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Recovery of Gallium from Aluminum Industry Residues

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ABSTRACT

A procedure is proposed to recover gallium from flue dust aluminum residues produced in plants by using solid-phase extraction with a commercial polyether-type polyurethane foam (PUF). Gallium can be separated from high concentrations of aluminum, iron, nickel, titanium, vanadium, copper, zinc, sulfate, fluoride, and chloride by extraction with PUF from 3 M sulfuric acid and 3 M sodium chloride concentration medium with at least a 92% efficiency. Gallium backextraction was fast and quantitative with ethanol solution. In all recovery steps commercial-grade reagents could be used, including tap water. The recovered gallium was precipitated with sodium hydroxide solution, purified by dissolution and precipitation, calcinated, and the final oxide was 98.6% pure.

INTRODUCTION

Gallium is currently recovered as a by-product from the bauxite refining process used to produce alumina and from some zinc ores processing. It is estimated that up to 25% of gallium world production is recovered from old scarp of intermetallic compounds to make solid-state diodes and other semiconductor industrial devices (1). Gallium is also recovered from scrubber dust removed from the fume extraction system in plants which produce aluminum by the electrolytic process (2). Thus the main producers of bauxite and zinc are the primary sources of gallium. Gallium is also found in minor quantities in many other materials. However, because of its low concentration, these ma-

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terials are not mined just for their gallium content. Bauxite is known to contain up to 0.01% gallium and may have an average of about 0.005% gallium. Brazil ranks third in the world in bauxite and gallium reserve base (1).

Aluminum plants produce considerable quantities of flue dust during the electrolysis process—for a fairly large plant in Brazil it may be more than a thousand metric tons a year. The dust from aluminum plants is a storage and waste problem. Its main constituents are such common elements as aluminum, sodium, iron, sulfur, fluoride, and carbon. The latter element accounts for about one-third of the total mass. In addition to these elements, rarer ones can also be present, notably gallium and vanadium, both of which seem to accumulate in the dust, probably by a sublimation process. In the case of gallium, a concentration range of from 0.1 to 1.0% (Ga_2O_3) has been reported (3).

It is known that $GaCl_3$ is easily extracted from hydrochloric acid solutions at various concentrations by a number of organic extractors including, among others, tertiary amines, organophosphorates, ethers, and ketones (4). Some of these extractors have been industrially used to separate and recover gallium from hydrochloric acid medium. They usually require large investments in reagents due to the loss of solvents and high cost of recovering them. Recently Mihaylov et al. (5) published a review about gallium solvent extraction in hydrometallurgy, pointing out gallium extraction as Ga^{3+}, $H^+GaCl_4^-$, and $Na^+Ga(OH)_4^-$ species in proper mediums.

Solid phase extraction (SPE) is an effective and inexpensive process which has been widely used in the analytical separation of many metals. Polyurethane foam (PUF) has received considerable attention in the last two decades as a solid extractor for the separation, preconcentration, and recovery of many inorganic and organic species from aqueous, nonaqueous, and gaseous mediums. Reviews in the literature that have reported PUF as a polymeric sorbent in separation chemistry have been compiled by Moody and Thomas (6) and Braun et al. (7, 8) since Bowen's first paper (9). Several chelating agents (10–12) and liquid ion exchangers (13, 14) have been used with PUF to increase selectivity in separation procedures.

Gesser et al. (16, 17) studied the extraction of gallium from chloride medium using unloaded PUF. These authors found that the best condition to extract gallium was in either 7.5 M hydrochloric acid or 7.0 M lithium chloride and 0.1 M hydrochloric acid solutions using PUF plugs systems at flow rates as high as 64 mL/min. They also found that iron(III) could be efficiently coextracted with gallium from these mediums, and gallium was stripped in a 2.0 M sodium hydroxide solution. Fang et al. (18) reported the recovery of gallium and some other elements from coal fly ash by using polyurethane foam. These authors studied the leaching parameters and used a muffle furnace to burn the coal ash in an air atmosphere at 500°C for 10 hours before leaching with 2 M hydrochloric acid solution at room temperature for 2 hours with shaking. Gallium was extracted by foam from 8.48 M chloride solution and 7 M hydrochloric or sulfuric acid. Carvalho et al. (19) used Brazilian commercial PUF to preconcentrate gallium whose presence had been directly determinated by x-ray fluorescence in aluminum, bauxite, and residues from the aluminum industry. Iron(III) was efficiently reduced by sodium dithionite. Commercial PUF was then used to sorb gallium: 1.86 mol Ga/kg PUF_{dried} as measured by sorption isotherms (20). Iron in the reduced form was coextracted only to a very small extent, less than 1%.

In this paper we propose the use of solid-phase extraction with commercial PUF as an efficient and adequate process to recover gallium from the flue dust removed from a fume collection system in plants that produce aluminum by the electrolytic process.

EXPERIMENTAL

Reagents

All reagents were of commercial grade unless otherwise stated. Water was from the laboratory tap. The polyurethane foam was a commercial, open cell, polyether type (Vulcan of Brazil-VCON 202, 42% resilience and 10–12 cells/linear cm). It was broken into small particles in a blender with water, squeezed, dried in a furnace at 70°C, and sifted through a domestic sieve of approximately 25 mesh before use. The flue dust was supplied from a large aluminum plant in Brazil.

Apparatus

A Rigaku-B3 wavelength dispersive x-ray fluorescence (XRF) spectrometer with a rhodium tube operated at 40 kV and 30 mA, a LiF crystal, and a scintillation counter were used to determine gallium by a thin layer technique in all experiments (19, 21).

Extraction and Backextraction Experiments

All solutions were prepared in this step by using analytical grade reagents and distilled water. Several different sulfuric acid concentrations in 100 mL solutions containing 7.5 mg of gallium were mixed with 0.3 g of PUF after sodium chloride concentration had been adjusted to 1.0, 2.0, and 3.0 M, respectively. Gallium extraction was carried out by a batch procedure previously described (19). The effects of sulfuric acid and chloride concentrations on gallium extraction were studied. The results are shown in Fig. 1.

Several systems to backextract gallium from PUF were tested. First, 7.5 mg of gallium was quantitatively extracted from 3.0 M H_2SO_4 and 3.0 M NaCl solutions in batch or column procedures. Then loaded PUF was washed with the same extraction solution without gallium, filtered off, and squeezed when batch procedure was used, or drained and submitted to a soft vacuum to re-

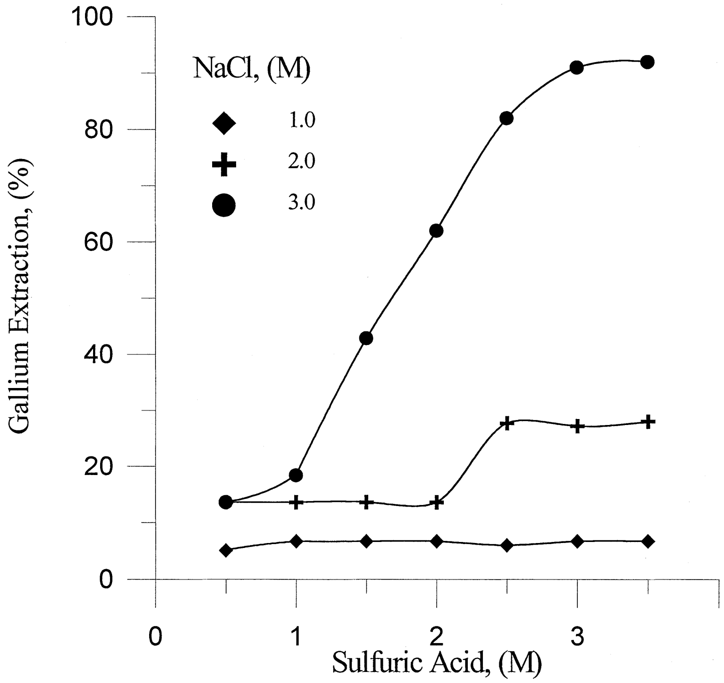

FIG. 1 Effect of sulfuric acid and sodium chloride on gallium sorption by PUF (100 mL solution, 75 μg Ga/mL, 0.30 g PUF).

move all air for column procedures. Gallium backextraction was tested with water, 2.0 M NaOH solution, and ethanol and acetone water solutions at different concentrations in percent volume–volume. The effect of time or temperature on backextraction was studied in some cases, and the concentration of the backextractor was studied in other cases. The results are shown in Table 1 and in Figs. 2 and 3.

TABLE 1
Effect of Temperature on Gallium Backextraction with 2.0 M NaOH (30 minutes shaking; 0.30 g PUF; 50 mL solution)

Temperature (°C)	Backextraction (%)	Type of procedure
25	5	Batch
35	28	Column[a]
45	34	Column
50	45	Batch
70	60	Batch
80	90	Column
80	88	Batch
80	93	Batch

[a] Column 35 × 5 mm; 2.0 g PUF.

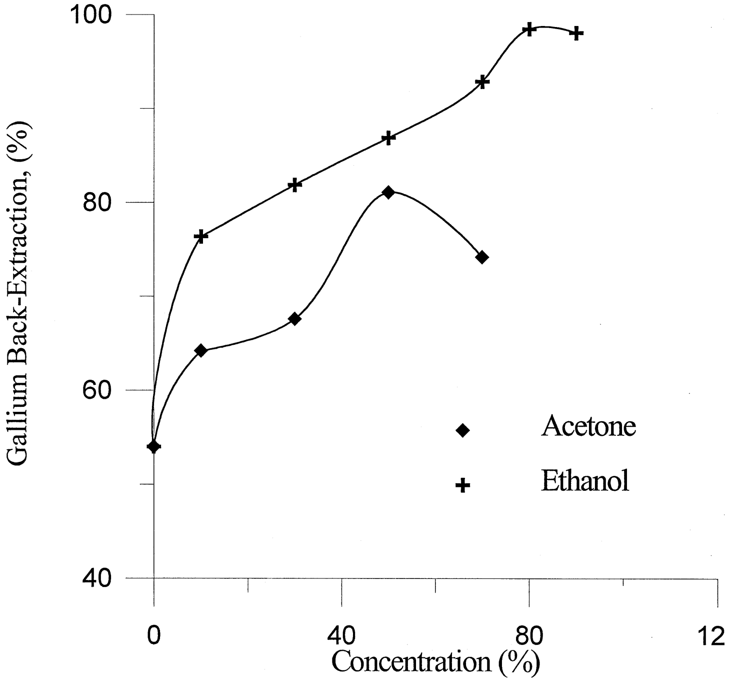

FIG. 2 Gallium backextraction with ethanol or acetone solution (0.30 g PUF loaded with 7300 μg of Ga, 50 mL solution, 30 minutes).

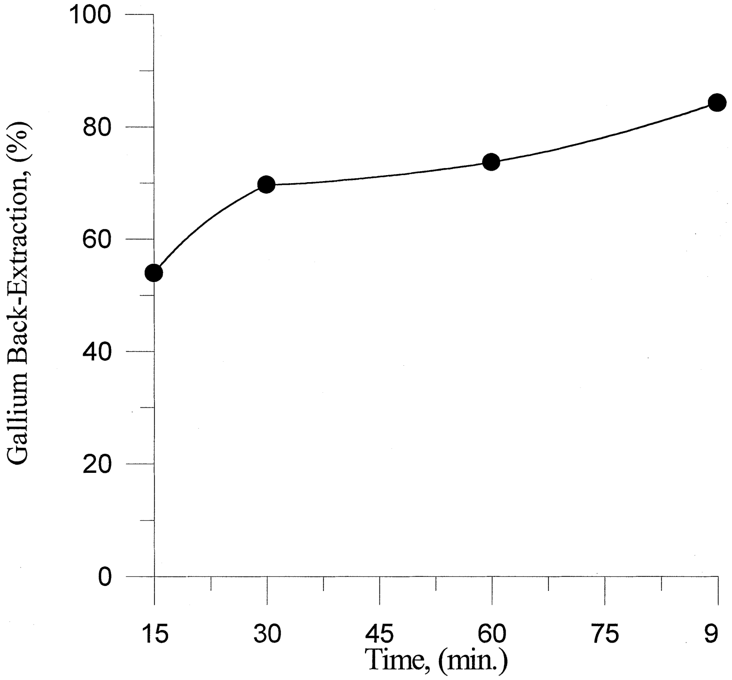

FIG. 3 Effect of time on gallium backextraction with water (same conditions as for Fig. 2).

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Characterization of Flue Dust and Gallium Acid Leaching

The flue dust was characterized by loss determination at 600°C, and the main elements were measured. The fluoride contents in both the original material and ash were determined using an ion selective electrode (ISE) of LaF (22). Aluminum, iron, and nickel contents were determined by EDTA titration (23). Gallium was determined by x-ray fluorescence (XRF) methods (19, 21). The results of material characterization are shown in Table 2. The percent weight loss in the flue dust at various temperatures was also measured and is shown in Table 2A.

A convenient amount of the flue dust put into an iron crucible was transferred to a furnace and calcinated at different temperatures. Afterward this material was weighed and submitted to different leaching procedures to solubilize gallium. Leaching with hydrochloric or sulfuric acid at different concentrations was tested, and the results are shown in Table 3. The mass/volume ratio, temperature, and leaching time were observed in all cases. Then the mixture was diluted with tap water, filtered off, and the acid and chloride concentrations were adjusted to 3.0 M with sulfuric acid and sodium chloride by adding the respective reagents when necessary. This liquor was used to extract gallium by PUF after reducing the iron by sodium dithionite. The gallium concentration in the final solution was determined by XRF.

TABLE 2
Characterization of Flue Dust

Main contents	Sample	Content (%)	Applied methodology
Loss at 600°C	Flue dust	43.85 ± 1.2	Calcination (600°C)
F^- (total)	Flue dust	22.18 ± 0.82	ISE
F^- (total)	Ash 600°C	18.72 ± 0.1	ISE
Aluminum	Ash 600°C	16 ± 1.3	EDTA, pH 3
Nickel	Ash 600°C	1.77 ± 0.8	EDTA, pH 10
Iron	Ash 600°C	1.84 ± 0.3	EDTA, pH 1.5
Gallium	Ash 600°C	0.22 ± 0.01	Polarography

TABLE 2A
Loss by Calcination of Flue Dust
(2.0000 g; 2 h)

Temperature (°C)	% Loss
200	13.4
400	23.2
600	50.3
800	53.0

TABLE 3
Acid Leaching of Flue Dust

Sample	Medium	Mass/volume	Temperature (°C)	Time (min)	% Ga leaching
Flue dust	HCl 1:1	1/3	27	420	58
Flue dust	H_2SO_4 conc	1/5	180	300	58
Ashes 600°C	HCl conc	1/5	60	180	72
Ashes 600°C	H_2SO_4 conc	1/5	180	180	88
Ashes 600°C	H_2SO_4 conc	1/3	180	180	55
Ashes 600°C	H_2SO_4 conc	1/3	180	180	51
Ashes 600°C	H_2SO_4 1:1	1/5	110	180	98
Ashes 600°C	H_2SO_4 1:1	1/5	120	120	96
Ashes 600°C	H_2SO_4 1:1	1/5	110	60	86
Ashes 200°C, 4 h	H_2SO_4 1:1	1/5	110	90	98
Ashes 300°C, 4 h	H_2SO_4 1:1	1/5	110	90	95
Ashes 300°C, 1 h	H_2SO_4 1:1	1/5	110	90	82
Ashes 200°C, 2 h	H_2SO_4 1:1	1/5	110	60	96
Ashes 200°C, 2 h	H_2SO_4 1:1	1/5	110	60	95
Ashes 200°C, 2 h	HCl 1:1	1/5	97	120	68
Ashes 200°C, 2 h	HCl 1:1	1/5	100	60	60
Ashes 200°C, 2 h	HCl 1:1	1/5	100	90	70
Ashes 300°C, 2 h	HCl 1:1	1/5	110	60	70
Ashes 300°C, 2 h	HCl 1:1	1/5	150	300	99.01
Ashes 300°C, 2 h	HCl 1:1	1/5	150	240	96.84
Ashes 300°C, 2 h	HCl 1:1	1/5	120	330	91.0

Recovery of Gallium

Gallium was extracted by PUF from 3.0 M sulfuric acid and 3.0 M sodium chloride liquor after iron had been reduced at 25°C. A mechanical WKS-100 shaker was used in the batch step for sample volumes up to 200 mL; for higher volumes of samples (up to 25 L) the system was stirred mechanically in a polyethylene reactor with rods that spun at 700 rpm. The mass of ground and dried PUF varied from 1.00 to 42.0 g as a function of sample volume and was based on 80 g Ga/kg PUF as reference of the gallium sorbing capacity of PUF (20). Two different types of columns were used: the first one was 3.50 × 0.50 cm, packed with 2.0 g of ground and dried PUF; the second one was 15.0 × 1.5 cm, with 13.0 g of PUF. Both columns were operated by vacuum at flow rates of 60 mL/min during extraction steps after removing all air. The gallium backextraction was carried out in a volume of 80% of ethanol solution (enough to cover the mixture in the batch procedure and at a flow of 6 mL/min in the column procedure). Gallium was analytically controlled in all steps by x-ray fluorescence or by EDTA complexometry.

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RESULTS AND DISCUSSION

Extraction and Backextraction of Gallium

The sulfuric acid concentrations for each 1.0, 2.0, and 3.0 M NaCl solutions ranged from 1 to 3.5 M. Gallium sorption on PUF was found to be strongly dependent on the acidity and chloride concentration, in agreement with literature (4, 16, 17) which identifies the ionic pair H^+ $GaCl_4^-$ as the extracted species. The system had maximum sorption at 3 M chloride concentration and sulfuric acid concentration within the 3 to 3.5 M range. As can be seen in Fig. 1, extraction was quantitative, little affected by sulfate content, and reached more than 95% of gallium extracted. Concentration solutions of 3 M H_2SO_4 and 3 M NaCl were used for all extraction steps in this work. Ions of such metals as Cu(II), Zn(II), Fe(II), Cd(II), TiO_2(II), Al(III), In(III), and Ti(III) were not coextracted from this medium. Fe(II) was coextracted only to a very small extent, in agreement with literature data (17–19).

The backextraction of gallium with 2.0 M NaOH solution was found to be efficient only at 80°C in both batch and column procedures (Table 1), which had not been reported in literature (15–17), and reached a maximum recovery efficiency of about 93%. When distilled water was used, the backextraction recovery efficiency was 84.3% and the procedure required as long as 90 minutes (Fig. 2). Backextraction with an 80% ethanol solution had a recovery efficiency of 98% while a 70% acetone solution had of a recovery efficiency of only 80%. There was a decrease in efficiency when a large concentration of acetone was used (Fig. 2). Backextraction was instantaneous in the batch process when ethanol or acetone solutions were used. In the column process, due to the swelling behavior of PUF in these mediums, the packed layer in the column imposed a maximum backextraction flow of 6 mL/min. This is about 10 times less than the extraction flow. In our work the system used to backextract gallium was an 80% ethanol solution.

Choice of Leaching Procedure

Table 2 shows the results of characterization tests of flue dust from an aluminum plant. As can be seen, there was a 43.85% weight loss at 600°C. This loss is mainly due to the main constituents: fluoride, sulfur, and carbon. The latter accounts for more than one-third of the total mass. The gallium content was 0.22 ± 0.01%.

To maximize acid leaching efficiency, parameters such as temperature, mass/volume ratio, acid type, and acid concentration were optimized. The choices and results are shown in Table 3.

Due to a high carbon-sulfur content in the flue dust, the shaking step in acid leaching was difficult to carry out because the dust has a large swelling gradient in this medium and therefore consumes a large amount of acid and decreases gallium leaching. A preliminary calcination of flue dust at different temperatures followed by the acid treatment was a very efficient way to overcome the problems of shaking and acid consumption. The most efficient condition was to burn the flue dust at 200°C for 2 hour and to leach it with a sulfuric acid 1:1 solution (v/v) at 110°C for 1 hour using a mass/volume ratio of 1:5. With this procedure the gallium leaching was in the 95 to 98% range as shown in Table 3. Following the acid leaching procedure, the liquor was diluted with tap water, filtered off, and the acid and chloride concentrations were adjusted to 3.0 M. Then enough sodium dithionite was added to reduce iron, which was controlled by the thiocyanate test. Then this liquor was used to recover gallium.

Recovery of Gallium from Flue Dust

The reproducibility and efficiency of the proposed procedure to recover gallium was tested. Aliquots containing 9.98, 15, 31.75, 34.92, and 44.25 mg of gallium were added to 100 mL 3 M H_2SO_4 and 3 M NaCl solutions. Table 4 shows the efficiency results for the recovery of gallium. As can be seen, an efficiency of better than 92% was reached when the gallium concentration in the solution was about 0.2 μg/mL and it was backextracted by a batch process with 2.0 M NaOH solution at 80°C. More than 98% of the gallium could also be recovered by a batch process with 80% ethanol solution.

The proposed procedure was applied to liquor samples whose volume ranged from 500 mL to 20 L. Gallium was quantitatively recovered from liquor containing up to 2800 mg Ga, as shown in Table 5. A higher salt content in the liquor contributed as a salt outing synergetic effect on gallium extraction by PUF. About 2.8 g of gallium were recovered using 42 g PUF in a batch procedure with 98% recovery efficiency. After gallium backextraction, it was precipitated with sodium hydroxide, purified by a dissolution reprecipitation step, and calcinated at 600°C. The oxide Ga_2O_3 was 98.6% pure and

TABLE 4
Recovery Efficiency of Gallium

Ga added (mg)	Ga found (mg)	Recovery (%)	Procedure characteristics
9.98	9.33	93.52	Column, 150 × 15 mm; 2M NaOH at 80°C
15.00	13.94	92.93	Batch, 2 M NaOH at 80°C
31.75	31.30	98.58	Batch, 80% ethanol; EPU reused
34.92	32.64	93.46	Column, 35 × 5 mm; 80% ethanol
44.25	41.45	93.67	Column, 35 × 5 mm; 80% ethanol; EPU reused

TABLE 5

Gallium Recovery from Residues of Aluminum Plants [backextraction: 80% ethanol, 30 min (batch); backextraction: 80% ethanol, 6.0 mL/min (column)]

Sample volume (L)	Gallium content (mg)	Mass PUF (g)	Gallium recovered (%)	Procedure used
0.50	31.0	1.00	97.7	Column
0.50	34.9	2.00	93.5	Column
0.50	44.2	2.00	98.1	Column
2.00	584.5	13.00	97.0	Batch
2.00	550.0	26.00	98.7	Batch
10.00	674.0	13.00	102.0	Column
10.00	818.0	18.00	91.0	Batch
20.00	2805.0	42.00	98.0	Batch

contained traces of molybdenum, vanadium, tin, and iron, detected qualitatively by x-ray fluorescence.

CONCLUSION

In this paper we proposed a procedure to recover gallium from flue dust residues of aluminum production plants by using solid-phase extraction with commercial polyether-type polyurethane foam. This procedure has simple laboratory operational steps, which means low costs, high efficiency, and good results compared with a conventional solvent extraction process.

Gallium could be separated from high concentrations of aluminum, iron, nickel, titanium, vanadium, copper, zinc, sulfate, fluoride, and chloride by extraction with PUF from 3 M sulfuric acid and 3 M sodium chloride solution with at least 92% efficiency of total recovery. The backextraction was fast and quantitative with an 80% ethanol solution. Commercial grade reagents could be used, including tap water, in all steps. The backextracted gallium was precipitated with sodium hydroxide solution, purified by reprecipitation, calcinated, and its final oxide was 98.6% pure.

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