

## Gallium Balance in a Greenfield Alumina Refinery

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### Abstract



Gallium chemistry and material balance across the Al Taweelah alumina refinery were investigated to identify the influential factors on gallium extraction from a complex chemistry perspective associated with high-temperature digestion, as well as the mechanisms of crystallisation in precipitation. The objective was to understand and improve the quality of produced alumina. In contradiction of the very limited literature on this subject, changes in the parameters of the precipitation circuit directly impacted the uptake of gallium into hydrate (the precursor product to alumina). A modelling approach was proposed to better describe the precipitation conditions that drive the incorporation of gallium into the product. Understanding and knowing how to manipulate this behavior is critical in any gallium management strategy that aims to avoid undesirable gallium contamination.

**Keywords:** Gallium extraction, High temperature digestion, Gibbsite precipitation, Alumina quality.

### 1. Introduction

Al Taweelah alumina refinery successfully started producing alumina in 2019 and has now significantly exceeded nameplate capacity. The quality of alumina produced is an important goal of this project and is largely dictated by the bauxite quality, the technology selected, and process conditions employed.

A more rigorous gallium balance investigation became important to understand the impacts of impurities and how to mitigate deviations. Gallium was selected as an in-focus element due to the desire to maintain lower contents in the product.

The aim of this paper is to provide a practical demonstration of gallium balance using plant data, to validate an observation. More fundamental work is required to understand the mechanisms involved in the observations from process information.

### 2. Gallium Review

The world's most important source of gallium is bauxite. Some authors have reported its main association with Ti minerals [1] and hematite [2,3], while the majority of the literature indicates that gallium is present primarily as a substituted element for aluminium in the aluminous minerals. Gallium is dispersed and associated with the aluminous minerals because of the similarities

between  $\text{Ga}^{3+}$  and  $\text{Al}^{3+}$ . The two occupy the same structural positions in minerals, maintaining a nearly constant Al:Ga ratio [4]. Therefore, it is likely that gallium in bauxite is distributed amongst the aluminium bearing mineralogy at a relatively constant Al:Ga ratio (i.e., within gibbsite, boehmite, and kaolin). Importantly, aluminium is also substituted in goethite and to a lesser extent in hematite. It's likely also that gallium is present in the iron mineralogy at a relatively constant ratio with the substituted aluminium. The constant Al:Ga ratio implies that the gallium content in various bauxite ores should also be relatively constant, tied more to the alumina content of the bauxite, rather than the source of the bauxite. In fact, a study of gallium concentrations for bauxite deposits worldwide found that the gallium concentrations in lateritic bauxites was on average 77 ppm  $\text{Ga}_2\text{O}_3$ , and, for karst bauxite deposits, an average of 78 ppm  $\text{Ga}_2\text{O}_3$ , indicating that there are no substantial differences in gallium concentrations between karst- and laterite-type bauxites [5].

Al Taweelah alumina refinery employs a high temperature digestion process (i.e., 280 °C). During digestion of bauxite for the production of alumina, a fraction of gallium is extracted along with the aluminium species. Within the literature, it is reported that approximately 70 % of the gallium is extracted from the bauxite into the liquor, the remaining 30 % being disposed with bauxite residue [6–8]. There is very limited information available in the literature regarding the digestion process conditions and liquor that would impact gallium extraction yield from the bauxite.

The aqueous chemistry of gallium is very similar to aluminium. In concentrated caustic solution, aluminium forms a monomeric tetrahedral hydroxo complex  $[\text{Al}(\text{OH})_4^-]$ , and in very concentrated aluminate solutions, an oxo-bridged dimer is also formed. Gallium is more soluble in caustic however, and it has been found that only the tetrahedral hydroxo complex  $[\text{Ga}(\text{OH})_4^-]$  species predominates. Despite the similarities between Al and Ga (very similar atomic/ionic sizes) this differing behavior was attributed to the different chemistry and physics of gallates and aluminates, with the study concluding that gallates are more compact structures than aluminates [6].

In the Bayer process, gallium will dissolve in the caustic liquor and only reaches quite low concentrations, typically between 100 to 500 ppm, far below its solubility. The pregnant Bayer liquor, containing this small amount of gallium will determine the incorporation in the product.

Shaw et al [7] examined the incorporation of gallium into precipitated gibbsite as a function of gallate concentration in batch precipitation tests (96 h, 50–200 g/L seed, alumina to caustic ratio (A/C) 0.5 to 0.7, total caustic level (C) 180g/L, caustic to total alkali ratio (C/S) 0.818, 60 °C). At these conditions they found that the gallate concentration is linearly related to the gallium content in product (4 % uptake) and that it is likely incorporated by isomorphous substitution. Isomorphous substitution is the substitution of atomic gallium for aluminium in the structure of gibbsite. While the authors claim that temperature also has no impact, the data in this paper is contrary to this finding.

A proper gallium removal system in an alumina refinery brings few benefits. The main direct benefit is the production of gallium metal for commercial application. The indirect benefit is a reduction in gallium in product, hence improving product quality. Understanding the balance well can provide a way to mitigate product quality issues, without necessarily installing a gallium removal process.

### 3. Gallium Balance in the Refinery

The main input of gallium is bauxite. Major outputs are with bauxite residue, both as physical phase (soluble) and as solid phase and majority of the output reports to the calcined alumina as a trace element. Figure 1 represents a simplified version of the Bayer process with the most relevant points for the balance of gallium. Measurements of bauxite, mud, and alumina were done via X-

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