Selective Extraction of Gallium from Bayer Liquor with Ion-Exchange Resin

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Abstract

Gallium is a rare and valuable raw material used in the semiconductor industry and is mostly extracted mostly from Bayer Process liquor. The dissolved gallium is removed as impurity in alumina as it coprecipitates with alumina trihydrate in the precipitation circuit. The undissolved gallium portion is removed as a small constituent of red mud. The high inventory of dissolved gallium within sodium aluminate liquor within an alumina refinery can be extracted through ion-exchange. Removal of this dissolved gallium can help in minimizing product impurity and can be used for additional revenue generation source for the refinery. The work presented in this paper is aimed at finding the most suitable liquor stream within the Bayer process and process conditions for maximum extraction of gallium using ion-exchange resins.

Keywords: Alumina refining, Sodium aluminate liquor, Gallium, Ion-exchange, Semiconductor.

1. Introduction

Gallium (Ga) is extensively utilized in integrated circuits and advanced electronic devices [2]. However, the Ga-bearing host minerals are scarce in nature. Gallium occurs in combination with several minerals, mainly aluminum, zinc, iron ores and coals. Bauxite and zinc ores as well as coals are the primary sources of Gallium [2,3] currently with the main commercial sources of Gallium presently being Bayer liquor and zinc residue.

Bayer liquor is the biggest raw material source for gallium production. It was estimated that about 90% of world's primary gallium is produced from Bayer liquor [1]. Gallium concentration in the bauxite ores is in the range of 20 to 80 ppm. In the Bayer process, approximately 70% of the Ga is leached from the bauxite into the caustic soda solution, while the remaining 30% gets disposed of with the red mud as waste [1,3]. Gallium accumulates in the Bayer liquor due to the continuous liquor recirculation and inventory, ultimately reaching to a concentration of 100–300 mg/L [3]. Ion exchange is used as a main method for gallium extraction from Bayer liquor.

Although the total installed capacity for alumina production in India is about 7 million MT, India is dependent on imported gallium. Indian bauxite contains approximately 60 ppm of gallium on average which if extracted can improve India's available gallium. Extraction from Bayer liquor will not only generate a source of revenue for the alumina refinery but also aid in improving the metal purity in product.

This study is aimed at finding suitable process conditions to remove gallium from Bayer liquor by using ion exchange resin. Experiments were conducted to select suitable liquor stream from process. Once the liquor stream was identified, experiments were conducted to find the optimum time and amount of resin required for a specified amount of liquor. Finally, the effect of temperature on recovery was studied.

2. Experiments and Results

Resin sample supplied by M/s Purolite (Puromet MTS9701), and water bath, as shown in Figure 1, was used in this test work. 100 mL of Bayer liquor samples loaded with specified amount of resin were kept at constant temperature for the required time. Samples were collected and filtered using filter paper for analysis. Separated resin was reused without washing to find adsorption capacity of the resin. Initial and final liquor samples were analyzed with ICP-OES to find Gallium concentration, caustic and alumina concentration were determined by auto titration. To test the impact of caustic and alumina concentrations, various liquor samples were taken from across the refinery, namely, aluminate liquor, spent liquor and green liquor samples. For the study, caustic soda concentration and A/C ratio were selected in usual range and is presented in Table 1.

Table 1. General concentration profile of liquor.

Liquor	*Caustic as Na_2O*	*A/C ratio as Al_2O_3/Na_2O*
Aluminate Liquor	~ 145 gm/L	~ 1.05
Spent Liquor	~ 155 gm/L	~ 0.55
Green Liquor	~ 225 gm/L	~ 0.55

Figure 1. Water bath used for test work.

2.1 Liquor Screening Test

For liquor screening, 1 g of resin was added to 100 ml of liquor and kept for 2 hours. at 60°C. Gallium recovery of different liquors is compared in Figure 2. The data indicated that the absolute maximum recovery was obtained with green liquor at 7.6 mg and 6.6 mg respectively for 100 mL. The recoveries for spent liquor were 6.9 & 6.2 mg respectively while the recoveries for aluminate liquor were 5.1 & 5.0 mg for 100mL. While absolute recovery is maximum for green liquor, recovery percentage is found to be maximum in case of spent liquor samples. Recovery percentage was calculated to be about 50% for spent liquor and around 40% for both aluminate liquor and green liquor. In view of availability of spent liquor at broad range of temperatures, further test work was conducted with spent liquor only.

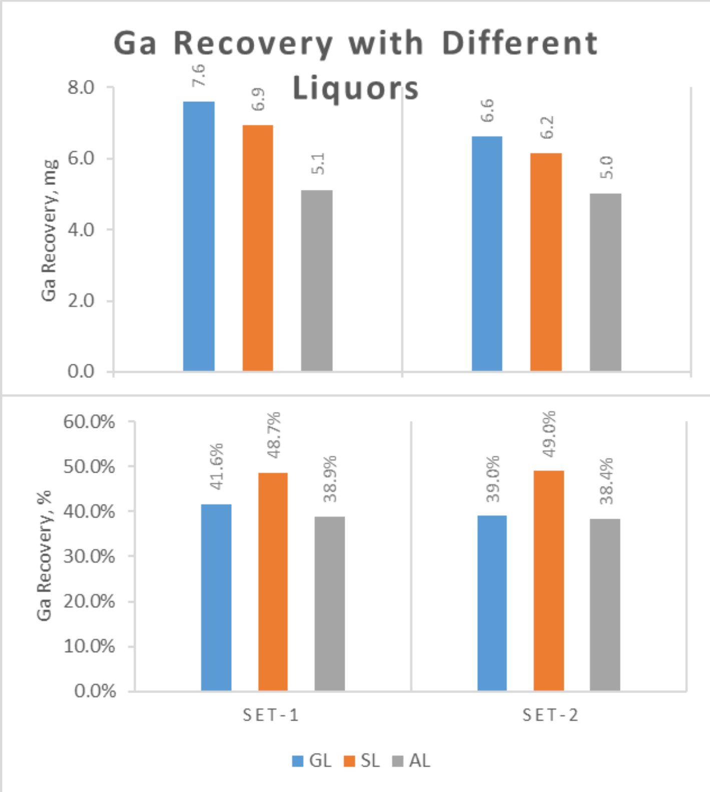

Figure 2. Gallium recovery with different liquors.

2.2 Effect of residence time on recovery

1 g of resin was added to 100 mL of spent liquor and kept for different periods to find optimum time required for maximum recovery. In the first set of tests, samples were withdrawn at 30 min, 60 min and 90 min intervals. Results are plotted at Figure 3. Results show increasing gallium recovery up to 90 minutes with maximum recovery of 49.7 %; this recovery was close to that achieved at 2 hr interval during the screening tests.

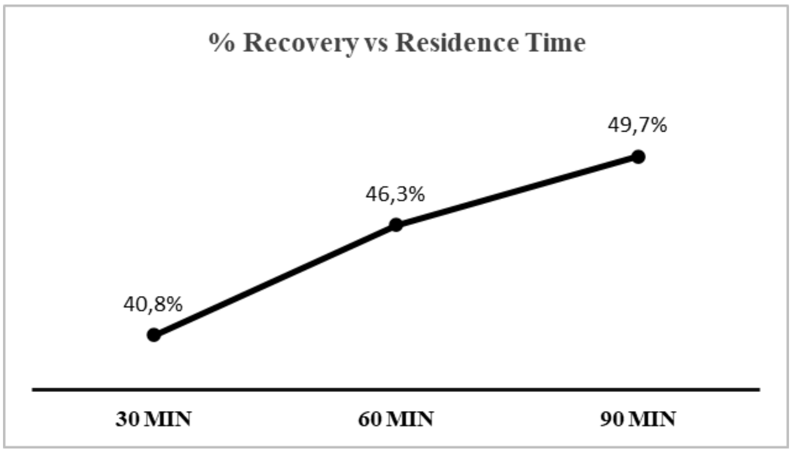

Figure 3. Gallium recovery at 30, 60 & 90 minutes.

During the second set, samples were collected at 60 min, 120 min and 180 min intervals. Results infer that the maximum recovery can be found between 60 min and 120 min time interval. Results are charted at Figure 4.

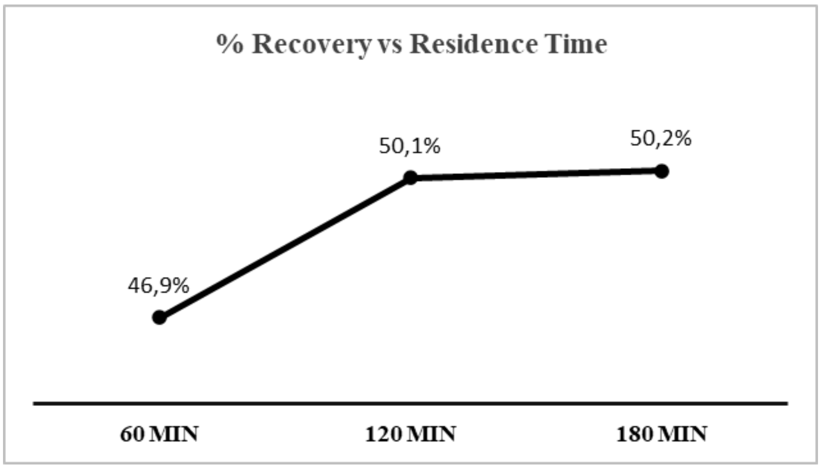

Figure 4. Gallium recovery at 60, 120 & 180 minutes.

It can be inferred from the two sets of data that optimum residence time for recovery is 90 mins as recovery did not improve significantly with higher residence time. To confirm this another set of tests is performed where samples were extracted at 45 min, 90 min and 135 min intervals. The data from set 3 confirmed the hypothesis of the optimum residence time being 90 mins with recoveries of 50.1% at 90 mins and 50.8% at 135 minutes. Results are presented at Figure 5.

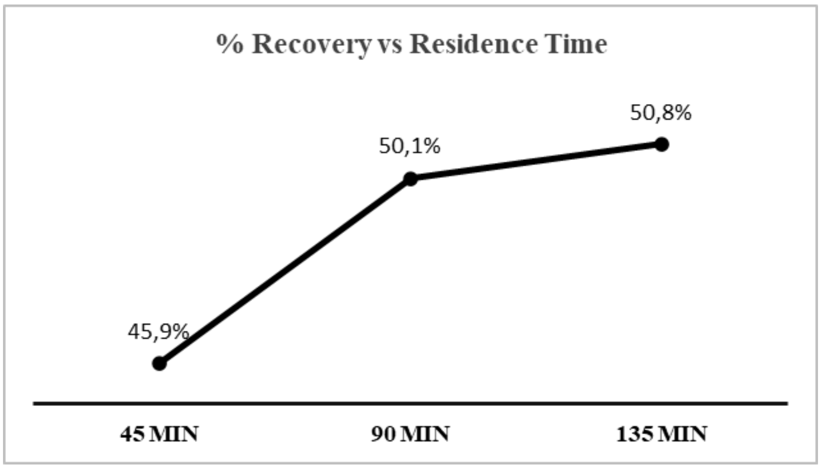

Figure 5. Gallium recovery at 45, 90 & 135 minutes.

2.3 Effect of Temperature on Recovery

To determine the impact of temperature on resin performance, 1 g of resin was added to the liquor and kept for 90 minutes at 40°C, 60°C and 80°C. Gallium recovery is plotted against temperature in Figure 6. The data indicates that gallium recovery decreases with temperature. However, there is not significant gain in recovery when temperature is reduced from 60°C to 40°C. At operating conditions, spent liquor is available at 50-55 °C.

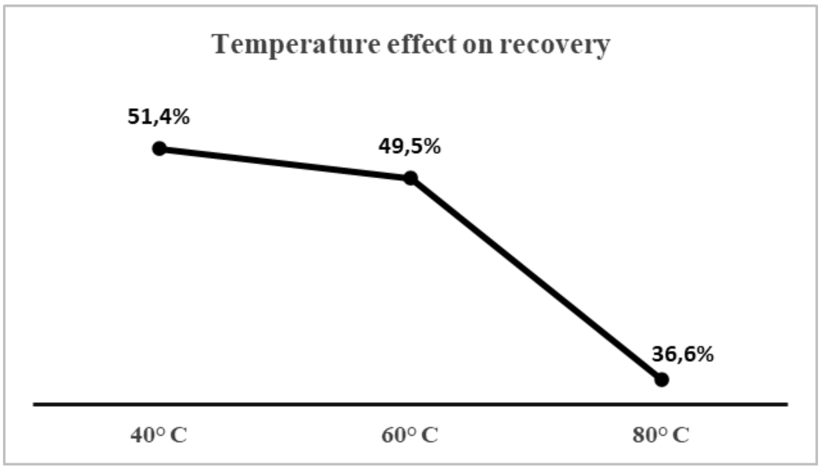

Figure 6. Effect of temperature on recovery.

2.4 Assessment of Resin Loading Capacity

To determine the resin loading capacity, 1 g of resin was added to 100 mL liquor and kept for 90 minutes at 60°C. The resin was filtered and then added to fresh liquor. It is found that the recovery reduced to about 20% for the reused resin.

The total loading capacity was calculated to be 9.2 & 9.1 mg of Ga/ g of resin. In another set, 1 g of resin was added to 200 mL of liquor and kept for 90 minutes at 60°C; the resin was then filtered and added to fresh liquor. Here recovery with filtered resin was found to be 7% and 11% with a total resin loading of 9.9 and 11.7 mg Ga/ g resin.

Table 2. Results of resin loading test.

Resin Conc, g/L		Ga_In, mg	Ga_Out, mg	Recovery, mg	% Recovery
10	Fresh Resin	12.8	6.3	6.5	50.6%
	Recycled Resin	12.8	10.1	2.7	21.0%
10	Fresh Resin	13.2	6.6	6.6	49.8%
	Recycled Resin	13.2	10.8	2.5	18.7%
5	Fresh Resin	25.6	17.6	8.1	31.5%
	Recycled Resin	25.6	23.8	1.8	7.0%
5	Fresh Resin	26.3	17.5	8.8	33.4%
	Recycled Resin	26.3	23.4	2.9	11.1%

3. Summary

Ion exchange resins can be used for selectively removing gallium ion present in Bayer liquor. Spent liquor (low caustic concentration and low A/C ratio) was found most suitable for the selected resin. It was found that a maximum recovery of 50% can be achieved at residence time of 90 minutes. Data showed that further increase in retention time did not result in significant recovery improvement. Low temperature conditions are favourable for ion exchange. However, reducing temperature below the operation temperature does not result in a sizeable improvement in recovery. Resin loading capacity is averaged at 10 mg gallium per g of resin.

4. References

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