

Liquid-Liquid Extraction of Gallium from Jajarm Bayer Process Liquor Using Kelex 100

Abdollahy, Mahmood*⁺; Naderi, Hojat

Department of Mining Engineering, Faculty of Engineering, Tarbiat Modares University, Tehran, I.R. IRAN

ABSTRACT: The solvent extraction of gallium from a concentrated Jajarm Bayer process liquor containing 164.90 g/l of Na₂O, 86.70 g/l of Al₂O₃ and 106.02 ppm of gallium was investigated using 10 vol.% Kelex100, a 7-alkyl substituted-8 hydroxyquinoline as an extractant, 10 vol.% ethanol as a modifier and kerosene as a diluent. At ($V_o : V_a = 1.0:1.0$) organic to aqueous phase ratio and at room temperature, 93.39% of gallium was recovered in 60 minutes. Back extraction studies of the loaded organic phase were carried out using hydrochloric acid, sulfuric acid and sodium hydroxide. Scrubbing of aluminium co-extracted into the organic phase was carried out with 5.0 M HCl and subsequently stripping of gallium was carried out with 1.5 M HCl. The final strip liquor was found to contain 490 ppm of gallium along with 141.73 ppm of aluminium.

KEY WORDS: Gallium extraction, Bayer process liquor, Kelex 100.

INTRODUCTION

Gallium is an important material used in the electronics industry, whose demand in the world market has been increasing due to its applications in semiconductors, high temperature rectifiers, transistors, batteries and other devices in which photoeffects may be used [1-3]. In recent years, the main way of obtaining gallium in viable conditions for the industry is via extraction as a by-product in the hydrometallurgical process of bauxite, the so-called Bayer process. This process consists of digestion of ores in a high concentrated solution of sodium hydroxide at high pressure and temperature. Finally aluminium will precipitated in the form of hydrate which is calcined to final product [4-6].

The Bayer process liquors normally builds up in

gallium concentrations from 100 to 300 ppm depending upon the gallium content of bauxite [7]. The solvent extraction of gallium from Bayer process liquors has been studied extensively by several authors from both thermodynamic and kinetic viewpoints.

Selective extraction of gallium from Bayer process liquors was first reported by *Leveque* and *Helegorsky* [7,8], using 8.5 vol.% of Kelex 100 (Sherex Chemicals, USA) in combination with 10.0 vol.% of *n*-decanol and 81.5 vol.% of kerosene, which were used as a modifier and diluent, respectively. When this organic phase was contacted with a Bayer process liquor containing 194 g/l of Na₂O, 75 g/l of Al₂O₃ and 270 ppm gallium, at 1:1 organic to aqueous phase ratio at room temperature, 80% of the gallium was recovered in 180 minutes.

* To whom correspondence should be addressed.

+ E-mail: minmabd@modares.ac.ir

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Table 1: Chemical composition of Bayer process liquor.

Ga (ppm)	Fe (ppm)	Al (g/l)	V (ppm)	Si (ppm)	Ti (ppm)	In
106.02	0.053	86.70	277.50	350	20.00	trace

Table 2: Gallium extraction at different conditions of organic to aqueous phase ratio and contact time.

Test No.	Aqueous to organic phase ratio (A/O)	Contact time (min)	Gallium concentration in aqueous phase after extraction	Extraction of gallium (%)
1	1:1	30	10.65	89.97
2	1:1	60	7.02	93.39
3	2:1	60	15.90	85.00
4	3:1	60	24.95	76.50
5	4:1	60	20.81	80.40
6	5:1	60	60.53	43.00

Iran Aluminum Company (IRALCo) is the first producer of alumina in Iran. Jajarm bauxite mines are located about 10 Km east of Jajarm in the Province of Khorasan, Iran. The Jajarm Alumina Plant processes diasporic bauxite into sandy alumina. The technology used for this purpose is known as Tube Digestion.

The recovery of gallium content present in alkaline aqueous solutions from Jajarm Alumina plant via liquid/liquid extraction and back extracting the gallium content by washing the organic phase using an aqueous acid solution was investigated.

EXPERIMENTAL

Materials

The Bayer process liquor was supplied by Jajarm Alumina. Kelex 100 was supplied by Nanjing Odessey, China. Etanol, hydrochloric and sulfuric acid was supplied by Merck, Germany, and the high grade kerosene (Density=0.78 g/cm³ at 20 °C, B.P.=190 - 250 °C) by Fluka, Germany.

Procedure

Experiments were conducted by preparing the organic phase of the required composition and mixing it thoroughly with the Bayer process liquor in a glass beaker using a mechanical stirrer at required aqueous to organic phase ratio and contact time. The organic and aqueous phase volumes were maintained at 50 ml. Scrubbing and stripping experiments of the loaded organic phase were conducted at 1:1 organic to aqueous phase ratio using various acid and alkaline solutions.

Aqueous samples were withdrawn and diluted for gallium, aluminum and sodium analysis of the raffinate and extract solutions using an inductively coupled plasma spectrophotometer. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Extraction

The Bayer process liquor was subjected to solvent extraction for the selective recovery of gallium using 10 vol.% Kelex100 as extractant, 10 vol.% etanol as modifier and kerosene as diluent. Four samples were taken at different time intervals from Jajarm alumina plant from which gallium was analysed. The results showed an increase in gallium concentration from 90 ppm in first sample to 170 ppm in last sample.

Chemical composition of liquor which was used in extraction processes is presented in table 1. The most important impurities were Al, V and Si. Extraction Percentage of gallium in various organic to aqueous phase ratio and contact time is presented in table 2. Extraction Percentage was calculated using relation 1. In these relations E = extraction percentage, W = initial concentration of metal in aqueous phase and W₁ = metal concentration in aqueous phase after extraction.

$$E = (W - W_1) / W * 100 \quad (1)$$

The effect of the contact time on gallium extraction, (tests 1 and 2) was studied. The gallium extraction was found to be increased from 89.97% to 93.39% with an increase in contact time from 30 to 60 min, respectively.

Table 3: Gallium, aluminium and vanadium concentrations in aqueous and organic phase before and after extraction(A/O:1.0:1.0,contact time:60 min).

		Ga (ppm)	Al (ppm)	V (ppm)
Before extraction	Aqueous phase	106.20	40644.00	275.70
	Organic phase	0.00	0.00	0.00
After extraction	Aqueous phase	7.02	30102.50	143.07

Table 4: Gallium concentration in aqueous and organic phases after extraction at different conditions of organic to aqueous phase ratio.

Test No.	A/O	Gallium concentration in organic phase (ppm)	Gallium concentration in aqueous phase (ppm)
2	1:1	99.18	7.02
3	2:1	180.60	15.90
4	3:1	243.75	24.95
5	4:1	340.84	20.81
6	5:1	228.37	60.53

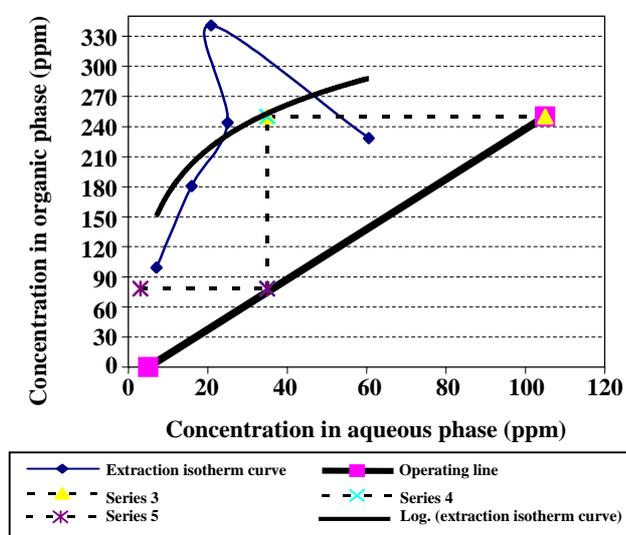


Fig. 1: Gallium extraction isotherm using kelex100.

In order to study the effect of aqueous to organic phase ratio (A/O) on gallium extraction, four tests (3 to 6) were carried out. Increasing aqueous to organic phase ratio from 1:1 to 3:1 were resulted in a decrease in gallium extraction. When aqueous to organic phase ratio increased to 4:1 gallium extraction increased to 80.40%. When aqueous to organic phase ratio increased to 5:1, gallium extraction decreased to 43.00%. Test No 5 was repeated. The result confirmed the trend.

The maximum gallium extraction was obtained at 1:1 organic to aqueous phase ratio in 60 min(93.39%).

Table 3 shows gallium, aluminium and vanadium concentrations in aqueous and organic phases before and after extraction.

The McCabe-Thiele diagram (Fig. 1) was plotted to determine the number of theoretical countercurrent stages required for maximum gallium extraction using gallium concentrations in aqueous and organic phases after each extraction test (table 4). For plotting the operating line gallium concentration were considered 105.00 and 5.00 ppm in aqueous phase and 0.00 and 200.00 ppm in organic phase, respectively. The McCabe-Thiele diagram indicated two theoretical countercurrent stages required to recover 95.00% of gallium.

Scrubbing and stripping of the organic phase

Back extraction of the gallium contained in organic phase can be carried out using an acid solution such as hydrochloric acid, nitric acid, sulfuric acid, or alkaline solution such as sodium hydroxide.

Back extraction studies of the loaded organic were carried out with the aid of hydrochloric and sulfuric acids and sodium hydroxide.

Back extraction of Ga and Al with acid solutions

Back extraction of gallium was carried out with 1.5, 3.0 and 5.0M HCl and H₂SO₄ at 1:1 aqueous to organic phase ratio and contact time of 15 min. The results are given in table 5.

Table 5: Back extraction of gallium and aluminium using acid solutions.

Back-extraction	HCl (M)			H ₂ SO ₄ (M)		
	1.5	3	5	1.5	3	5
Ga (%)	100.00	84.27	1.00	55.60	100.00	100.00
Al (%)	18.20	16.67	15.20	13.27	13.20	13.89

Table 6: Back extraction of gallium and aluminium using NaOH solute.

Back-extraction percentage	NaOH (N)				
	3	6	9	12	15
Ga (%)	1.10	0.28	8.26	43.33	44.98
Al (%)	2.71	4.40	8.67	1.95	1.91

From results it is evident that back extraction of gallium using concentrated solution of H₂SO₄ or dilute solution of HCl is possible.

The back extraction of gallium was found to be maximum when a 1.5 M HCl was used (100%) and decreased with an increase in HCl concentration. Increasing concentration of HCl solution to 3.0 and 5.0M has been resulted in a gallium extraction percentage of 84.27 and 1.00, respectively.

The results showed that selective back extraction of aluminium was possible using concentrated solution of HCl. Therefore it was possible to extract only the aluminium with a concentrated solution of HCl at first step followed by back extraction of gallium with a dilute solution of HCl.

Results showed that the selective back extraction of aluminium was not possible using H₂SO₄ solution.

Behavior of NaOH solutions

Back extraction of gallium was carried out with 3, 6, 9, 12 and 15N NaOH. Experiments were conducted at 1:1 aqueous to organic phase ratio and contact time of 15 min. The results are given in table 6.

From these tables it was evident that it was not possible to back extract the gallium and aluminium effectively using NaOH solution. The back extraction of gallium was 44.98% for 15N NaOH. The maximum back extraction of aluminium was obtained for 9N NaOH (8.67%). Any increase or decrease in concentration of NaOH resulted in a decrease in aluminium extraction.

Preparation of enriched gallium solution

Previous results showed that 5.0M HCl can be used as a scrub solution to remove impurities such as aluminium and then 1.5M HCl can be used as a strip solution to recover gallium.

The process must produce a gallium solution which is compatible with the processes for the production of gallium metal, from the point of view of purity and gallium content.

In order to increase gallium content in final strip solution, suitable aqueous to organic ratios were chosen in extraction and stripping stages. The results obtained for extraction, scrubbing and stripping stages at different aqueous to organic phase ratios are given in tables 7 to 9.

The final strip liquor was found to contain 490 ppm of gallium along with 141.73 ppm of aluminium. The overall recovery of gallium in the strip liquor was found to be 87.02% from a Bayer process liquor containing 106.02 ppm of initial gallium while 99.82% of aluminium was removed.

CONCLUSIONS

The solvent extraction of gallium using 10 vol.% Kelex 100, 10 vol.% ethanol and kerosene from a Bayer process liquor containing 106.02 ppm has resulted in 93.39% gallium recovery in 1 h. Back extraction studies of the loaded organic were carried out using hydrochloric and sulfuric acids and sodium hydroxide. The results showed that extraction of only the aluminium with a concentrated solution of HCl in scrubbing stage followed

Table 7: Aqueous to organic phase ratios and contact times for extraction, scrubbing and stripping stages.

	Extraction	Scrubbing	Stripping
Aqueous to organic phase ratio (A/O)	2:1	1:1	1:2
Contact time (min)	60	15	15

Table 8: Results obtained for extraction process.

		Feed	Aqueous phase	Organic phase
Gallium(Ga)	Concentration(ppm)	106.02	13.27	185.00
	Extraction percentage	100.00	12.50	87.50
Aluminium(Al)	Concentration(ppm)	40644.00	28102.00	24996.00
	Extraction percentage	100.00	69.22	30.78

Table 9: Results obtained for scrubbing and stripping processes.

		Scrubbing			Stripping		
		Feed (loaded organic phase)	Scrub solution	Organic phase after scrubbing	Feed (organic phase after scrubbing)	Strip solution	Organic phase after stripping
Ga	Concentration (ppm)	185.00	1.01	184.00	184.00	490.00	00.00
	Extraction percentage	100.00	0.55	99.45	100.00	100.00	00.00
Al	Concentration (ppm)	24996.00	2381.23	22614.78	22614.78	141.73	22473.05
	Extraction percentage	100.00	9.53	90.47	100.00	0.63	99.37

by back extract the gallium with a dilute solution of HCl is possible. The final strip liquor contained 490 ppm of gallium along with 141.73 ppm of aluminium. The overall recovery of gallium was 87.02%.

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