

## Lanthanides as impurities in the Bayer production cycle of the aluminum hydroxide from Sierra Leone bauxite

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### Abstract

This paper is describing a careful study on content and distribution of rare elements in the fluid and solid phases involved in dry and classified aluminum hydroxide production through Bayer process at Alum SA, Tulcea, Romania. The source of rare elements in Bayer process is the bauxite from Sierra Leone, a particular type of aluminous goethite-lateritic bauxite, not fully studied yet. Rare earth elements are fairly abundant in the nature, but their distribution is very large, encompassing hundreds of types of minerals where rare element appears as minor crystalline and amorphous compounds, solid solutions, or as ions adsorbed on the surface of common natural rocks. This study data show that Sierra Leone bauxite has only a small content in rare elements. Mainly, only the scandium and cerium concentrations (44.84 mg/kg and 11.49 mg/kg in bauxite residue) may reach the expected values required for eventually valorization. On the Bayer cycle, the rare metals enter with bauxite and concentrate in bauxite residues. Solubility of the rare element compounds in the Bayer process fluid phases is close to zero. In the final product, the aluminum hydroxide dried, milled and classified grades, the rare metals appear only as occlusion contaminants.

**Keywords:** aluminum hydroxide, lanthanides, bauxite, bauxite residue, Bayer process

### INTRODUCTION

Rare earth elements (REE) denominate a group of seventeen elements with similar physical and chemical properties. Fifteen of them, called lanthanides are: Lanthanum-La (138.91), Cerium-Ce (140.12), Praseodymium (140.91), Neodymium-Nd (144.24), Promethium-Pm (146.92), Samarium-Sm (150.36), Europium-Eu (151.96), Gadolinium-Gd (157.25), Terbium-Tb (158.93), Dysprosium-Dy (162.5), Holmium-Ho (164.93), Erbium-Er (167.26), Thulium-Tm (168.93), Ytterbium-Yb (173.04) and Lutetium-Lu (174.97) and are taking up the positions 57 to 71 in the table of elements. Another two elements (Scandium-Sc (44.95) and Yttrium-Y (88.90) have been attached to the above group, because they share similar properties and were found together with lanthanides in the natural lanthanide resources. Promethium, a radioactive metal whose most stable isotope has a short half-life of 17.7 years, is not regarded as a naturally occurring element, even if some irrelevant quantities sometimes accompany cerium radioactive ores [1]. In literature, the REEs are grouped regularly into two rows: light rare earth elements (LREEs) from lanthanum through to europium, and the heavy rare earth elements (HREEs) from gadolinium through to lutetium. Their occurrence and similar properties are presented usually separately [2]. Rare earth elements are fairly abundant in the earth's crust, varying from 0.3 ppm of thulium to 60 ppm of cerium [3]. The REEs similar chemical reactivity results in straightforward ionic substitutions in the crystal structures of other

minerals and occurrence of multiple REEs within a single mineral or the each of REEs distribution between more minerals. Thus, the availability of many REEs are somewhat limited by the overextended distribution in the earth's crust [4, 5]. The most important lanthanide resources are found in four groups of minerals with high lanthanide content, exploitable in various geographical areas: carbonate ores, phosphate ores, silicate ores, oxide ores and materials. In these resources, the lanthanides are most often in the form of the following natural mineral phases [3]:

a) *Carbonate minerals*: Bastnaesite  $(\text{Ce,La})(\text{CO}_3)\text{F}$ ; Parisite  $\text{Ca}(\text{Ce,La})_2(\text{CO}_3)_3\text{F}_2$ ; Synchysite  $\text{Ca}(\text{Ce,La})(\text{CO}_3)_2\text{F}$  and Cebaite  $\text{Ba}_3\text{Ce}_2(\text{CO}_3)_5\text{F}_2$  containing lanthanides [6-8]; and Breunerite  $(\text{Mg,Fe,Sc})\text{CO}_3$  or Dolomite  $(\text{Ca,Mg,Sc})\text{CO}_3$  (accompanying the silicate albite mineral phase) containing scandium [9]; Yttrium bonded to 25 carbonates compounds.

b) *Phosphate minerals*: Lanthanides in calcium substituted in phosphates as fluoride, chloride or hydroxide)  $\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$ : Polymetallic monazite;  $(\text{Ce,La,Nd,Th})\text{PO}_4$ : Aluminum phosphates florencite  $\text{CeAl}_3(\text{PO}_4)_2(\text{OH})_6$  containing lanthanides [10-12] and Scandium phosphate anhydrous and hydrous species, such as Pretulite  $(\text{ScPO}_4)$  and Kolbeckite  $(\text{ScPO}_4 \cdot 2\text{H}_2\text{O})$  [13]; Yttrium phosphate minerals - Xenotime  $(\text{YPO}_4)$  and also, other 9 phosphates, vanadates and arsenates [14];

c) *Silicate minerals*: Kainosite  $\text{Ca}_2(\text{Y,Ce})_2\text{Si}_4\text{O}_{12}\text{CO}_3\text{H}_2\text{O}$ ; Ritholite  $(\text{Ce,Ca})_5(\text{SiO}_4)_3(\text{OH,F})$ ; Gadolinite  $(\text{Ce,La,Nd,Y})_2\text{Fe}^{2+}\text{Be}_2\text{Si}_2\text{O}_{10}$ ; Allanite  $(\text{Ce,Ca,Y})_2(\text{Al,Fe}^{3+})_3(\text{SiO}_4)_3\text{OH}$ , containing lanthanides and yttrium [15-18]; Scandium as an essential element in the following silicate minerals mono silicate Cascandite  $\text{Ca}(\text{Sc,Fe}^{2+})\text{Si}_3\text{O}_8(\text{OH})$ , Cyclosilicate bazzite  $\text{Be}_3(\text{Sc,Al})_2\text{Si}_6\text{O}_{18}$ , Disilicate thortveitite  $(\text{Sc,Y})_2\text{Si}_2\text{O}_7$ , and Orthosilicate eringaite  $\text{Ca}_3\text{Sc}_2(\text{SiO}_4)_3$  [19].

d) *Oxide minerals*: Fergusonite  $(\text{Ce,La,Nd})\text{NbO}_4$ , Loparite  $(\text{Ce,La,Na,Ca,Sr})(\text{Ti,Nb})\text{O}_3$ ; Euxenite  $(\text{Y,Ca,Ce,U,Th})(\text{Nb,Ta,Ti})_2\text{O}_6$ ; Brannerite  $(\text{U,Ca,Y,Ce})(\text{Ti,Fe})_2\text{O}_6$  containing lanthanide and yttrium. The main scandium oxide mineral phases are: Ixiolite  $(\text{Sc,Ta,Nb,Sn,Fe,Ti})_4\text{O}_8$ ; Bazzite  $(\text{Be}_3\text{Sc}_2\text{Si}_6\text{O}_{18})$ , Pyrochlore  $(\text{Ca,Sc,Y,Sn,U})_2(\text{Ta,Nb,Ti})_2\text{O}_6(\text{O,OH,F})$ , and Columbite  $(\text{Fe}^{2+}\text{Nb}_2\text{O}_6$  up to  $\text{Mn}^{2+}\text{Nb}_2\text{O}_6)$  [20, 21].

The ever-increasing growth in the electronics industry, the production of light-weight electric vehicles and devices for generating renewable energy have imposed an accelerating demand for specific raw materials such as rare earth elements (REEs). In several economic regions, like the European Union, Japan or USA have been identified raw materials labeled as "critical" relating to their supply risk and economic importance. The search for new natural resources of critical metals has encouraged research works about identifying some new available raw materials supply and new strategies for intensive valorization. The recent published reviews are available on such subjects as occurrence, exploration and analysis of the critical lanthanides minerals [4-6, 22-31], as well as the new strategies to bring all these resources in the circular economy [32-35]. Also, valuable reviews cover different subjects concerning the mobilization of huge deposits residual materials from other large-scale industries, like red mud and other poly-metallic resources [36-47], phosphate materials and phospho-gypsum [10-12, 18, 27, 48-51] and the coal and coal ashes [52-56]. Furthermore, some interesting published papers on this subject are relating about researches on the environmental problems encountered in the lanthanide extraction technologies and the realistic ways toward to zero waste, and the end of waste by sustainable solutions [4, 33, 35, 56-60].

The purpose of this paper is to conduct a rigorous study on the lanthanides concentrations, as well as on the scandium and yttrium content in Sierra Leone bauxite and in the Bayer cycle of manufacturing the aluminum hydroxide dried, milled and classified on particle sizes classes basis. Also, the paper aims to highlight the purity of the aluminum hydroxide grades as industrial products. Additionally, the second goal of this research is to characterize the bauxite residue and identify it as a possible secondary resource of rare elements. Bauxite from Sierra Leone is still a little-known raw material for the Bayer's alumina production, even if the first information about its composition and petrography were published many years ago [61, 62]. In the last 10 years, only a few papers were published by Alum SA, Tulcea, Romania, mainly related to the use of this bauxite as raw material for the production of Bayer alumina [63-66]. For a careful analysis of the minor elements from materials with complex mineralogy, such as the bauxite and bauxite residue, the literature recommends two ways of preliminary treatment: alkali fusion followed by the acid

digestion [67-69], respectively, the acid baking followed by extraction with water [70-72]. Both methods may be improved by an intensive microwave-assisted process before, during or after digestion [46, 70-73]. In this paper, experiments followed a modified acid baking method, also taking, the advantage of assisted microwave digestion process.

## EXPERIMENTAL PART

### Materials

The lanthanides and (additionally) scandium and yttrium content in a fluid and solid phases from the aluminum hydroxide production cycle were measured after the onset of all research facilities to develop of a technology for obtaining dry, milled and classified aluminum hydroxide. Representative samples of bauxite concentrated and spent Bayer liquors and different sorts of aluminum hydroxide dried, milled and classified were collected in many rounds for different purposes [65, 66]. From this large number of samples, there were selected two sets of data representing the best results concerning: the mineralogy of both Sierra Leone bauxite (BA1, BA2) and bauxite residues (BR1, BR2), the composition of concentrated Bayer liquor and, impurity concentration in some of in the commercial grades of aluminum hydroxide. Sample BA1 belongs to the usual quality of bauxite from Sierra Leone, processed by Alum SA, Tulcea. The sample BR1 is the bauxite residue from this bauxite sort. Also, this bauxite residue was washed and filtered on an experimental pilot high-pressure filter. Sample BA2 is low-quality bauxite from the same source. The sample BR2 is the bauxite residue sample coming out from this low-quality source. Actually, this was the washed sample, separated by deep thickening. Data from Table 1 and 2 will serve to better understand the concentrations of the lanthanides, scandium and yttrium in the Bayer cycle of aluminum hydroxide production. Sampling and analyses of each element of interest were done in accordance with European standards [74-77].

The table 1 and 2 are disclosing the complex ranges of phases in both types of bauxite, as raw materials and in bauxite residues involved in the Bayer processing of Sierra Leone bauxite. The Al-goethite, Al-hematite and ilmenite, as well as the new born phases during Bayer process, like sodalite and katoite phases are well known as metal oxides phases ready to immobilize the lanthanides compounds [19-21]. Also, the amorphous phases (30-40 mass per cent in bauxite and bauxite residues) may have substantial contribution in adsorption and immobilization of any ion of lanthanides or fragments of the molecular complex carrier compounds of lanthanides.

**Table 1.** Mineralogical composition of bauxite samples BA1 and BA2

Mineralogical phases	Bauxite sample BA1		Bauxite sample BA2	
	Composition, (%)	Crystalite dimension Lvol-IB, (nm)	Composition, (%)	Crystalite dimension Lvol-IB, (nm)
Gibbsite	43.9±2.5	98.1±2.0	31.3±1.7	90.7±2.0
Al-Goethite-fine	17.07±0.99	9.63±0.88	24.9±1.4	9.55±0.76
Al-Goethite-coarse	2.20±0.13	49±2.9	2.89±0.16	42±1.8
Al-Hematite	4.81±0.28	28.5±1.7	3.35±0.19	22.8±1.9
Kaolinite	1.379±0.080	15.7±0.59	4.28±0.24	6.4±1.1
Quartz	0.618±0.036	46±1.8	1.85±0.10	127±26
Zircon	0.750±0.044	12.7±2.8	0.640±0.036	12.7±3.2
Ilmenite	0.298±0.017	40±2.8	0.606±0.034	66±2.8
Anatase	0.178±0.010	38±2.6	0.189±0.011	38±2.6
Amorphous	28.7±4.6		30.0±4.3	

Al-Goethite:  $(\text{Fe}_{0.7564} \pm 0.0037 \text{ Al}_{0.2436} \pm 0.0037)\text{O}(\text{OH})$ ;

Al-Hematite:  $(\text{Fe}_{0.9202} \pm 0.0046 \text{ Al}_{0.0790} \pm 0.0046)_2\text{O}_3$

**Table 2.** Mineralogical composition of bauxite residue samples BR1 and BR2

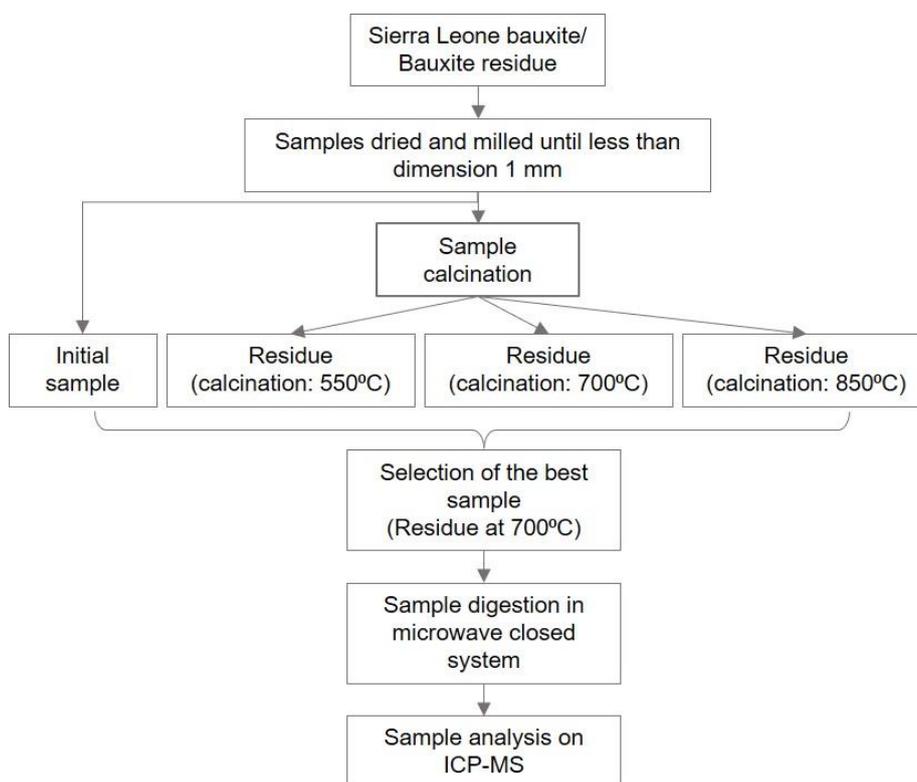
Mineralogical phases	Sample BR1	Sample BR2
	Mass composition, (%)	Mass composition, (%)
Gibbsite	1.247± 0.020	2.927±0.065
Al-Goethite-fine	34.15±0.55	31.31±0.696
Al-Goethite-coarse	1.161±0.019	0.025±0.001
Al-Hematite	12.46±0.20	11.61±0.258
Ilmenite	3.118±0.051	1.754±0.039
Katoite	2.506±0.041	5.919±0.132
Sodalite	2.315±0.038	5.164±0.115
Calcite	1.012±0.016	0.612±0.014
Rutile	0.759±0.012	-
Anatase	0.498±0.008	0.674±0.015
Quartz	0.392±0.006	1.238±0.028
Magnetite	0.120±0.002	-
Amorphous	40.3±1.100	38.7±1.474

These particular chemical characteristics of the Sierra Leone bauxite and of bauxite residues come from the history of metamorphic transformations and mechanical wearing of the bauxite-associated minerals. Accordingly, much attention should be paid to the analytical method selected for processing the mineral samples to make possible the total dissolution of lanthanides, scandium and yttrium elements during digestion of minerals for analysis.

#### Methods

The entire procedure for determination of the total content of lanthanides, scandium and yttrium was applied for samples BA1, BR1 and BR2, according to SR EN 17294-2:2017, “*Application of inductively coupled plasma mass spectrometry (ICP-MS). Part 2. Determination of 62 elements*”. This procedure has gone along with the following stages: a) drying samples at 105°C and grinding them until dimensions less than 1 mm, before calcination; b) samples calcination at three different temperature values (550°C, 700°C, 850°C) and selection of the temperature of 700°C as the best for being applied before the microwaves assisted acid baking of the samples BA1, BR1 and BR2 (Figure 1); c) selection of the best chemical formulation for acid baking sample composition: 0.5g sample + 9 ml HNO<sub>3</sub> (65%) + 1ml H<sub>2</sub>O<sub>2</sub> (30%); d) selection of the best program of microwaves assistance into digestion cell: two steps at 190 °C and respectively, 100 °C, for 20 and respectively 25 minutes, both under a 1500W microwaves power consumption; e) after the digestion was complete, the solution in the digestion cell was filtered through a ceramic filter with a pore diameter of 0.45µm and brought to a 25 ml volumetric flask); f) determination of the elements using the ICP-MS equipment. All these parameters have been optimized to eliminate any interference that may occur during the analysis and may influence the data about real concentrations of lanthanides.

In addition, representative samples of concentrated sodium aluminate solution were collected from the production line before aluminum hydroxide precipitation. Samples of aluminum hydroxide dried, milled and classified (five products with different particles size dimensions) from the last production batch, and bauxite residue have been collected from the production line, during a period of time, when all the process parameters were quite enough closed to usual values, common for the steady state production.



**Fig. 1.** Flow chart of bauxite sample preparation

### Equipment

For the analysis of rare metals (lanthanides, scandium and yttrium), it was used: the equipment Agilent ICP-MS 7900, model G8403A with Mass Hunter 4.4 measurement program. The operating parameters of this equipment are presented in Table 3. For plotting the calibration curve required for determining the concentrations of Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, on a range of concentration 10-50  $\mu\text{g/L}$  there were used a multi-element MRC (16 rare metals) with a concentration of 10 mg/L (in 5%  $\text{HNO}_3$ ). This MRC is a certified reference material from batch BCBZ4903 and is traceable to NIST. All reagents used have the appropriate analytical quality.

**Table 3.** Operating parameters of the ICP-MS 7900 Agilent

<i>ICP-MS spectrometer parameters</i>			
Delay time:	60 s	Purge gas flow:	normal
Replicates:	3 times	Peristaltic pump:	1.5 mL/min
<i>Tune parameters</i>			
<i>Plasma parameters</i>			
Plasma flow rate:	15 L/min	Power RF:	1550 W
Auxiliary flow rate:	0.90 L/min	Plasma view:	axial
Nebulizer Pump:	0.10 rps	RF matching:	1.30V
<i>Plasma mode</i>			
Plasma Mode:	general purpose	Sample Depth:	10 mm
<i>Cell parameters</i>			
He flow:	4.3 mL/min	OctpBias:	-8.0 V
<i>Spectral peak processing</i>			
Peak algorithm:	peak area	Peak pattern:	3 points
Replicates:	3	Integration time:	0.2001 sec
<i>Sample acquisition</i>			
Sample uptake:	30 sec	Stabilize:	40 sec
<i>Post run</i>			
Probe rinse (Sample):	10 sec	Probe rinse (Standard):	10 sec

The ICP-MS concept is based on the combination of inductively coupled plasma, as an ionization method, with mass spectrometry as a method of ion separation and detection. Unlike the atomic absorption spectrometry concept (AAS), ICP-MS can detect all elements simultaneously at very low concentrations at 1-10 ppt. The microwave closed system is an ETHOS UP digestion system from Milestone.

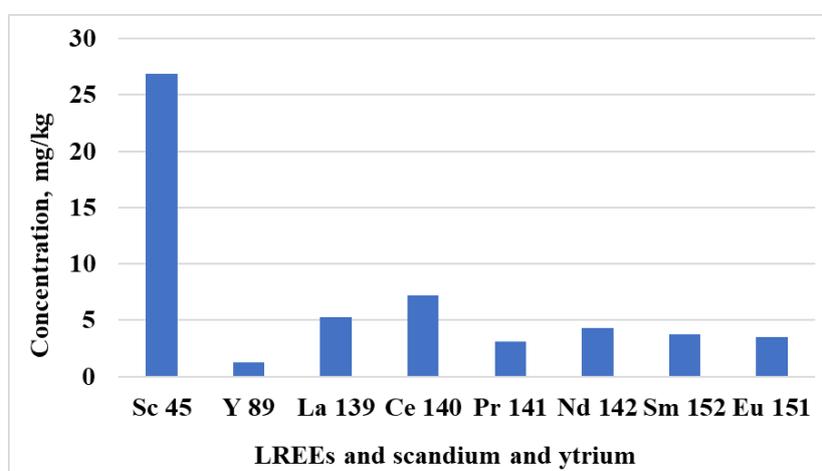
## RESULTS AND DISCUSSION

### *Rare elements content in bauxite and bauxite residue*

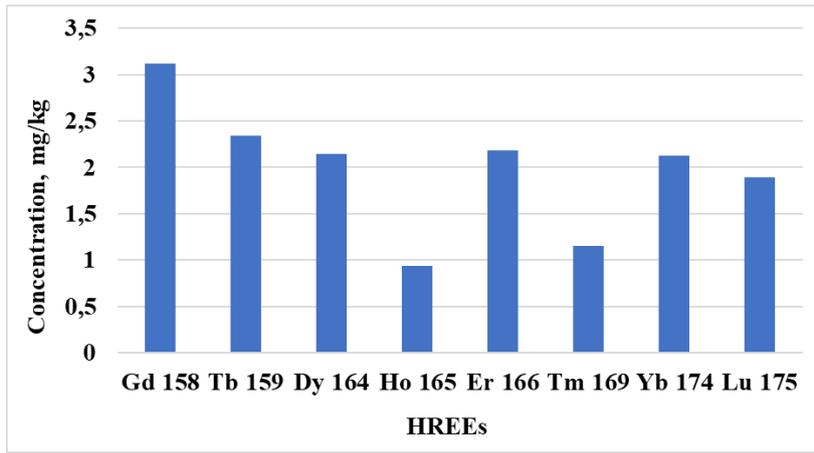
In the table 4 is presented the total collected data, parted distinctly, as Low mass lanthanides (and Scandium and Yttrium) and respectively, High mass lanthanides. A better view of the ratios between low mass lanthanides (also adding the scandium and the yttrium) and high mass lanthanides, as well as the contribution of each element to the total content of rare elements in bauxite and bauxite residue, can be easily seen in the figures 2-5.

**Table 4.** Lanthanides, Scandium and Yttrium in Sierra Leone bauxite and bauxite residues, mg/kg

<b>Samples</b>	<b>BA1</b>	<b>BR1</b>	<b>BR2</b>
<b>Scandium and Yttrium</b>			
Scandium 45	26.86	40.19	44.84
Yttrium 89	1.27	1.39	7.14
<b>Low mass lanthanides</b>			
Lanthanum 139	5.30	8.07	11.49
Cerium 140	7.19	15.25	18.32
Praseodymium 141	3.14	4.54	6.02
Neodymium 142	4.30	9.03	10.16
Samarium 152	3.78	6.81	5.33
Europium 151	3.53	5.60	5.24
<b>High mass lanthanides</b>			
Gadolinium 158	3.12	3.56	5.48
Terbium 159	2.34	3.90	4.65
Dysprosium 164	2.14	4.28	5.47
Holmium 165	0.94	1.18	4.67
Erbium 166	2.18	4.01	5.18
Thulium 169	1.15	1.27	4.58
Ytterbium 174	2.13	3.68	5.02
Lutetium 175	1.89	3.64	4.92

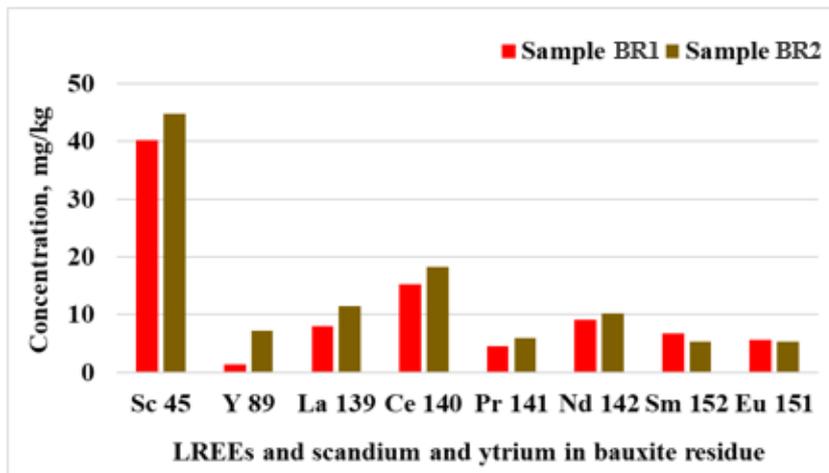


**Fig. 2.** LREEs in Sierra Leone bauxite (Sample BA1)

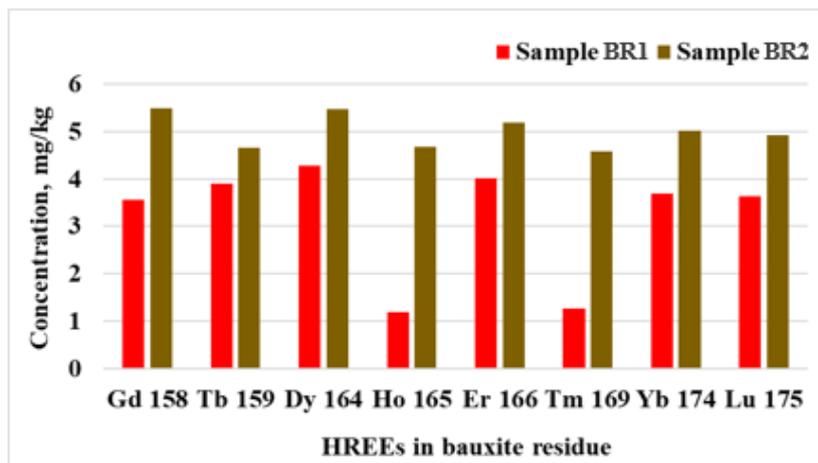


**Fig. 3.** HREEs in Sierra Leone bauxite (Sample BA1)

From figures 2 and 3, results one of the most important characteristics of the Sierra Leone bauxites, the concentrations in LREEs are higher than concentrations in HREEs. Because all the rare elements are passing almost totally in the bauxite residue, this characteristic remains valid for the bauxite residue, and this can be easily seen in Table 4 and in Figures 4 and 5, standing for the content of rare elements in the bauxite residues. The mineralogy of the two samples of bauxite, BA1 and BA2, are quite different, especially in the content of Al-Goethite-fine particles (Table 2). This significant mineralogical component of the bauxites can be associated with higher concentrations of HREEs in the bauxite residue BR2, coming from sample BA2 (Table 4).



**Fig. 4.** LREEs in Sierra Leone bauxite residues



**Fig. 5.** HREEs in Sierra Leone bauxite residues

Consequently, the content of rare elements in Sierra Leone bauxite and bauxite residues is low. Only the scandium in concentrations of 40–45 mg/kg, found in both bauxite residues, might be extracted with a simple technology, when the performances of this technology will be able to deliver the product at reasonable prices.

*Rare elements content in concentrated sodium aluminate and aluminum hydroxide grades*

In the tables 5 and 6 are given the data on rare elements in the most concentrated solution of sodium aluminate from the Bayer cycle. The recorded value from ISP-MS determinations shows that lanthanides compounds are completely insoluble in all fluid phases from the Bayer alumina process (Table 5). Analysis of the rare metals in four classified dry aluminum hydroxide size fractions, also using, the ISP-MS method of determination, is presented in Table 6.

Minor contamination with scandium and all LREEs lanthanides was observed for the smallest dimension fraction (10  $\mu\text{m}$ ). Only scandium, lanthanum and cerium contaminate the other size fractions, but the concentrations are below 0.25 mg/kg.

**Table 5.** Lanthanide, scandium and yttrium in Bayer alumina concentrated fluids, mg/Kg

Elements	Concentration	Elements	Concentration
Scandium	<0.003	Gadolinium	<0.002
Yttrium	<0.002	Terbium	<0.001
Lanthanum	<0.001	Dysprosium	<0.002
Cerium	<0.001	Holmium	<0.002
Praseodymium	<0.001	Erbium	<0.002
Neodymium	<0.002	Thulium	<0.001
Samarium	<0.001	Ytterbium	<0.001
Europium	<0.002	Lutetium	<0.002

**Table 6.** Lanthanide, scandium and yttrium in aluminum hydroxide samples, mg/kg

Elements	Samples under 10 $\mu\text{m}$	Samples under 20 $\mu\text{m}$	Samples under 45 $\mu\text{m}$	Samples under 150 $\mu\text{m}$
<b>Scandium and Yttrium</b>				
Scandium 45	0.17	0.16	0.11	0.12
Yttrium 89	<0.11	<0.11	0.12	<0.11
<b>Low mass lanthanides</b>				
Lanthanum 139	0.09	<0.06	0.20	<0.06
Cerium 140	0.23	0.21	0.12	0.10
Praseodymium 141	0.09	<0.07	<0.07	<0.07
Neodymium 142	0.11	<0.09	<0.09	<0.09
Samarium 152	0.09	<0.07	<0.07	<0.07
Europium 151	<0.10	0.10	<0.10	<0.10
<b>High mass lanthanides</b>				
Gadolinium 158	<0.09	<0.09	<0.09	<0.09
Terbium 159	<0.14	<0.14	<0.14	<0.14
Dysprosium 164	<0.08	<0.08	<0.08	<0.08
Holmium 165	<0.13	<0.13	<0.13	<0.13
Erbium 166	<0.10	<0.10	<0.10	<0.10
Thulium 169	<0.12	<0.12	<0.12	<0.12
Ytterbium 174	<0.08	<0.08	<0.08	<0.08
Lutetium 175	<0.13	<0.13	<0.13	<0.13

*Performance parameters and validation of the analysis method*

The performance parameters of a specific analysis method are: the detection limit (LOD), the quantification limit (LOQ), the repeatability, the intermediate accuracy, the extended uncertainty,

and the recovery. The “in-house” validation of the lanthanide, scandium, and yttrium analysis method was performed by evaluating the performance parameters mentioned above (concentration range: 10 - 50 µg/L). In Table 7, a recommended experimental program for calculating these parameters is given.

**Table 7.** Experimental program for validation of the performance parameters for rare elements

Performance parameters	Experimental measurements
LOQ si LOD	5 blank independent samples fortified by solutions with rare elements concentrations of 5 µg/L
Repeatability	10 standard independent solutions with rare elements concentration of 25 µg/L 4 experiments (3 standard solutions per experiment analyzed by 2 laboratory chemists in 4 different days)
Intermediate accuracy	12 standard independent solutions with rare elements concentration of 25 µg/L
Recovery	10 solutions with real independent samples, fortified by solutions with rare elements concentration of 35 µg/L.

The calculation of the extended uncertainty was done according to the method (GUM: 1995), using the following formula [78]:

$$U_{extended} = k \cdot U_{combined} \quad (1)$$

where:

$k$  is the coverage factor equal to 2, for a 95% confidence level and  $U_{combined}$  is the combined standard uncertainty.

Thus,

$$U_{extended} = k \cdot \left[ (U_c^2 + U_v^2 + U_{rep}^2) + \left( \frac{1}{U_{mas}} \right)^2 + \left( \frac{1}{U_{rec}} \right)^2 \right]^{1/2} \quad (2)$$

where:

$U_c$  is the uncertainty given by the concentration measurements (instruments calibration, glassware calibration and reference standard materials);

$U_v$  is the uncertainty given by volumetric flask 25 ml;

$U_{rep}$  is the uncertainty given by repeatability (volume mass, concentration, recovery achieved by extraction);

$U_{mas}$  is the uncertainty given by weight (balance calibration linearity);

$U_{rec}$  is the uncertainty given by recovering from the real samples;

LOQ is the quantification limit and LOD is the detection limit.

The bauxite residue marked BR2 was selected for performance parameters due to its higher content of rare metals. The results are given in Table 8.

Based on results from Table 8, it can be stated that the lowest detection and quantification limits have been recorded for lanthanum and cerium. Thus, the lowest measurement uncertainty is identified for cerium, and the highest is for ytterbium. A certified reference material (MRC) appropriate to the analyzed matrix is usually used in the recovery study. In this case, there is no certified reference material (MRC) for bauxite and bauxite residues. Under these circumstances, one of the samples already studied (sample BR2 containing bauxite residue) was fortified with a known rare elements concentration of 35 µg/L. The sample was analyzed by ICP-MS, and the recovery yields were computed. The best recovery yields were obtained for scandium (87%), lanthanum (82%), cerium (75%), neodymium (69%), praseodymium (68%), and yttrium (65%). The percentage order of recovery yields is as follows: Sc > La > Ce > Nd > Pr > Y > Lu > Ho > Dy > Er > Tb > Gd > Sm > Eu > Tm > Yb.

**Table 8.** Performance parameters for rare metals concentrations (lanthanides, scandium and yttrium) by the ICP-MS method

Elements	LOD (mg/kg)	LOQ (mg/kg)	Accuracy (mg/kg)	RSD <sub>r</sub> * (%)	RSD <sub>Ri</sub> ** (%)	U <sub>ex</sub> *** (%)	Recovery (%)
Scandium	0.025	0.10	0.060	0.95	3.53	16.99	85.24
Yttrium	0.028	0.11	0.035	1.00	3.97	17.83	85.68
Lanthanum	0.015	0.06	0.016	1.66	4.01	17.61	98.20
Cerium	0.014	0.06	0.018	0.79	2.70	15.14	98.90
Praseodimium	0.017	0.07	0.019	1.08	2.46	15.33	85.13
Neodimium	0.022	0.09	0.054	0.91	2.18	16.18	85.39
Samarium	0.017	0.07	0.052	1.23	2.99	19.12	86.21
Europium	0.025	0.10	0.028	0.72	1.50	19.31	80.25
Gadolinium	0.022	0.09	0.057	0.96	2.42	18.79	82.56
Terbium	0.046	0.14	0.017	0.64	2.14	17.67	80.63
Dysprosium	0.020	0.08	0.045	0.61	1.92	18.33	81.54
Holmium	0.043	0.13	0.020	0.81	1.95	16.52	80.46
Erbium	0.026	0.10	0.031	1.16	2.33	18.19	80.78
Thulium	0.040	0.12	0.024	0.99	2.18	15.16	80.96
Ytterbium	0.020	0.08	0.051	0.95	1.60	19.39	80.62
Lutetium	0.043	0.13	0.019	0.60	1.90	15.42	83.25

\*Repeatability; \*\* Intermediate accuracy; \*\*\* Measurement uncertainty

## CONCLUSIONS

The lanthanides and additionally scandium and yttrium content along to production cycle of the aluminum hydroxide dried, milled and classified has been determined with a performant spectrometric analysis using ICP-MS method. Experimental data have been shown that the LREEs / HREEs percent ratios in Sierra Leone bauxite are greater than 1.0 as happen in the case of lateritic bauxites, according to literature. Mainly, the entire quantity of lanthanides, scandium and yttrium from bauxite is passing almost totally into bauxite residues, keeping up with the same ratios between LREEs and HREEs in bauxite. Only insignificant concentrations of all the rare elements were found in concentrates aluminum hydroxide solution, independently of the aluminum concentrations. In all the particle size fractions of the aluminum hydrate dried, milled and classified, the rare elements can contaminate the final products only by occlusion. Low contamination with scandium and all LREEs lanthanides was noticed in the fraction with particle size less than 10  $\mu\text{m}$ . Also, scandium, lanthanum, and cerium contaminate the other fractions, but only at a concentration less than 0.25 mg/kg.

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