

## AA31 - Extraction of Gallium from Jamaican Bayer Process Operations

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### Abstract

Gallium is emerging as a next generation metal that has multiple applications in the semiconductor and solar photovoltaic industry. It is mostly extracted as a byproduct of the production of aluminum and zinc metals. Gallium normally dissolves in the dominant process liquor and is recovered via processes such as solvent extraction and electrolytic processes. As the net-zero initiatives are becoming more pertinent in the global landscape, there is a need for materials that will facilitate green technologies. Gallium is one of those critical minerals that will enable this vision to become a reality. The aim of this paper is to identify the optimum path for the extraction of gallium from Jamaican Bayer process operations. Jamaica has both low and high temperature refinery operations, and there are opportunities to initiate the production of gallium in the future. Gallium in Jamaican bauxite is found to occur in the range of 48–75  $\mu\text{g/g}$ , classifying the resource as a medium gallium content bauxite. With an average of 60  $\mu\text{g/g}$  of gallium in bauxite, studies have shown that the critical metal is accumulating in the sodium aluminate process liquor as alumina is produced. This paper outlines the dispersion of gallium through a low temperature Jamaican Bayer process operation and proposes key design elements for optimizing a process that will extract the metal.

**Keywords:** Gallium, Bayer process, Gallium process balance, Gallium dispersion in the Bayer process.

### 1. Introduction

A study of the associations of gallium with aluminum and iron minerals has identified that Jamaican bauxites contain gallium concentrations in the range of 48-75  $\mu\text{g/g}$  [1]. The average concentration of gallium in Jamaican bauxites is approximately 60  $\mu\text{g/g}$ . According to global standards, this classifies Jamaican bauxites as medium gallium content bauxites. Chemical studies have also been identified that other crystallo-chemical factors can influence the presence of gallium in the crystal lattices of gibbsite, boehmite or goethite. This interaction has led to potential theories about the origin of bauxites in Jamaica.

The bauxite/alumina industry represents the greatest source of gallium in the world. This discovery is influenced by the fact that gallium concentrates in the sodium aluminate process liquor during the extraction of alumina. During Bayer process operations, the gallium concentration builds up to a steady state concentration that can be detected by analytical methods such as wet chemistry methods or via the utilization of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) [2].

A 1983 survey of gallium steady state concentrations in four (4) Jamaican alumina refineries revealed that there is a variation in gallium concentrations across operations [3]. Table 1 highlights these details below:

**Table 1. 1983 Jamaican Bayer process gallium survey [2].**

Plant	Concentration in liquor (ppm Ga)
Plant A	53
Plant B	48
Plant C	85
Plant D	185

The survey indicates that as gallium accumulates in the Bayer process liquor, it is possible to extract it using existing industrial scale gallium extraction methods. The two predominant impactors to the concentration of gallium in liquor include (i) bauxite mineralogy (ii) Bayer process plant design and operating conditions.

Temperature is a key parameter in maximizing the extraction of gallium. It is notable that Plant D, a high temperature alumina refinery, has more than two times the gallium content in its process liquor as its low temperature counterparts. Plant D also had the additional advantage of a higher caustic concentration due to higher evaporation rates.

These findings, identified in the 1980-1990 decade in alumina refining in Jamaica, show that there are good prospects for the Jamaican Bayer process operations to be expanded to extract gallium. Ongoing efforts in the research and development programs at the Jamaica Bauxite Institute aim to:

- (i) Investigate the feasibility in 2023 and beyond, of extracting gallium as a by-product of Jamaican Bayer process operations.
- (ii) Evaluate existing methods for gallium extraction (solvent extraction and ion-exchange resin) and establish the most economic method for extracting gallium from Jamaican Bayer Process liquors.
- (iii) Conduct bench scale, pilot scale and full-scale commissioning of gallium extraction operations as an appendage to Jamaican Bayer process operations.

## **2. Experiments and Results**

Preliminary studies on gallium in Bayer process operations only highlighted the presence of gallium in one sample of sodium aluminate liquor. They did not indicate the dispersion of the gallium through the entire Bayer circuit. In order to get a more thorough understanding of the dispersion of gallium through the Bayer process, a gallium profile was created. Samples collected from plant B in 2022 are highlighted below.

The samples were submitted to the Jamaica Bauxite Institute Laboratory, where the samples were filtered, diluted, and analyzed using the Agilent 5800 ICP-OES.

**Table 2. Sample collection points for Bayer process samples (Plant B).**

Sample Number	Location
1	Test Tank
2	Digester Feed
3	Digester Blow Off
4	Liquor to Precipitation
5	Liquor Decanter Underflow
6	Mud to Lake
7	Liquor from Precipitation

### 2.1 Summary for Liquor Preparation for Analysis on ICP-OES Instrument

The collected Bayer process liquor was separated from mud by a filtration process. A Whatman filter paper #1 (24.0 cm), Buchner funnel, Buchner flask and access to a vacuum pump was used to carry out the filtration. The liquor sample filtrate was transferred into a clean bottle and was labeled: straight. From this straight sample a  $\times 25$  dilution was prepared. This method was repeated for all liquor samples collected. Five Gallium (Ga) working calibration standards were prepared, at concentrations of 0, 100, 180, 260, 300 ppm, from a stock solution of 1000 ppm Gallium (Ga). They were stored in 50 mL volumetric flasks. The Agilent 5800 ICP-OES instrument was used to analyze all liquor samples for the presence of Gallium at 3 different wavelengths: 287.423; 294.363; and 417.202.

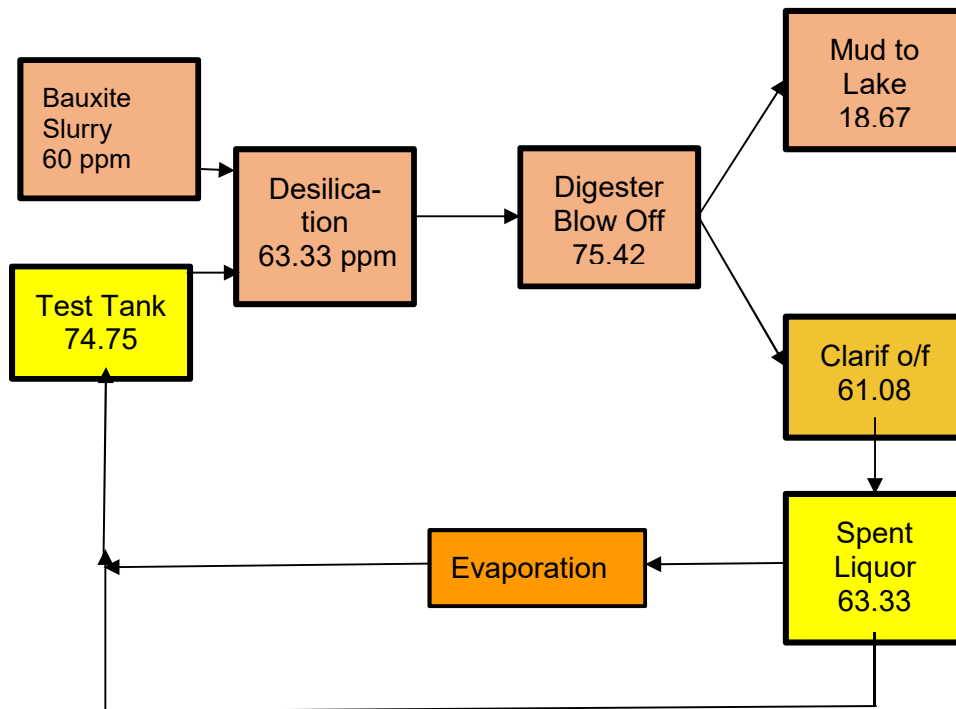
The results of the analysis are outlined below in Table 3.

**Table 3. Gallium dispersion in plant B Bayer process operations.**

LABEL	Element	Concentration /ppm
Gallium Standard	Ga (287.42) Ga (294.36) Ga (417.20)	180
Test Tank		74.75
Desilication		58.91
DBO#1 (Digester Train 1)		75.42
DBO#2 (Digester Train 2)		74.83
Decant #1 (Clarification O/f)		61.08
Decant #2 (Clarification O/f)		65.66
Mud to Lake (Clarification U/f)		18.87
Spent Liquor		63.33

Plant B is a low temperature Bayer process facility and has a two-digester operation. The dispersion of gallium in one digester train can be visualized in the process flow diagram in Figure 1.

The general process flow entails the mixing of sodium hydroxide liquor from the test tanks with bauxite slurry. This is the preparatory phase of digestion, and enables the desilication process to be initiated. After desilication, the slurry is sent to the digester unit for alumina extraction into the high temperature caustic solution. Post digestion, mud and liquor streams are collected and sent to the mud lake and to the precipitation processes respectively.



**Figure 1. Preliminary gallium Bayer process mass balance (plant B).**

### 3. Discussion

The preliminary data that was collected from Plant B is indicating that the gallium concentration is congruent with previously collected process data for a low temperature Bayer process facility (Plant C). There is clear evidence of accumulation of gallium in the digestion process to a peak of 75.42 ppm in this example of a low temperature alumina refinery. Further validation of this data, with a full profile of all operating refineries in Jamaica, will be conducted in 2023. The sodium aluminate liquor profile from Plant C, a low temperature facility, is highlighted in Table 4.

Noting that the concentration of gallium in sodium aluminate liquors is congruent across low temperature refineries, the next steps of this exercise involve identifying the factors that will maximize gallium recovery. The data will be used to facilitate the engineering design of an actual gallium extraction facility.

**Table 4. Process liquor profile for plant C [3].**

Component	Concentration
Caustic (Na <sub>2</sub> CO <sub>3</sub> )	208.22 g/L
Alumina (Al <sub>2</sub> O <sub>3</sub> )	81.08 g/L
Phosphorous (P <sub>2</sub> O <sub>5</sub> )	882.05 ppm
Vanadium (V)	360.00 ppm
Gallium (Ga <sup>3+</sup> )	85.00 ppm
Organic Carbon	1.53 g/L
Total Soda (Na <sub>2</sub> O)	141.25 g/L

### 3.1 Operating Factors that Maximize Gallium Extraction Methods

There are various methods for gallium extraction from the Bayer process, including the Carbonation, Alusuisse process and Sumitomo processes. There are also similar extractive methods for the extraction of gallium from zinc ores [4].

According to the liquor profile of Jamaican Bayer process operations, there are a few preparatory factors that will maximize gallium extraction. Preliminary studies have identified that process impurities have been found to inhibit the electrochemical deposition of gallium at the cathode, during electrolysis. For Jamaican refineries, it is therefore best to remove impurities such as vanadium and phosphorus, prior to extraction of gallium from the process feed. A prior Jamaica Bauxite Institute study [3], indicates that the ideal pre-treatment for gallium process feeds includes the key steps:

1. Evaporation (25%)
2. Causticization Phase 1
3. Inorganic Removal
4. Causticization Phase 2

Evaporation impacts the general plant water balance, and concentrates the gallium in solution, for maximum recovery. From the Plant B gallium process balance prepared above, evaporation effects are evident as the concentration of gallium increases between spent liquor and test tank liquor. There is an 11.43 ppm increase in the concentration of gallium in the Test Tank liquor in comparison to the spent liquor. The unit operation that links these two process streams is the evaporation process. Plant D, significantly benefits with its higher temperature operations, higher caustic concentration, which ultimately increases its gallium concentration.

Process feed pre-treatment, and evaporation effects will therefore be a standard for future plant designs for gallium extraction in Jamaica. The current quantification exercise will enable engineers to see how gallium accumulates in the local process, and further facilitate the engineering design for plant commissioning in the future.

#### 4. Summary

Gallium concentrations in Jamaican Bauxites were found to be in the range of 48–75 µg/g. This level is found to be comparable to other bauxite rich regions of the world such as Australia, Suriname, Greece and the USA.

Gallium in Jamaican bauxites was found to disperse in the Bayer process during alumina extraction, and predominantly remains in the sodium aluminate liquor. The concentration of the gallium in the liquor continues to increase until a steady state equilibrium concentration is achieved. This equilibrium concentration is dependent on temperature and liquor concentration.

As the global demand for gallium increases, and the relatively high concentration of gallium is detected in Jamaican bauxites, there is room for growth in Jamaican alumina refinery operations to expand to include gallium production as part of its alumina refining activities.

The next phase of this study will aim to operationalize the information that has been collated over the past four decades, via bench scale, then pilot scale extractions of gallium.

#### 5. References

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