Abstract

Bauxites contain trace elements which have not been leached from their parent rock, but have instead remained in the composition of bauxite. During the refining of alumina from bauxites, these trace elements will also be introduced to the Bayer process along with the major bauxite constituents. This paper describes a study on the distribution of the trace elements gallium (Ga), vanadium (V), cerium (Ce), yttrium (Y) and thorium (Th) through the Bayer process. The first four elements can potentially be extracted as Bayer process by-products, whereas Th should be analysed due to its potentially adverse impact. Case-by-case examination showed that most of the trace elements end up entirely in bauxite residue. It was found that Ga accumulation was in an average range compared to previous reports and there is potential for the economic extraction of this metal. V was also found to accumulate in Bayer liquor in a similar amount to that reported previously, but was absent from the aluminium hydroxide product, with the majority ending up in bauxite residue. Practically all of the Ce, Y and Th were found in bauxite residue after bauxite processing. For the trace elements entirely ending up in bauxite residue, a method is proposed for predicting their content in residue based on their concentration determined in bauxite feed.

Keywords: Bayer process, trace elements, bauxite residue, cerium, yttrium.

1. Introduction

The presence and importance of many trace elements found in bauxites has been acknowledged decades ago, as well as their transfer into bauxite residue or product alumina during the Bayer process [1 – 3]. When entering the process, the significance of trace elements can be one or more of the following: 1) control over undesired impurities that might end up in the product (e.g. V); 2) extracting a trace element as a by-product of alumina production (e.g. Ga); 3) environmental and occupational health considerations (e.g. Th).

Along with existing and emerging trace element extraction technologies from the Bayer circuit and bauxite residue, some aspects of the mechanisms of partitioning needs be broadened to better describe and predict the behaviour of these trace elements in the Bayer process.

Bauxites of karstic type are known to be more enriched in trace elements compared to lateritic bauxites [4]. This fact has led to many studies with regards to rare earth element distribution and their extraction from bauxite residue, especially with respect to the Mediterranean bauxite belt of karstic type deposits [5, 6]. In this study, we also give attention to the refinery of Aluminium of Greece (AoG) processing Parnassos-Ghiona karstic bauxite as well as imported lateritic bauxite.
Bauxite ores are the main source of present day Ga production, whereas a lesser amount is produced from zinc ores [7]. It is estimated that 8 – 21 % of the Ga recovery potential from alumina refineries is being exploited based on year 2011 data, indicating a growth potential for this industrial process [8]. Ga is recovered from a Ga-enriched side stream of Bayer liquor which is returned to the process after the extraction of Ga [9]. Feasible methods for the recovery of Ce and Y from Bayer process solids exist, but are currently not exploited industrially, while V by-products are being commercialised to some extent [10 – 13].

Several studies have analysed trace element concentrations in various bauxite types and derived residues. Commonly, the authors synonymously conclude that most trace elements are enriched into bauxite residue except for Ga [2, 14 – 16]. In addition, Ochsenkühn-Petropulu et al. report enrichment factors of rare earth elements from bauxite to residue, ranging from 1.7 to 2.3 with an average of 2.0 [17]. Ga and V concentrations in Bayer process liquors are given in several sources [18 – 25]. One of the pioneering overviews examining Ga as a Bayer process by-product is compiled by Hudson and an examination of the system is given there [3].

In addition to analysing Bayer solids, Sato. et al. have analysed the concentration of Th and uranium (U) in Bayer liquors [26]. A mass balance approach, where all significant material flows are considered to describe the distribution of trace elements, is used by Adams and Richardson for describing Th and U behaviour [1], by Derevyankin et al. to report the routes taken by scandium and lanthanum [27], and Papp et al. which details the mass balance of molybdenum and zinc in the Bayer process [28]. Th partitioning in bauxite and derived residue has also been explained in mineralogical and beneficiation terms [29 – 31].

While Th has been covered to some extent, to the best to our knowledge, the distribution of Ga, V, Ce and Y throughout the Bayer process using a mass balance approach has not been presented in the open literature. This study’s aim is to analyse the mass distribution of these trace elements as well as to examine if some distribution patterns are different from those previously reported, especially when high temperature digestion (255 °C) is applied, as is the case for AoG due to exploitation of boehmitic/diasporic bauxites. Our literature review revealed that while there are many publications available indicating trace element concentrations in bauxites, aluminium hydroxide and in Bayer liquors, they can’t be related to their mass flows during bauxite processing. Ga has recently received attention from a resource availability point of view [7, 8, 32]. Frenzel et al. published an analysis “On the current and future availability of gallium”, which reviewed Ga production from several sources and provided relevant economic estimations. They specifically emphasized the lack of information available regarding Ga mass balance data related to alumina industry, in their words [7]:

“Authors never state relative mass or even volume flow rates.”

This deficit clearly made their, and other authors’ task more complex and caused higher uncertainties [7, 8, 32]. Frenzel et al. did, however, compile a mathematical mass balance model of Ga distribution based on available facts and knowledge, while mass flow data, which are a crucial input for estimating resource availability, were deduced as indirect estimates [7]. This study hopes to provide a critical input for future Ga and other trace metals availability estimations.

Ga and V were chosen because of their well-known attribute of being enriched in Bayer liquor, as well as their present and prospective economic value. Ce and other rare earth elements may also become valuable bauxite processing by-products in the near future due to an increasing demand for these elements and their availability in some bauxite residues [10, 33, 34]. Thus, Ce was chosen as a representative of the ceric or light rare earth elements (lanthanum to gadolinium) as, of these elements, it exists in the highest concentration. Y was chosen to
process liquor is above the suggested cut-off concentration of 240 mg/l, indicating a possibility for economic extraction of Ga from the circuit.

The accumulation of V in process liquors is comparable to previous analyses. It is effectively controlled as a side benefit of lime added to the process, that precipitates excess V and thus avoids its unwanted transfer to alumina product. Since the range of V concentrations in Bayer liquors was 300 – 400 mg/l, it can be concluded that the accumulation of V into process liquor is not affected by its relatively higher abundance in karstic bauxite.

Although Ga and V are found and known to accumulate in Bayer liquor, no presence of liquor Ce, Y or Th was detected. Almost the entire mass of V, Ce, Y and Th entering the process from the bauxites are separated with the balance of bauxite residue at the end of the cycle. Combining this property and the stability of iron oxide phases during the Bayer process, a simple method for predicting trace element concentration in bauxite residue based on iron oxide concentration in bauxite and derived residue as well as average trace element concentration of the bauxite feed is proposed. The given mass balances of trace elements in the Bayer cycle that were previously absent from the open literature can be used as inputs to availability and resource estimations.

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6. References


