Quantitative Chemical Analysis of Red Mud and Products of its Processing to Scandium, Zirconium and REE Oxides by ICP AES

Tatyana Golovanova[1], Tatyana Mukina[2], Yulia Chernyshova[3], Alexander Suss[4] and Alexander Damaskin[5]
1. Head of analytical laboratory,
2. Sr. Analytical Chemist,
3. Analytical Chemist
4. Director Technology Department
5. Sr. Scientist
RUSAL Engineering and Technology Center (VAMI), 86 Sredny pr., Saint Petersburg, Russia
Corresponding author: aleksandr.suss@rusal.com

Abstract

Establishment of scandium production from the red mud of the Ural alumina refineries by RUSAL required implementation of effective process control and quality assessment of the pure scandium oxide produced. To this end, techniques for scandium, zirconium and REE determination in bauxites, muds, semi-products and commercial products using the existing equipment and methods of the facility's central laboratory (i.e. without the purchase of new equipment and/or adoption of additional methods of analysis) were developed by RUSAL's Engineering and Technology Center. Investigations were performed to develop the quantitative chemical analysis of red mud and products of its processing for determination of Sc, Zr and REE oxides by inductively coupled plasma-atomic emission (ICP-AES) on the PerkinElmer OPTIMA 8000 CROSS FLOW-L15 model. The possibility to analyse a wide range of concentrations from 1 ppm to 10% is shown. Comparative determinations of basic element oxides, trace contamination and REE by various analytical methods were performed.

Keywords: scandium, REE, zirconium, ICP-AES, analytical methods.

1. Introduction

The unique chemical and physical properties of scandium and REE are widely used in various fields of science and industry: electronics (superconductors), optics and nuclear (filters for quasi–monochromatic neutron beam production, neutron tube and generator targets, β-particles source). Scandium is used for the production of halogen lamps. Scandium is also used as alloying material in production of high-strength cast iron, low-alloyed steel and special alloys, most promising of which are alloys with aluminium. Adding Sc to aluminium alloys can increase their strength by 2 times, increases its plasticity and corrosion resistance, and most importantly, makes alloys weldable with seam properties the same as base alloy material. This opens new areas of aluminium use in civil aviation (shifting to welded construction significantly reduces the weight of aircraft), shipbuilding, etc.

At present scandium is produced in small quantities (world production is about 14 tpy) and mainly extracted from liquors of the uranium and titanium dioxide industries, where it is contained in trace quantities. One of the factors limiting production is the absence of a large raw material base. One potentially huge source are bauxites, which accounts for more than half of the world's Sc. When bauxites are processed in alumina production, soluble scandium forms are concentrated in bauxite residue – red mud, so scandium production from bauxite residue has very good prospects. Due to the amounts of red mud produced and accumulated annually and the possibility to implement Bayer process friendly scandium extraction technology as an addition to alumina production process, it almost has no capacity constraints.

2. Tasks and Objectives

In 2014 UC RUSAL established a trial plant for scandium oxide production from the red mud of Sredny Timan bauxite processing (Komi Republic, Russian Federation). After two years of plant operation a number of tasks were defined, including prompt chemical and analytical control on all stages of technological process and quality control of high purity scandium oxide (> 99 %). Zirconium is one impurity that accumulates in the Sc concentrate due to technology applied, and its determination is as important as other REEs.

3. Experimental

Establishment of high-purity scandium (> 99 %) production from red mud requires implementation of effective methods of determination of Zr, Sc and rare-earth elements (REE) in a wide range of concentrations. REE qualitative analysis is one of the most challenging tasks in analytical chemistry. These elements possess similar physical and chemical properties which causes specific challenges for their joint determination. Many determination methods are time-consuming and labour-intensive, requiring additional chemical process stages of separating and concentrating.

Methods such as inductively coupled plasma-atomic emission (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP MS) are used for direct determination of Zr, Sc and REE, and these determinations are preferable for analytical control. But these methods have both advantages, such as low detection limits and wide linear concentration range, and a number of limitations due to spectral aliasing and matrix effects.

Consequently, investigations were performed to determine the possibility of direct determination of Zr, Sc and REE in the red mud and intermediate products (various concentrates), extracted during the production of scandium oxide from red mud.

As a rule, to develop a determination method using ICP AS, the following three main tasks are required:

- sample preparation;
- matrix effects minimization;
- spectral lines selection.

Investigations were performed using the PerkinElmer OPTIMA 8000 model (USA).

ICP AS operating parameters:

- RF Power, W ………..…………………………………………..1500;
- Outer argon flow, L/min…………………………………….….12;
- Intermediate argon flow, L/min ……………………….………0.5;
- Inner argon flow, L/min …………………………………………..0.7;
- Torch Fassel-type quartz torch;
- Nebulizer Meinhard concentric nebulizer;
- Spray chambers Scott-type spray chamber.

Sample preparation. When using an ICP method, the sample solution shall be added to the argon plasma as aerosol. That is why various methods of transforming solid samples into solutions were implemented:

- acid digestion;
- fusion.

When analyzing the acid digestion method it was determined that some Zr is present in the samples as zirconate that is difficult to digest with acids, and due to this, the sample cannot be fully dissolved and can lead to invalid results.

All determined elements are fully dissolved when the sample is fused with lithium tetraborate. The melt can then be leached with 5 % HCl. Following this method, a 0.1 g sample was added to the platinum crucible with 0.4 g lithium tetraborate and mixed carefully. Then the sample was fused at 1000 °C in a muffle furnace for 10 minutes. The melt was digested in a heated 5 % HCl solution, and then the solution was added to 100 cm^3 flask. Macro and micro components of one weighed sample can be determined using such method.

Minimization of matrix effect. Investigation of the elimination of matrix effects of macro components (Fe, Ca, Al, Na, Ti), showed that the effects only appear if matrix elements in solution exceed 100 μ/cm^3 and this shall be taken into account in future studies.

Spectral lines selection. Atoms and ions of zirconium, scandium and rare-earth elements possess large quantity of emission spectrum. Accordingly, when selecting the analytical spectral line for the determined element, the following criteria should be applied:

- high line sensitivity;
- absence of spectral aliasing from the sample matrix elements.

Based on the conducted investigation the following analytical spectral lines for the elements were selected (Table 1).

Table 1. Analytical lines for the analysis of red mud and intermediate products by ICP AS

Element	Wave length, nm
Zr	339.197; 343.823
Sc	361.384; 424.683
Ce	413.764; 418.660
Dy	353.170
Er	369.265
Eu	393.048; 412.970
Gd	376.839
Ho	345.600
La	379.478; 408.672
Lu	261.542
Nd	406.109; 430.358
Pr	414.311; 422.293
Sm	359.260
Td	350.917
Tm	346.22
Y	360.073; 371.029
Yb	289.138; 328.937

A method for determination of Zr, Sc and REE by ICP AP was approved using the samples of bauxite, red mud, Zr and Sc concentrate. The method’s accuracy was checked by several methods:

- sample weight variation;
- addition method;
- comparison of results acquired by using ICP MS method in the certified laboratory of Russian Geological Research Institute (VSEGEI, named after A.P. Karpinsky). The results are specified in Tables 2, 3 and 4.

Table 2. Determination of Sc, Zr and REE in bauxite and red mud samples by ICP AS and ICP MS

Element	**Timansky bauxite (STBR)**				**Severo-Uralsky bauxite (SUBR) GB-1+10 % STBR**				**Guinea bauxite CBK**			
	bauxite		mud		bauxite		mud		bauxite		mud	
	Determined components content, ppm											
	AS	MS	AS	MS	AS	MS	AS	MS	AS	MS	AS	MS
Sc	46	53.6	75	85	47	54	101	111	14.4	15.6	35.3	31.3
Zr	470	540	740	814	375	339	540	542	267	310	703	659
Ce	355	288	488	418	252	216	416	378	56	49	152	128
Dy	22.6	23.5	27	26.9	19.1	21	39.9	42.1	<5	5.1	12	10.3
Er	14	12.4	15.5	13.9	14.4	12	28.3	25.9	<5	3.3	7	5.9
Eu	<5	5.3	5.9	6.8	<5	5	8.9	10.6	<5	0.94	<5	2.23
Gd	35	25.4	35	28.8	25.7	21.1	53	42.5	<5	4.3	11	9.03
Ho	5.2	4.4	<5	4.64	<5	3.8	7.2	8.3	<5	0.99	<5	1.9
La	172	151	223	195	150	128	271	240	34	28.8	80.1	69
Lu	<5	1.6	<5	2	<5	1.5	<5	3.3	<5	0.4	<5	0.96
Nd	153	157	209	179	123	111	235	205	21.1	18	52.4	48.9
Pr	39.5	34.1	40.1	46.3	23	27.7	30.7	49.6	<5	5.3	16	13.8
Sm	30.7	27	40	33	25.6	21.6	45.1	39.3	<5	3.4	9.1	9.4
Tb	5.2	3.8	<5	4.3	<5	3.1	7.1	6.1	<5	0.76	<5	1.6
Tm	<5	2.1	<5	2.3	<5	1.9	<5	4.1	<5	0.51	<5	1
Y	134	124	150	137	173	154	391	372	29.1	30.7	51.9	53
Yb	13.3	11.6	16	13.5	12.4	10.6	20.1	22	<5	2.99	6.5	6.4

Table 3. Determination of Sc, Zr oxides in Zr and Sc concentrates by ICP AS and ICP MS

Sample designation	**Element, mass. %**			
	Sc		Zr	
	AS	MS	AS	MS
Zr - concentrate	0.75	0.71	7.6	7.4
Sc - concentrate	13.7	13.4	16.8	17.1

Table 4. Determination of REE in Zr and Sc concentrates by ICP AS and ICP MS

Element	Determined components content, ppm			
	Sc - concentrate		Zr-concentrate	
	AS	MS	AS	MS
Ce	4139	3800	180	162
Dy	956	799	142	120
Er	1156	990	248	234
Eu	37	31,4	13	11,6
Gd	275	238	60	50
Ho	295	250	50	42
La	41	34	136	138
Lu	578	475	43	29
Nd	239	234	145	151
Pr	45	37,2	53	46
Sm	120	105	10	11,1
Td	95	72	490	444
Tm	179	214	50	41
Y	8696	7350	1882	1677
Yb	2554	2200	288	246

Results specified in Tables 2, 3 and 4 show that the results obtained using ICP AS and ICP MS methods are similar and the discrepancy between methods is within 5-20 %.

4. Conclusion

The conducted studies proved the possibility to determine Zr, Sc and REE simultaneously by using ICP AS method in bauxites, red mud, Zr and Sc concentrates without any additional chemical processing. The possibility to analyse them in a wide range of concentrations from 1 ppm to 10% is shown.

For quality control of scandium oxide, an ICP MS method should be used. It provides for significant reduction of REE determination limits as required for analytical control of pure scandium oxide (≥ 99.9 %). Also it allows a reduction in the time and cost required for the analysis.

5. References

1. K.V. Zhernokleeva, V.B. Baranovskaya, Analysis of pure scandium, yttrium and their oxides by inductively coupled plasma-atomic emission and inductively coupled plasma-mass spectrometry methods, *Plant laboratory. Materials diagnostics*, 2011. Vol.76, No 11, 20-26.
2. I.V. Glinskaya et al., Analytical control of red mud processing, *Iron and steel industry*, 2013, No 9, 17-21.
3. A. Premadas, Determination of trace level lanthanides and thorium by inductively coupled plasma atomic emission spectrometry in different types of geological, red mud,

and coal fly ash samples after separation as oxalates using calcium as carrier, JAAS: *Atomic Spectroscopy*, 2012, Vol. 33, # 1, 14-24.

4. L.N. Komissarova, Inorganic and organic chemistry of scandium, URSS, 2001, 512.