Specific Features of Scandium Behavior during Sodium Bicarbonate Digestion of Red Mud

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Abstract

Bauxite ore contains ~ 65 % of world Scandium recoverable reserves. From Bayer extractable alumina > 96 % of Scandium merges into red mud (RM). In smelter grade alumina produced from the bauxites Sc_2O_3 content ranges from 1.2 to 2.3 ppm. Sc content in initial bauxite has little influence on its content in alumina. Scandium that is present in red mud after processing of Middle Timan bauxite and Nothern-Ural bauxite has two forms. Part of Scandium (~ 65%) can be readily extracted from boehmite and diaspore. Sc_2O_3 content in Al monohydrates amounts to 80-100 ppm. During autoclave digestion Sc goes into red mud as extractable form (Sc_{av}) and is adsorbed on the RM surface in form of oxyhydroxide ScO(OH). Sorbed scandium can be present on the surface of any RM phase or mineral. And due to this property concentrating of Sc_{av} during RM treatment is inefficient. Sc_{av} can be easily digested with sodium bicarbonate solution under "mild" conditions. Chemically bonded Scandium in the structure of mainly iron-containing minerals of bauxite (30 ± 15 %) can be extracted by "severe" acid leaching with breaking of crystal structure of hematite and other minerals. When bauxite is digested in autoclave (Bayer process) new phases are formed (calcium hydrogarnet (HG) and sodium hydroalumosilicate (DSP). Hydrogarnets and DSP do not bind Scandium chemically and it indirectly confirms Scandium sorbing properties in RM. Tests on development of sodium bicarbonate digestion modes of scandium from RM showed significant range of values of Sc extraction into the solution (from 10 to 65 %). One of the most important factors affecting Sc extraction is Sc secondary losses due to formation of new phases (incl. aragonite, dawsonite, etc.) These phases are in equilibrium under such conditions. The mechanism of Sc secondary losses during sodium bicarbonate digestion of red mud was analyzed, and some practices to increase of extraction values were offered.

Keywords: Red Mud, scandium, bicarbonate digestion.

1. Introduction

In 2014 UC RUSAL commissioned Pilot plant at Urals aluminium smelter (Pilot plant) for production of scandium oxide (purity grade $Sc_2O_3 \geq 99.5$ mass. %) from red mud. Also a large amount of laboratory tests was performed. Based on the test results the Pilot plant was upgraded several times to improve its technical and economical properties and establish design data for construction of industrial plant with throughput of 3 tpa Sc_2O_3.

The results of these activities ensured better understanding of properties of scandium in red mud (RM) produced from Middle Timan bauxite (STBR) and North Urals bauxite (SUBR) and behavior of scandium during sodium bicarbonate digestion.

To determine factors influencing scandium behavior during sodium bicarbonate digestion (SBD) model experiments were performed to study the influence of phase changes in the RM on scandium extraction.

1.2. Scandium in Bauxites and Red Mud

Scandium is a typical trace element. Its geochemical behavior changes wave-like in the course of formation of bauxites and laterites by weathering of parent rocks and further carbonization processes. In case of small changes in pH level and depending on the presence of different anions and cations in the solution, temperature and other factors various minerals can serve as geochemical traps for scandium.

The following are the data on the content and form of scandium in bauxites and red mud from their processing.

1.3. Boehmite and Diaspore

Studies by All-Russian Research Institute of Mineral Resources, n.a. N.M. Fedorovski (VIMS) [1] showed that in STBR bauxites Al_2O_3 is present as boehmite [ɤ-AlO(OH)] and amounts to 50 - 55 %. Sc_2O_3 content in boehmite is ~ 100 - 110 ppm. So the amount of Sc_2O_3 that goes to red mud is 75 - 80 g/t RM provided that ~ 100 % of boehmite is digested. It is so called extractable scandium (Sc_{av}) and it can be easily digested with sodium bicarbonate solution under "mild" conditions. Total content of Sc_2O_3 in red mud from STBR bauxite amounts to ~ 140 ± 10 ppm and extractable scandium (Sc_{av} – from boehmite) amounts to ~ 55 - 60 %.

High content of scandium in Al - minerals is not typical for other bauxites. In particular, in bauxites from Parnassus bauxite mine scandium content amounts to 10-23 ppm (i.e. < 10 % from total Sc content in bauxite).

1.4. Chamosite

The amount of chamosite[1] in Urals bauxite reaches 30 % and it contains scandium [3] but the average amount is not established. During the autoclave digestion chamosite partially dissolves [4] and the amount of Sc_{av} in RM might reach 60 - 65 %.

1.5. Zircon

In STBR bauxites (Shugorskaya deposit) zircon (ZrO_2) is present as accessory mineral in form of fine grains of < 5 µm. Article [5] shows that it is metamict zircon (i.e. with amorphized structure) and the content of Sc_2O_3 amounts to 1.5 - 3.3 mass. %. Metamict fine-grained zircon decomposes during sodium bicarbonate digestion and scandium dissolves into the solution.
Greek bauxites contain higher amount of ZrO_2 (up to 1 mass. %) as large ZrO_2 crystals [2]. The content of scandium in such zircon is also higher but Zr coarse grains precipitate with red mud unchanged and scandium is hard to extract.

1.6. Titan Minerals and Phases

[1] Chamosite in STBR and SUBR bauxites has an "ideal" formula: $4FeO \times Al_2O_3 \times 3SiO_2 \times 4H_2O$. Research showed the chamosite structure actually contains the following: up to 4.4 % MgO, up to 1.6 % CaO, up to 1.1 % TiO_2 and up to 2.5 % CO_2. Also part of chamosite in bauxite is oxidized that is why up to 20 % Fe^{2+} is oxidized to Fe^{3+}, and it affects its crystal structure, behavior during autoclave digestion and decomposition.

Table 7. Solids chemical composition.

Experiment No	TCA dosage	Precipitation weight, gram	Oxide content in the solids, mass. %											
			Sc_2O_3	ZrO_2	TiO_2	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	P_2O_5	SO_3	LOI
Initial RM		50 gram	0.0140	0.11	4.5	13.1	14.9	45.6	6.4	0.85	5.1	0.51	1.2	7.2
266	1	52.08	0.0094	0.053	3.9	11.5	13.3	40	6	0.86	8.3	0.44	1.1	13.2
267	3	51.91	0.0094	0.079	3.9	11.6	13.9	39.6	7	0.77	6.9	0.44	1	12.8
268	5	52.33	0.0098	0.074	3.8	11.3	13.4	38.5	6.9	0.82	8.5	0.43	1	14.3

The results showed that due to addition some extra amount of TCA (~10-50 % from present HG) scandium extraction reduced by ~ 4÷5 %.

5. Conclusions

1. During sodium bicarbonate digestion of red mud (at pH = 9 ± 0.2) calcium hydrogarnets decompose by 50 % and more and form new phases – dawsonite, calcite, aragonite, vaterite. First 30 minutes of digestion are of key significance. This process causes the secondary losses up to > 50 % of extractable scandium. Scandium bound in hydrogarnet is also lost as it goes into new phases: dawsonite, calcite, and aragonite.

2. In course of preliminary treatment of red mud with sodium solution hydrogarnet decomposes to calcium carbonates by established reaction. Also pH value increases above 12 - 13 and caustic and sodium aluminate are formed. They can be returned to alumina production process. This method can be used to avoid increase of alkali content in red mud after sodium bicarbonate digestion and to improve extraction of scandium bound with dawsonite.

3. Digested mud shall be washed to dissolve dawsonite. Due to that alkali can be returned to the process and scandium extraction increases.

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