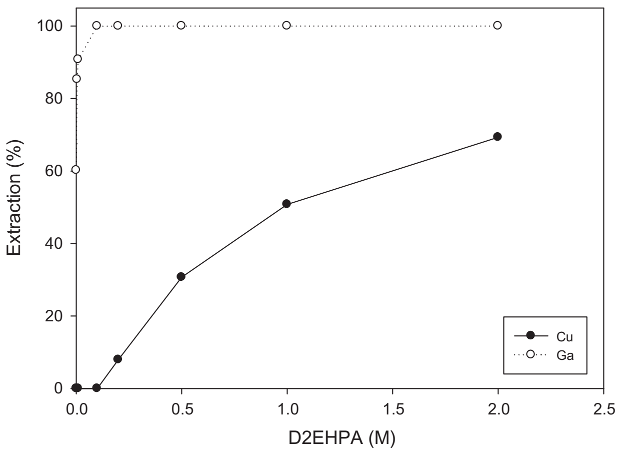

Fig. 6. Effect of D_2EHPA concentration on extraction efficiency (Aqueous phase: pH 2; O/A = 1/1; Shake frequency: 500 min^{-1}; Shake time: 30 min).

In terms of single-stage extraction, the optimal extraction operating conditions of this technique were copper-gallium solution with pH 2, 0.1 M D_2EHPA, oil-aqueous volume ratio of 1/1 and 30 min oscillation at 500 times per min. The extraction percentage of gallium was higher than 99.9% as a result. The gallium metal of organic phase can use HCl solution for stripping successfully, in order to facilitate subsequent electrolytic recovery of gallium.

In comparison to literatures, as an extractant, the D_2EHPA extracts trivalent gallium very selectively. Its extraction mechanism is mainly the exchange between hydrogen of extractant and metal ion, which is cation exchange form. The percentage extraction of the extractant D2EHPA is higher than that of Cyanex272 [1], Cyanex923 [2,3,9] and Cyanex925 [3], as well as neutral extractant TBP [7,10]. Therefore, the D_2EHPA as an extractant has excellent efficiency in separating copper-gallium alloy target material.

Table 1
Stripping reagents and stripping efficiency

Stripping reagent	Stripping rate (%)
0.1 M HCl	0
0.5 M HCl	57.7
1 M HCl	100
0.1 M HNO_3	12
0.5 M HNO_3	97
1 M HNO_3	99.7

4. Conclusions

According to the experimental results of this technique:

(a) The increase in the pH value of copper-gallium solution helps the D_2EHPA release hydrogen ion for exchange reaction with gallium ion, so that the extraction efficiency increases. The extraction percentage is approximately 100% when pH 3.5.

(b) Within the same operating time, when the extraction shake frequency is high, the contact between water phase and organic phase is more complete, which is helpful to the extraction of metals. The extension of the extraction shake time is helpful to the extraction of metals.

(c) The metal extraction capacity increases with the D_2EHPA concentration. In terms of single-stage extraction, the better extraction operating conditions of this technique are copper-gallium solution of pH 2 with at least 0.1 M D_2EHPA, oil-aqueous volume ratio of 1/1 and 30 min oscillation at frequency of 500 times per minute. The extraction percentage of gallium is higher than 99.9%.

(d) The gallium containing organic phase is stripped by 1 M HCl, and the stripping efficiency is as high as 100%.

(e) The solvent extraction can recover low concentration metals selectively, and the separating effect of high distribution coefficient can be obtained by changing parameters. Therefore, this technique provides an effective method for separating and recovering gallium metals.

Acknowledgement

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References

[1] B. Gupta, N. Mudhar, I. Singh, Separations and recovery of indium and gallium using bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), Sep. Purif. Technol. 57 (2007) 294–303.

[2] B. Gupta, N. Mudhar, Z. Begum, I. Singh, Extraction and recovery of Ga(III) from waste material using Cyanex 923, Hydrometallurgy 87 (2007) 18–26.

[3] I.M. Ahmed, Y.A. El-Nadi, N.E. El-Hefny, Extraction of gallium(III) from hydrochloric acid by Cyanex 923 and Cyanex 925, Hydrometallurgy 131–132 (2013) 24–28.

[4] S.V. Mahamuni, P.P. Wadgaonkar, M.A. Anuse, Liquid–liquid extraction and recovery of gallium(III) from acid media with 2-octylaminopyridine in chloroform: Analysis of bauxite ore, J. Serb. Chem. Soc. 75 (2010) 1099–1113.

[5] Z. Zhao, Y. Yang, Y. Xiao, Y. Fan, Recovery of gallium from Bayer liquor: A review, Hydrometallurgy 125–126 (2012) 115–124.

[6] R. Dumortier, M.E. Weber, J.H. Vera, Removal and recovery of gallium from aqueous solutions by complexation with sodium di-(n-octyl) phosphinate, Hydrometallurgy 76 (2005) 207–215.

[7] J. Liu, Y.T. Yan, K.R. Lai, Extraction and separation of gallium from high concentration HCl solution with TBP, Hydrometallurgy China 21 (2002) 189–191.

[8] M.S. Lee, J.G. Ahn, E.C. Lee, Solvent extraction separation of indium and gallium from sulphate solutions using D_2EHPA, Hydrometallurgy 63 (2002) 269–276.

[9] B. Gupta, A. Deep, P. Malik, Liquid–liquid extraction and recovery of indium using Cyanex 923, Anal. Chim. Acta 513 (2004) 463–471.

[10] S. Virolainen, D. Ibana, E. Paatero, Recovery of indium from indium tin oxide by solvent extraction, Hydrometallurgy 107 (2011) 56–61.