

## Distribution of Trace Elements Through the Bayer Process and its By-Products

Johannes Vind<sup>1</sup>, Vicky Vassiliadou<sup>2</sup> and Dimitrios Panias<sup>3</sup>

1. PhD Candidate, National Technical University of Athens, School of Mining and Metallurgical Engineering, Athens, Greece

2. Head of Continuous Improvement and Systems Management, Aluminium of Greece, Agios Nikolaos, Boeotia, Greece

3. Professor, National Technical University of Athens, School of Mining and Metallurgical Engineering, Athens, Greece

Corresponding author: johannes.vind@alhellas.gr

### 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

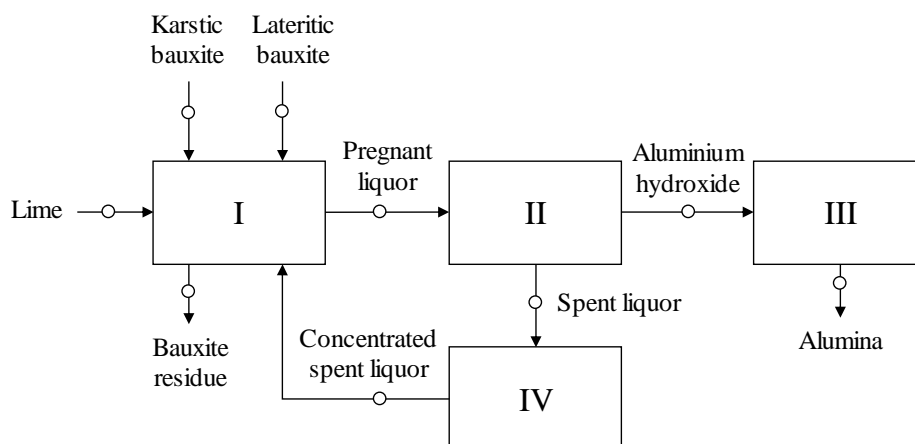
represent the distribution of yttric or heavy rare earth elements (Y and terbium to lutetium) [35]. Based on this analysis, suggestions as well as systemic assumptions are given for predicting trace element behaviour in the Bayer process.

## 2. Materials and Methods

### 2.1. Sampling and Technological Data

Samples were collected in the Aluminium of Greece (AoG) refinery located in Agios Nikolaos, Boeotia, in central Greece. Sampling took place over a two-day period and materials were collected from key points in the process flow sheet to provide a snapshot of the whole process (Figure 1). AoG uses mainly two types of feed bauxites: locally mined karstic bauxite and imported lateritic bauxite. The Greek karstic bauxite samples originate from the Parnassos-Ghiona B3 horizon, which is the youngest and most exploited horizon of the deposit [36]. The Greek karstic bauxite sample in our study at AoG is the result of mixing bauxites from two different mining locations and subjecting them to beneficiation by removing limestone by heavy media separation [37]. The lateritic bauxite used at AoG originates from Trombetas.

Bauxite samples were collected from stockpiles as composite samples as a best representation of the feed material. Bayer liquors, aluminium hydroxide, alumina and lime samples were collected from the appropriate sampling points according to the internal protocols of AoG. A composite sample of bauxite residue was collected after the filter pressing of the residues. Fresh sodium hydroxide addition to the process was negligible during the sampling period and was therefore excluded from the analysis. Process data for both solid and the liquid mass flows were acquired for the same period as sampling.



**Figure 1. Simplified flow sheet of the Bayer process indicating the sampled materials.**

The following production units are depicted in Figure 1 above: I — digestion, settling, washing; II — precipitation; III — calcination; IV — evaporation.

### 2.2. Chemical Analysis

Solid samples were fused with lithium metaborate/tetraborate flux along with lithium bromide as non-wetting agent and the resulting beads were dissolved in 10 % nitric acid to ensure the total dissolution of the material matrix. Derived solutions were analysed by inductively coupled plasma mass spectrometry (ICP-MS) for Ga, Ce, Y and Th. Ga in alumina, and V in all solids were determined by X-ray fluorescence (XRF) spectrometry on the fused glass beads, the method applied in AoG. Fusion was chosen because this method has been proven to provide

total dissolution of nearly all chemical elements over a range of tested certified bauxite reference materials, bauxite and bauxite residue samples compared to different acid digestion methods [16, 38]. In XRF, fusion beads provide a more reliable analysis compared to powder scans because grain size heterogeneity and mineralogical effects are minimised [39]. Bayer liquor samples were acidified with nitric acid by the following method: 1) sample was diluted 1:10 with distilled water; 2) 5 ml of concentrated nitric acid was added to 5 ml of diluted sample while gently heating it; 3) resulting solution was made up to 50 ml mark of volumetric flask with distilled water [40]. Ga and V were subsequently analysed in inductively coupled plasma atomic emission spectroscopy (ICP-OES), and the detection of Ce, Y and Th were attempted by ICP-MS. All analyses with a few exceptions were in duplicate.

### 2.3. Compiling of the Mass Balance

The results from chemical analysis were used in combination with mass flow data and normalised to the mass of produced alumina ( $\text{Al}_2\text{O}_3$ ) according to Equation (1). The mass balance approach to describing trace element distribution were based on the method given by Papp et al. [28].

$$a = \frac{c \times m_1}{m_2} \quad (1)$$

Where: a                      normalised concentration of trace element, mg/kg  $\text{Al}_2\text{O}_3$   
 c                              measured concentration of trace element in solid, mg/kg; or liquid, mg/l  
 $m_1$                         mass flow of material on dry basis, kg/d; or liquor flow  $\text{m}^3/\text{d}$   
 $m_2$                         mass flow of alumina, kg/d

### 3. Results and Discussion

The measured trace element concentrations are given in Tables 1 and 2 for both solid and liquid samples. Enrichment factors express the ratios of bauxite residue, alumina or pregnant liquor concentration to feed bauxite concentration to express the magnitude of enrichment or depletion (Table 2). Error margins, reported as one standard deviation ( $\sigma$ ), are slightly high for the analysed liquors, but generally remain within the 10 % relative limit. The mass balance for trace elements is given in Table 3, presented on alumina normalised basis as mg/kg  $\text{Al}_2\text{O}_3$ . The section *Internal balance* considers both solids and liquids entering and exiting the process. The section *External balance* considers only solid materials as the inputs and outputs of process.

**Table 1. Trace element concentrations in the analysed materials in mg/kg.**

	<b>Ga</b>	<b>V</b>	<b>Ce</b>	<b>Y</b>	<b>Th</b>
	mg/kg				
Karstic bx	$62 \pm 2$	474	$199 \pm 0.2$	$48 \pm 0.4$	$56 \pm 0.1$
Lateritic bx	$60 \pm 2$	258	< 2	$11 \pm 2$	< 2
Weighted average of total bauxite feed	61	428	157	40	44
Lime	< 2	$64 \pm 0.6$	< 2	< 2	< 2
Bauxite residue	$41 \pm 0.2$	1020	$363 \pm 9$	$90 \pm 1$	$105 \pm 3$
Aluminium hydroxide	85*	< 10*	< 2*	< 2*	< 2*
Alumina	85	< 10	< 2	< 2	< 2

Error margins are reported as 1 sigma; where missing, it is due to absence of duplicate measurements; \* on calcined basis.

**Table 2. Trace element concentrations in liquor samples given in mg/l.**

	<b>Ga</b>	<b>V</b>	<b>Ce</b>	<b>Y</b>	<b>Th</b>
	mg/l				
Concentrated spent liquor	367 ± 51	426	< 0.04	< 0.04	< 0.2
Pregnant liquor	267 ± 26	295 ± 13	< 0.04	< 0.04	< 0.2
Spent liquor	280 ± 15	315 ± 20	< 0.04	< 0.04	< 0.2
	<b>Enrichment factors</b>				
	<b>Ga</b>	<b>V</b>	<b>Ce</b>	<b>Y</b>	<b>Th</b>
Alumina / bauxite	1.39	-	-	-	-
Bauxite residue / bauxite	0.66	2.38	2.31	2.23	2.37
Pregnant liquor / bauxite	25.1	3.97	-	-	-

Error margins are reported as 1 sigma; where missing, it is due to absence of duplicate measurements. In the lower section are given the enrichment factors.

**Table 3. Mass balance of selected trace elements in different Bayer process units, normalised and expressed as mg/kg of produced alumina (Al<sub>2</sub>O<sub>3</sub>).**

		<b>Ga</b>	<b>V</b>	<b>Ce</b>	<b>Y</b>	<b>Th</b>
		mg/kg Al <sub>2</sub> O <sub>3</sub>				
<b>I Digestion</b>	In: Karstic bx	94 ± 3	726	305 ± 1	74 ± 1	86 ± 0.1
	Lateritic bx	24 ± 1	105	bdl	4 ± 1	bdl
	Concentrated spent liq.	2729 ± 388	3168	bdl	bdl	bdl
	Lime	bdl	4 ± 0.04	bdl	bdl	bdl
	<b>Sum</b>	<b>2847 ± 377</b>	<b>4003</b>	<b>305 ± 1</b>	<b>78 ± 1</b>	<b>86 ± 0.1</b>
	Out: Bauxite residue	33 ± 0.2	830	296 ± 7	73 ± 1	86 ± 2
	Pregnant liq.	2981 ± 284	3292 ± 146	bdl	bdl	bdl
	<b>Sum</b>	<b>3014 ± 284</b>	<b>4122 ± 146</b>	<b>296 ± 7</b>	<b>73 ± 1</b>	<b>86 ± 2</b>
	<i>Difference</i>	<i>6 %</i>	<i>3 %</i>	<i>- 3 %</i>	<i>- 6 %</i>	<i>- 0.6 %</i>
	<b>II Precipitation</b>	In: Pregnant liq.	<b>2981 ± 284</b>	<b>3292 ± 146</b>	bdl	bdl
Out: Aluminium hydroxide		85	bdl	bdl	bdl	bdl
Spent liq.		2910 ± 152	3274 ± 212	bdl	bdl	bdl
<b>Sum</b>		<b>2995 ± 152</b>	<b>3274 ± 212</b>			
<i>Difference</i>		<i>0.5 %</i>	<i>- 0.6 %</i>			

**Table 3 (continued).**

			<b>Ga</b>	<b>V</b>	<b>Ce</b>	<b>Y</b>	<b>Th</b>
			mg/kg Al <sub>2</sub> O <sub>3</sub>				
<b>III Calci- nation</b>	In:	Aluminium hydroxide	<b>85</b>	bdl	bdl	bdl	bdl
	Out:	Alumina	<b>85</b>	bdl	bdl	bdl	bdl
		<i>Difference</i>	0.0 %				
<b>IV Evapo- ration</b>	In:	Spent liq.	<b>2910 ± 152</b>	<b>3274 ± 212</b>	bdl	bdl	bdl
	Out:	Concentrated spent liq.	<b>2729 ± 377</b>	<b>3168</b>	bdl	bdl	bdl
		<i>Difference</i>	- 6 %	- 3 %			
<b>Internal balance</b>	In:	Karst bx	94 ± 3	726	305 ± 1	74 ± 1	86 ± 0.1
		Lateritic bx	24 ± 1	105	bdl	4 ± 1	bdl
		Concentrated spent liq.	2729 ± 377	3168	bdl	bdl	bdl
		Lime	bdl	4 ± 0.04	bdl	bdl	bdl
		<b>Sum</b>	<b>2847 ± 377</b>	<b>4003</b>	<b>305 ± 1</b>	<b>78 ± 1</b>	<b>86 ± 0.1</b>
	Out:	Alumina	85	bdl	bdl	bdl	bdl
		Spent liq.	2910 ± 152	3274 ± 212	bdl	bdl	bdl
		Bauxite residue	33 ± 0.2	830	296 ± 7	73 ± 1	86 ± 2
		<b>Sum</b>	<b>3028 ± 152</b>	<b>4104 ± 212</b>	<b>296 ± 7</b>	<b>73 ± 1</b>	<b>86 ± 2</b>
		<i>Difference</i>	6 %	3 %	- 3 %	- 6 %	- 0.6 %
<b>External balance</b>	In:	Karst bx	94 ± 3	726	305 ± 1	74 ± 1	86 ± 0.1
		Lateritic bx	24 ± 1	105	bdl	4 ± 1	bdl
		Lime	bdl	4 ± 0.04	bdl	bdl	bdl
		<b>Sum</b>	<b>118 ± 4</b>	<b>835</b>	<b>305 ± 1</b>	<b>78 ± 1</b>	<b>86 ± 0.1</b>
	Out:	Alumina	85	bdl	bdl	bdl	bdl
		Bauxite residue	33 ± 0.2	830	296 ± 7	73 ± 1	86 ± 2
		<b>Sum</b>	<b>118 ± 4</b>	<b>830</b>	<b>296 ± 7</b>	<b>73 ± 1</b>	<b>86 ± 2</b>
	<i>Difference</i>	- 0.6 %	- 0.5 %	- 3 %	- 6 %	- 0.6 %	

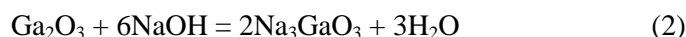
Error margins are reported as 1 sigma; where missing, it is due to absence of duplicate measurements; bdl — below detection limit.

### 3.1. Distribution of Ga

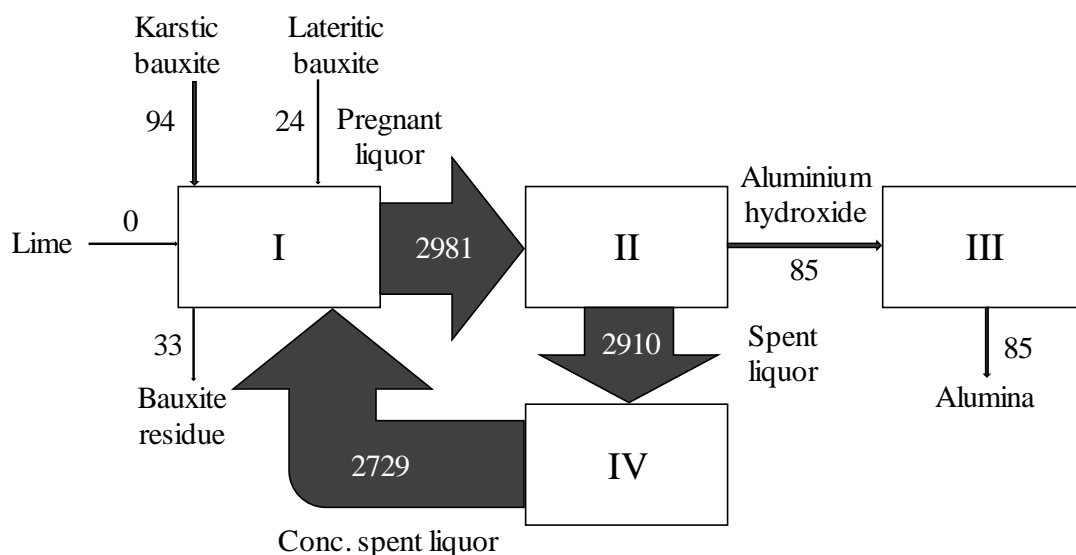
There was virtually no difference in the Ga concentrations in the two bauxites of different origin. This is in line with the report by USGS, where they found a similar presence of Ga in karstic and lateritic bauxites. They summarise the world average Ga concentration in all analysed bauxite deposits as being 57 mg/kg, which is similar to this analysis — 62 mg/kg and 60 mg/kg, in karstic and lateritic bauxites respectively [41]. The Ga concentration in Greek

bauxite residue is comparable to a recent publication (41 mg/kg in present work and 39 mg/kg in literature) [30].

The mass distribution of Ga is mainly controlled by process liquors (Figure 2). During bauxite digestion, Ga is released from aluminium-bearing minerals like gibbsite, boehmite and diaspore [42]. The Ga digestion reaction is described by Equation (2) [43]:



Ga accumulates in process liquors, achieving saturation at levels exceeding 300 mg/l. This is about the average of that reported across earlier publications (60 – 600 mg/l Ga), yet typically shown values remain between 100 – 200 mg/l Ga [18 – 23]. The present Ga saturation levels are prospective for economic extraction given that Frenzel et al. suggest a conservative cut-off concentration for profitable production of Ga from process liquor being 240 mg/l [7]. The enrichment factor is 25 (Ga in liquor compared to Ga in bauxite). Even though the highest concentration of Ga was detected in concentrated spent liquor, the highest relative amount of Ga (allowing for volumetric changes from gibbsite precipitation and liquor evaporation) was found in pregnant liquor. This is because freshly leached Ga in digestion is present in pregnant liquor, while some Ga is precipitated along with gibbsite during precipitation and so removed from the concentrated spent liquor stream.



**Figure 2. Distribution of Ga in the Bayer process, expressed in mg/kg  $\text{Al}_2\text{O}_3$ .**

From the pregnant liquor, 71 % of Ga entering the process is precipitated with aluminium hydroxide (85 mg/kg  $\text{Al}_2\text{O}_3$ ) (Table 2). This impurity, however, has no adverse effect on the quality of smelter grade alumina [43]. A smaller proportion of 28 % reports to bauxite residue (33 mg/kg  $\text{Al}_2\text{O}_3$ ). The mass difference between the entering and exiting portion of Ga is negligible. For the purposes of modelling of Ga distribution, Hudson has indicated, and Frenzel et al. have applied the partitioning of Ga as 35 % going to bauxite residue and 65 % to hydrate product [3, 7]. From this analysis, the partitioning is more in line with that reported by Figueiredo et al., with 30 % of Ga going to bauxite residue, and 70 % to hydroxide product. This analysis therefore supports the literature that suggests about 70 % of bauxite Ga is digested in the Bayer process, that this part is subsequently precipitated into aluminium hydroxide, and roughly 30 % of Ga is separated with bauxite residue [3, 18].

### 3.2. Distribution of V

Almost twice as much V is contained in the karstic bauxite (471 mg/kg) compared to the lateritic bauxite (258 mg/kg). Given the different proportions of bauxites in the feed, the major input of V is therefore from karstic bauxite (87 %). Of the trace elements studied, only V has a minor secondary process input from the lime feed. In a recent report, V concentration in Greek bauxite residue has been reported as 1081 mg/kg, our measurement is slightly lower at 1020 mg/kg, indicating a fluctuation over time [30], and/or sampling and analysis variations.

The mass distribution of V is again mainly regulated by process liquors, where the concentration of V exceeds 400 mg/l in concentrated spent liquor (Figure 3). This is in accordance with the range of V saturation levels in Bayer liquors reported in several publications (100 – 2800 mg/l V) [18, 22, 24, 25]. Authier-Martin et al. refer to earlier studies indicating that V is about 30 % soluble during Bayer digestion [43]. Compared with bauxite feed on alumina normalised basis, V is enriched in pregnant liquor up to 4 times in this study. In process liquors, V appears in the form of  $\text{VO}_4^{3-}$  [43]. This impurity is unwanted in hydroxide and metal production due to its known property of decreasing the electric conductivity of metallic aluminium, causing a green hue in fused alumina, and the scale it can form in the piping of a Bayer refinery when precipitated from the liquor in the cooler parts of the circuit [25, 43, 44]. The removal of V from process liquors is a side benefit of process lime addition. V precipitates as calcium vanadate, as an impurity in tri-calcium aluminate ( $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ ), or as  $\text{Na}_7(\text{VO}_4)_2\text{F}\cdot 19\text{H}_2\text{O}$ , as identified by Okudan et al. [25, 45, 46]. Our study did not detect any V in the aluminium hydroxide product (< 10 mg/kg). Therefore, lime addition that mainly reduces soda losses among other beneficial effects, is simultaneously providing a way to remove excess V from the Bayer cycle and preventing V precipitation to product. In the existing case study, V is separated from the process and is accumulated in the bauxite residue (99.5 % of total V input). No other significant V-containing by-product is formed.

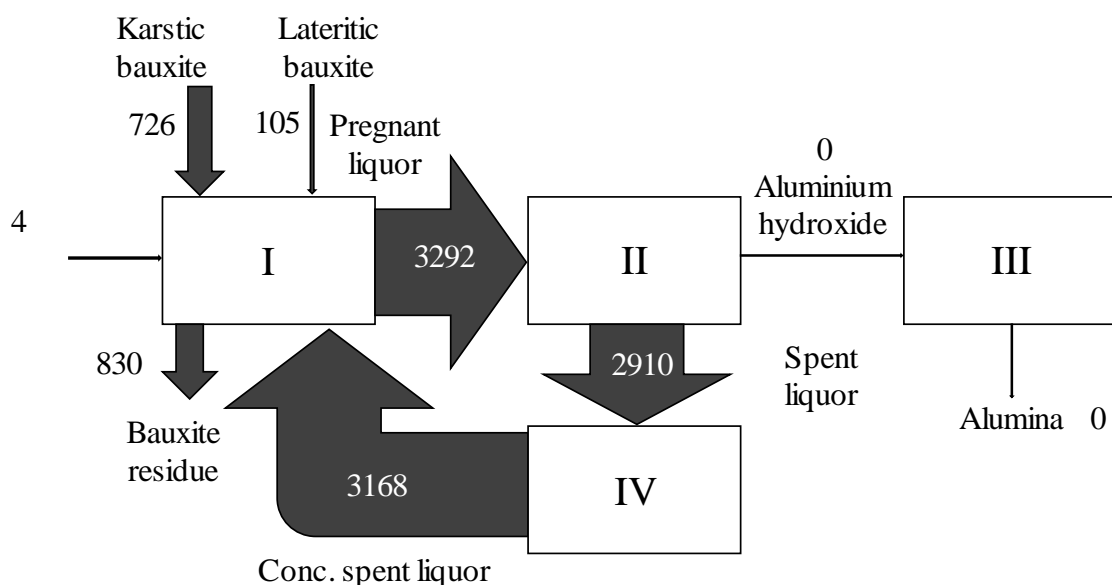


Figure 3. Distribution of V in the Bayer process, expressed in mg/kg  $\text{Al}_2\text{O}_3$ .

### 3.3. Distribution of Ce, Y and Th

Although chemically different, Ce, Y and Th can be discussed as one group given their similar mass distribution in alumina production. Clearly the sole input of Ce and Th is from karstic bauxites, whereas a minor contribution (6 %) of Y comes from lateritic bauxite. The differences

in bauxite residue concentrations compared to earlier reports are broader for this group of elements. For instance, 439 mg/kg of Ce has been reported in bauxite residue while our estimation is 363 mg/kg, a 17 % of difference [30].

In Bayer liquors, Ce, Y and Th were not found (Ce, Y < 0.04 mg/l; Th < 0.2 mg/l). For Th, this behaviour was indicated earlier [26]. This leaves the conclusion that the only route for these elements is into bauxite residue, since neither were these metals found in product samples (Figure 4). At the end of the cycle, 3 % of the initial amount of Ce, 0.6 % of Th and 6 % of Y are missing and accounted as losses or errors in estimation, but the possibility of minute amounts passing to processing liquor or alumina also remain.

While the differences between the input and output masses of Ce and Th are within reasonable limits, the Y balance discrepancy is slightly too high. It could be argued that the Y concentration found in lateritic bauxite is a result of an erroneous analysis. The question also arises, why should lateritic bauxite contain Y yet no Ce, while light rare elements are commonly more abundant in various rock types [47]? This would explain the mismatch between Y input and output. Regardless of this discrepancy, it can be concluded that basically all Ce, Y and Th ends up in bauxite residue after bauxite processing, and their distribution is controlled only by solid flows. If no Ce, Y and Th was dissolved into the processing liquor during high temperature digestion, it is reasonable to assume that same is true for the significantly milder conditions of lateritic bauxite digestion.

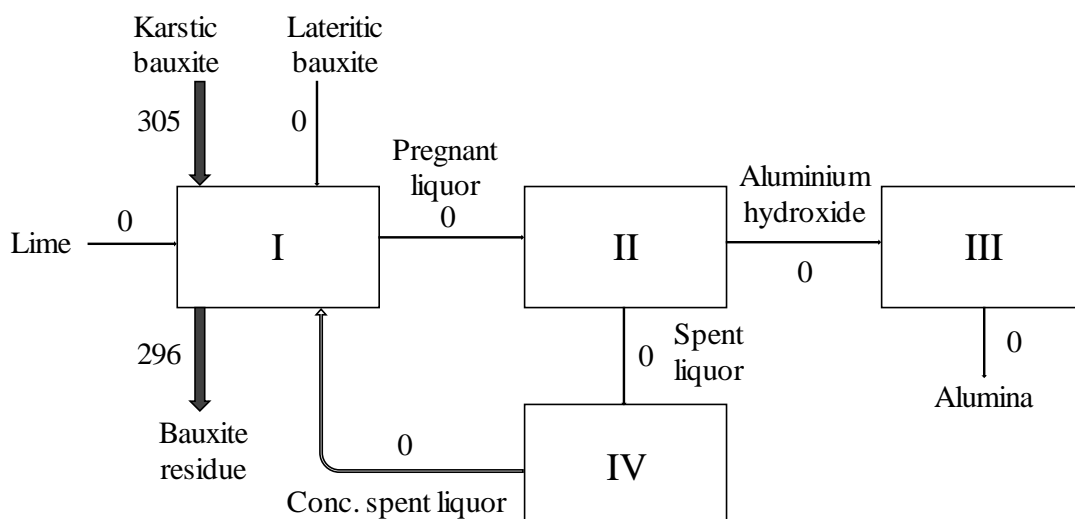


Figure 4. Distribution of Ce in the Bayer process, expressed in mg/kg  $\text{Al}_2\text{O}_3$ .

### 3.4. Possibilities for Predicting the Distribution of Trace Elements

In the case of Ga, we observed that the concentrations in the process liquors were around the average of reported values while the concentrations given in literature have quite a high range. Therefore, the amount of Ga in processing liquors should be analysed on a case-by-case basis due to the variable processing conditions across different refineries. However, this study supports the previously proposed behaviour of Ga being 70 % soluble during the digestion process and the remaining 30 % ending up in bauxite residue, and this can be used as one of the main assumptions for assessing the distribution of Ga in the Bayer process in the absence of more specific information [3, 18].

The other metal that accumulates in process liquors is V. Its saturation level was observed to be similar to earlier reports and its accumulation factor in liquor is about 4.

The rest of the trace elements — Ce, Y and Th — were found to be inert during the processing of bauxites, in the sense that all their mass ended up in bauxite residue. V is soluble to an extent, but it can be grouped with Ce, Y and Th, since the V mass balance on a solids basis indicated complete transfer into bauxite residue.

Among the main bauxite components, iron oxide is largely considered inert during the Bayer process as it is fully recovered in bauxite residue, leaving aside its minute dissolution into liquor and known conversions of iron oxyhydroxides to iron oxides during processing [45]. Its concentration in bauxite and its residues after processing can be used in mass balance calculations with over 99 % accuracy [48]. Feret and See explain that the maximum enrichment level of trace elements from bauxite to residue is limited by the enrichment factor of iron oxide [16]. It is with this limit that we can be more certain of how much any compound can be enriched into bauxite residue on a solid basis.

Within the period of our assessment, the enrichment factor of iron oxide was 2.40 which is comparable to the enrichment factors of V (2.38), Ce (2.31), Th (2.37) and a lesser extent to Y (2.23). A more conservative and representative iron oxide enrichment factor can be used, derived from yearly average iron oxide concentrations, which in this case was calculated to be 2.31, also closely resembling enrichment factors of the studied trace elements.

From the preceding, a simple estimation tool can be proposed to predict the concentration of an inert trace element concentration in bauxite residue, based on iron oxide concentration in bauxite and bauxite residue as well as bauxite trace element concentration as presented in Equation (3). By an inert element we mean here an element that does not pass into alumina or exit the process by any other means, which does not imply absolute chemical inertness. Caution should be exercised in determining a reliable, representative average trace element concentration for the bauxite feed.

$$C_{BR} = \frac{C_{Fe\_BR}}{C_{Fe\_BX}} \times C_{BX} \quad (3)$$

Where: $C_{BR}$	Predicted concentration of trace element in bauxite residue, mg/kg
$C_{Fe\_BR}$	$Fe_2O_3$ concentration in bauxite residue, %
$C_{Fe\_BX}$	$Fe_2O_3$ concentration in bauxite, %
$C_{BX}$	Average concentration of trace element in bauxite feed, mg/kg

Such an estimation method might become useful when the trace element concentrations in bauxite feed fluctuates over time due to variation in the bauxite deposit, or even changes of bauxite origin. As trace element recovery is envisaged from bauxite residue, economic feasibility studies should also consider variable trace element concentrations that are not uniform over time and are dependent mostly on the bauxite feed [49].

#### 4. Conclusions

Analysing the distribution of trace elements confirmed previously reported behaviours and expanded the understanding of trace element distribution after high temperature (255 °C) bauxite digestion. The study did not indicate any significant differences compared to lower digestion temperatures reported in the literature.

Ga is about 70 % soluble in the Bayer process and the same proportion passes to aluminium hydroxide, the remaining 30 % of its initial mass ends up in bauxite residue. Its accumulation into Bayer liquor is around the average of previously known values. Also, the accumulation 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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