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 [ɣ-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

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[1] Chamosite in STBR and SUBR bauxites has an "ideal" formula: $4FeO \times Al_20_3 \times 3SiO_2 \times 4H_2O$. 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.

Article [6] shows high Ti – Sc correlation (titan – over 70 % as perovskite, $CaTiO_3$, and some amount as rutile and anatase) in RM from Greek bauxite. The form of scandium in perovskite is not determined.

We did not establish any correlations between Sc and Ti content in red mud from STBR bauxite. During sodium bicarbonate digestion up to 20 % of red mud dissolves into the solution. Consequently we can state that scandium absorbed on the surface of rutile, anatase, hydrocassite ($CaTi_2O_4(OH)_2 \times nH_2O$) and perovskite and partially in crystal lattice can be extracted.

1.7. Hematite and Goethite

It is believed that hematite is the main carrier for scandium in bauxite. As work [2] shows hematite and goethite in Greek bauxites contain up to 80 % of scandium. In Bayer process hematite is nonreactive, i.e. > 80 % of scandium remains poorly extractable and disposed with red mud.

1.8. Apatite

Some scholars believe that scandium can associate with apatite. Our studies proved the correlation between the content of scandium and phosphorus in RM from SUBR bauxite.

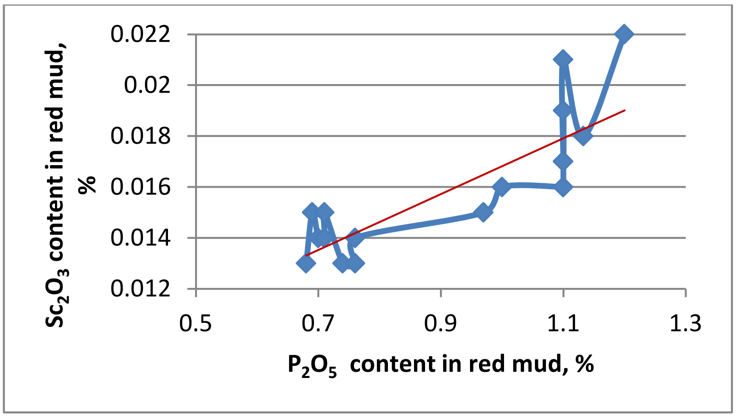

Figure 1. Dependence of Sc_2O_3 content in red mud on P_2O_5 (samples of RM are taken over the period from January 2015 to March 2017.

1.9. Scandium Migration from Bauxite to Red Mud

From boehmite, diaspore and chamosite scandium is digested into alkali solution with high caustic concentration ($Na_2O_{caustic}$). Sc_2O_3 solubility in pure caustic solution (concentration by NaOH ~ 250 g/dm^3) at ambient temperature is about 1 g/dm^3 and improves at higher temperatures [7]. If scandium could be fully dissolved the concentration of dissolved scandium in the fluid of strong digested slurry would be up to 20 mg/dm^3 expressed as Sc_2O_3. But as per the analysis data of the fluid of strong digested slurry the actual Sc_2O_3 amount is < 1 mg/dm^3. It can be assumed that scandium is removed from strong alkali-aluminate liquor due to one or several processes such as the following:

- formation of independent insoluble phase, most likely $Sc(OH)_3$ or ScOOH that is adsorbed on some phase. A number of researches believe that the main sorbing agent for Sc is the surface of fine haematite;
- scandium isomorphously enters the structure of forming phases, for example, DSP and/or calcium hydrogarnet (HG).

In Bayer process during decomposition of Si - minerals (kaolinite, chamosite, quartz etc.) only two following stable phases are formed in significant amount:

- calcium hydrogarnet (HG) represented by formula **$3CaO \times 2(Al,Fe)_2O_3 \times n(Si,Ti)O_2 \times (6\text{-}2n)H_2O$**
- sodium hydroalumosilicate (DSP) of sulphate-cancrinite type with general formula **$Na_6[SiAlO_4]_7(SO_3) \times 1.7\ H_2O$**

Mud from STBR bauxite contain about 30 % of DSP and HG that are constantly changing at all stages of Bayer process incl. recrystallization and isomorphous substitution [8].

During STBR and SUBR bauxite processing with Bayer method only two initial minerals remain in significant quantity in RM:

- fine hematite (the amount in RM is up to 45 %) that deemed to sorb scandium on its surface;
- chamosite (the amount in RM is > 15 mass. %) partially changed on the surface. Study of red mud from STBR bauxite with the use of scanning electron microscope performed by M.V. Lomonosov Moscow State University showed that relatively larger amounts of scandium are correlated with changed chamosite surface.

Haematite concentrate was extracted from RM from STBR bauxite with the number of methods (disintegration, enrichment in magnetic fields of medium and high intensity, gravity segregation etc.). Analysis of concentrate showed that Sc_2O_3 content amounts to 140 - 160 ppm i.e. it matches the average amount of scandium in RM. So the information that fine hematite is the main sorbing agent for Sc_{av} was not confirmed.

It can be stated that depending on bauxite type and process parameters of Bayer cycle the mud contains several forms of scandium:

- easily extractable scandium, adsorbed or precipitated on the surface. The amount varies from 5 to 70 %;
- heavily extractable scandium chemically bonded in the structure of mainly iron-containing minerals, from 95 to 30 %;
- chemically bonded in the phases formed during the reactions with other compounds, incl. Al, Ca, CO_2, Fe, etc.

1.10. Scandium Balance in Bayer Process

Balance of scandium distribution between product alumina and solid and liquid phases of red mud shall be specified.

As work [2] shows during the processing of mixture of diaspore and gibbsite bauxites at AoG (Greece) 16 % of scandium goes to alumina during the decomposition so scandium content in SGA amounts to about 40 ppm (expressed as Sc_2O_3). ~ 80 % of scandium goes into red mud.
Study of SGA from 7 refineries of UC RUSAL (Sc_2O_3 content in bauxites varies from 25 to 100 ppm) showed that Sc_2O_3 content amounts to 1.2 - 2.3 ppm. Any correlation between scandium content in bauxite and alumina was not determined. So over 95 - 99 % of scandium goes into red mud.

Analysis of pond water form UAZ (Urals aluminium plant) recycled from the mud disposal area indicated that it contains up to 1 mg/dm^3 Sc_2O_3.

2. Research Objective

Due to scandium type generated during processing of STBR and SUBR bauxites by sodium bicarbonate digestion Sc_2O_3 concentration in liquid phase shall be > 25 - 50 mg/dm^3. Development of modes for sodium bicarbonate digestion of scandium from RM in laboratory and at pilot plant showed significant difference in values of scandium recovery into the liquor (from 10 to 65 %). Sc_2O_3 amount in the liquor does not exceed 15 - 20 mg/dm^3. Reasons for poor repeatability of digestion shall be explained. Scattered results on digestion efficiency affect performance indicators of Sc_2O_3 production. It was assumed that one of the main factors determining scandium recovery is scandium secondary losses during new phase formation that remain stable during sodium bicarbonate digestion. This work specifies the results of verification of such assumption.

3. Experimental

3.1. Fixation of Scandium Recovered from RM

Due to scandium secondary losses during sodium bicarbonate digestion we developed method for recovered scandium fixation that allows minimizing the impact of secondary reactions. As per this method the excessive amount of ion - exchange resin is added to mud slurry so that the resin quickly absorbs dissolved scandium. Due to that scandium does not enter into reaction and does not form new compounds. After completion of digestion process the resin was washed from red mud and sodium bicarbonate solution and analyzed for Sc and other elements content by ICP MS and/or ICP AS as per method [9].

3.2. Red Mud Changes During Sodium Bicarbonate Digestion

The comparative analysis of X-ray diagrams of red mud after alumina production and red mud after SBD showed that calcium hydrogarnet (HG) or tricalcium aluminate hydrate (TCA) decomposition occurs. It was established that during the reaction with soda and bicarbonate calcium hydrogarnet dissolves into the following:

- calcite and its low temperature forms – aragonite and vaterite;
- sodium and aluminium hydrogencarbonate, of dawsonite type $Na_2O\times Al_2O_3\times 2CO_2\times 2H_2O$;
- alikali (sodium) hydrosilicate.

Red mud from UAZ (Urals aluminium smelter) contains 8 - 15 mass. % of calcium hydrogarnet. It is undefined if scandium is bound into forming calcium carbonates (calcite, aragonite and vaterite) and dawsonite during HG decomposition. Also reaction rate and produced products are not determined.

3.3. Calcium Hydrogarnet Decomposition by Sodium Bicarbonate Solution

Two samples were studied:

- initial red mud from UAZ (Urals aluminium smelter);
- tricalcium aluminate hydrate (TCA) – prepared in the laboratory with use of process spent liquor and fresh calcium hydroxide, $Ca(OH)_2$.

Chemical composition of the samples is indicated in Table 1:

Table 1. Chemical composition of UAZ red mud, initial TCA, forming compounds, and Al_2O_3 content in solutions.

Sample description	Al_2O_3 in liquid phase, g/dm^3	Chemical analysis of solids, mass. %										
		TiO_2	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	P_2O_5	SO_3	LOI	incl. CO_2*
Initial UAZ red mud	init. liquor 0	4.4	13.4	15.6	43.2	7.3	1.2	4.6	0.56	1.0	7.9	1.3
Initial synthetic TCA	0	<0.05	<0.06	20.5	0.11	48.2	0.17	0.25	0.03	0.2	30.2	1.4
experiment 2 TCA + CO_2 bubbling for 1.5 hours at 22 °C	**0.036**	0.06	<0.06	17.8	0.16	44.2	0.45	2.0	0.06	0.13	35.9	19.1
experiment 3 TCA, digestion for 2 hours at 85 °C	**22.1**	0.08	<0.06	9.0	0.26	50.5	0.42	0.65	0.05	0.10	38.5	26.0
experiment 4 TCA, digestion for 4 hours at 85 °C	**26.1**	0.08	<0.06	8.6	0.12	51.1	0.39	0.85	0.06	0.10	39.3	28.6
experiment 5 TCA, digestion for 6 hours at 85 °C	**32.0**	0.09	<0.06	6.9	0.13	51.7	0.45	0.57	0.06	0.08	39.6	31.0

Conditions of experiments on HG decomposition: Digestion was performed with sodium bicarbonate solution. Solution composition (g/dm^3): Na_2O_{total} – 70.91, pH – 9.33, in all experiments L : S = 4 : 1 (by weight).

Filtrate after experiments was analyzed for Al_2O_3 and Na_2O content, muds were analyzed by X-ray spectral analysis (XSA) and X-ray diffraction analysis (XRD) methods and also tested for CO_2 content (Table 2 and Table 3).

Experiment 2 – 3.5 grams of TCA mixed with 15 cm^3 of sodium bicarbonate solution and bubbled through 100 % CO_2 from the vessel for 1.5 hours at ambient temperature while stirring. pH in slurry liquid part amounted to 8.6.

As can be seen during the bubbling through 100 % CO_2 at ambient temperature in an hour CO_2 content in the precipitation increased by 13 times from 1.9 to 19.1 mass. % due to formation of calcite. The amount of calcite in the sample reached over 50 % that was confirmed by X-ray diffraction analysis (Table 2). There is almost no alumina in the solution (Table 1).

Experiments 3, 4 and 5 – 3.5 grams of TCA added to 15 cm^3 of sodium bicarbonate solution and digested while stirring at 85 °C for 2, 4 and 6 hours. CO_2 bubbling was not performed.
As can be seen HG dissolves at 85 °C and in 2 hours over 70 % of HG goes into calcite. After 6 hours of reaction with sodium bicarbonate solution HG dissolution value reaches 85 %. And due to CO_2 binding into calcite there is no sodium bicarbonate in the solution and Na_2CO_3 partially causticizes to NaOH. Due to caustification pH increases to > 13.7. Al_2O_3 content in the solution increases from 0 to > 30 g/dm^3 and simultaneously Al_2O_3 content in the precipitation decreases from ~ 20 to ~ 6 %.

In practice under limited CO_2 input conditions calcium hydrogarnet is dissolved by sodium solution: solid calcium carbonate precipitates, part of soda goes into caustic and alumina dissolves as sodium aluminate ($NaAlO_{2aqv}$).

If during the digestion CO_2 bubbling is performed alumina from TCA does not dissolve as sodium aluminate but it forms dawsonite that probably acts as Sc precipitator; the assumption is tested in the present section (Table 2).

Table 2. Semiquantitative phase composition of red mud and Ca-compounds.

Sample description	**Intensity of characteristic peaks of phases and minerals, d/n, Å / I, imp/s**											
	Boehmite, 6.11 Å	**Diaspore, 4.0 Å**	**Al- goethite, 4.18 Å**	**Haematite, 2.70 Å**	**Calcite, 3.03 Å**	**Portlandite, 4.9Å $Ca(OH)_2$**	**$3CaO\cdot Al_2O_3\cdot 6H_2O$, 5.10Å (TCA)**	**$3CaOAl_2O_3CaCO_3\cdot 11$ $_2O$, 7.60Å (TCA)**	**Mica, 10.0 Å**	**DSP, 6.30 Å**	**Hydrogarnet, 5.10 Å**	**Chamosite, 7.05 Å**
No 7 Init.RM	сл.	105	235	3030	160	-	-	-	160	250	110	705
Initial TCA	-	-	-	-	90	610	1820	195	-	-	-	-
Experiment No 2	-	-	-	-	4145	95	1315	-	-	-	-	-
Experiment No 3	-	-	-	-	6080	100	885	сл.	-	-	-	-
Experiment No 4	-	-	-	-	6320	90	710	-	-	-	-	-
Experiment No 5	-	-	-	-	7785	60	570	-	-	-	-	-

Scandium binding by calcium hydrogarnet decomposition products (TCA)

To conduct **experiment 6** the following was used:

- TCA prepared in the laboratory (chemical composition is specified in Table 1, phase composition is specified in Table 2);
- Sc-containing sodium bicarbonate solution.

Experiment conditions:

- temperature – 85 °C
- volume of digestion solution - 100 cm^3;
- TCA dosage rate – 4 g (on dry basis);
- residence time while stirring – 3 hours;
- slight bubbling with 100 % CO_2 from a vessel to maintain $pH \leq 9.0$ in operating medium.

After completion of the experiment the slurry was filtered using Buchner funnel and washed with ~10 cm^3 of water. Process water was mixed with the filtrate (~ 92 cm^3). Filter cake was dried to constant weight and analyzed by XSA, XRD, ICP AS methods. Chemical compositions of solids and liquid phases and phase compositions of the precipitations are specified in Table 3 and Table 4.

As the experiment showed > 80 % TCA dissolves due to soda impact and significant amount of alikali and carbon acid react to form dawsonite $Na_2O\times Al_2O_3\times 2CO_3\times 2H_2O$ and calcium carbonate (calcite, aragonite and vaterite). It causes significant reduction of concentration of digestion solution expressed by Na_2O_{total} from 70 to 41 g/dm^3.

Table 3. Chemical composition of the solutions.

Sample description	Content, g/dm^3				
	Na_2O_{total}	Al_2O_3	Sc_2O_3	ZrO_2	TiO_2
Initial solution	70.0	0.019	0.032	0.11	0.38
After experiment 6	41.1	0.0034	0.0078	0.0026	0.0096

> **75 % scandium, zirconium and titan are removed from the solution** (Table 3) and significant amount of alkali is bound. Chemical composition of the precipitation is specified in Table 4.

Table 4. Chemical composition of the precipitation after the contact with Sc - containing sodium carbonate solution, mass. %.

Sc_2O_3	ZrO_2	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O
0.035	<0.0005	1.4	14.5	0.23	0.06	27.4	0.42	11.1

As can be seen Sc_2O_3 content in the precipitation amounts to 350 ppm.

By its phase composition the precipitation comprises calcite, dawsonite and low-temperature calcium carbonate, aragonite and vaterite.

It is confirmed that part of scandium digested from red mud can be repeatedly bound in new phases. Further we will establish if dawsonite and calcium carbonates affect this process. Variations (by two times or more) in scandium recovery values during sodium bicarbonate digestion (22 - 25 %) and bicarbonate-sorption digestion (38 - 55 %) can be attributed to this very feature. If resin is present in the slurry scandium attaches to it and does not enter the structure of forming dawsonite or calcium carbonate.

To confirm this assumption TCA dissolution kinetics in Sc - solution was tested (**experiments No 7**).

Experimental conditions:

- residence time of TCA and Sc - solution – 0.5, 1, 2 and 3 hours with and without resin;
- volume of digestion sodium bicarbonate solution - 100 cm^3**;**
- TCA dosage rate – 4 grams i.e. this value is close to calcium hydrogarnet content in the red mud during bicarbonate digestion;
- during the residence time the slurry was stirred with the propeller agitator;
- experiment temperature – 85 °C.
- CO_2 was continuously fed to maintain pH = 8.8÷9 in the reaction zone;
- the amount of resin added for the number of experiments - 4 cm^3 per 100 cm^3 of the solution.

After the completion of the experiment the slurry was filtered using Buchner funnel under vacuum and washed with 10 cm^3 of hot water. The filtrate was analyzed for Na_2O_{total}, Na_2O_{carb}, $Na_2O_{bicarbonate}$, Al_2O_3, Sc_2O_3. The mud was analyzed by XSA, XRD, ICP AS methods. The results are specified in Table 5 and Table 6.

Table 5. Chemical composition of the solutions after interaction with TCA.

Experimen No	Time, hour	V, cm^3	pH	Content, g/dm^3				
				Na_2O total	Al_2O_3	Sc_2O_3	ZrO_2	TiO_2
Initial solution **without resin**			9.2	68.9	0.0017	**0.031**	0.0024	0.011
223	3	116.5	8.85	55.0	0.0078	0.015	0.0019	0.016
224	2	111	8.97	58.1	0.0025	0.016	0.0019	0.012
225	1	116	9.0	54.3	0.0063	0.016	0.002	0.011
226	0.5	128	9.0	48.8	0.012	0.013	0.0017	0.0089
Initial solution **with resin**			9.35	76	0.0011	0.031	0.0023	0.011
228	3	145	8.9	50.4	0.0024	0.0008	0.0015	0.003
230	2	110	8.93	55.0	0.0014	0.0009	0.0015	0.0031
227	1	119	9.0	58.12	0.002	0.0015	0.0018	0.0041
229	0.5	112	8.97	62	0.0024	0.0030	0.0017	0.0054

Table 6. Chemical composition of the solids and resin after reaction with Sc – solution.

Time, hour	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 TCA		<0.0001		<0.05	<0.06	20.5	0.11	48.2	0.17	0.25	0.03	0.2	30.2 incl. CO_2=1.4
3	5.203	0.1	0.0019	0.06	0.99	17.7	0.26	33.4	0.42	6.1	0.06	0.06	40.5
2	5.06	0.06	0.0009	<0.05	1	18.7	0.24	34.9	0.44	5.3	0.06	0.07	39.8
1	5.02	0.053	0.008	0.06	1	18.5	0.25	34.7	0.44	5.7	0.06	0.07	39.1
0.5	5.05	0.04	0.0006	0.06	1	18.8	0.26	34.9	0.5	5.0	0.06	0.06	38.4
3	4.30 (precipitation)	0.0085	0.0054	<0.05	0.91	16.4	0.2	29.9	0.32	8.5	0.07	0.04	43.5
	1.2737 (resin)	0.14	0.0016										
2	4.92 (precipitation)	0.004	0.0005	0.06	0.92	16.7	0.22	31.4	0.34	8.2	0.09	0.05	42.4
	1.1967 (resin)	0.13	0.0015										
1	5.18 (precipitation)	0.0072	0.011	0.05	0.89	16.3	0.21	30.7	0.36	8.6	0.08	0.05	42.9
	1.3348 (resin)	0.14	0.0021										
0.5	5.19 (precipitation)	0.011	0.003	<0.05	0.93	17.3	0.21	31.7	0.41	7.6	0.09	0.05	41.2
	1.2558 (resin)	0.11	0.014										

4. Discussion

As can be seen from the results main part (~ 70 %) of TCA dissolves and greater part of calcite, aragonite and dawsonite form within the first 30 minutes (Figure 2 and Figure 3). It shall be taken into account the actual amount of dawsonite is consistent with the amount of newly formed calcium carbonates but X-ray amorphous phase is also formed and that influences the intensity of diffraction peaks.

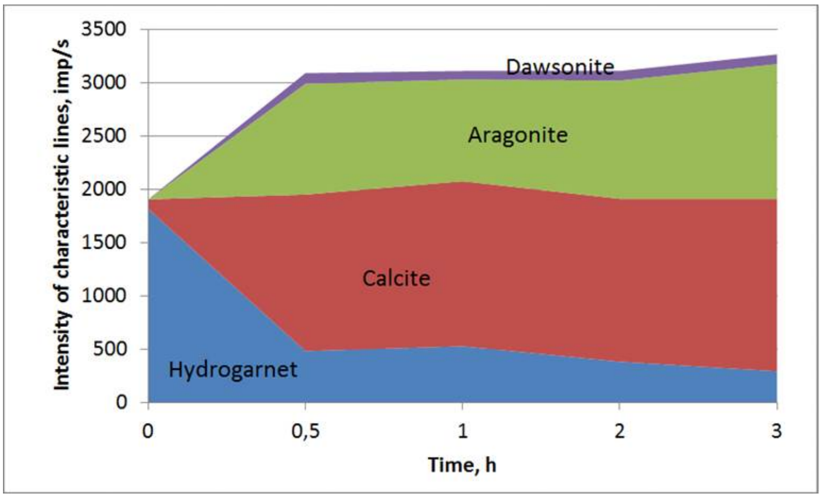

Figure 2. Results of semiquantitative X-ray diffraction analysis on TCA dissolution and formation of new phases in sodium bicarbonate solution depending on the time (Conditions: 85 °C, without resin).

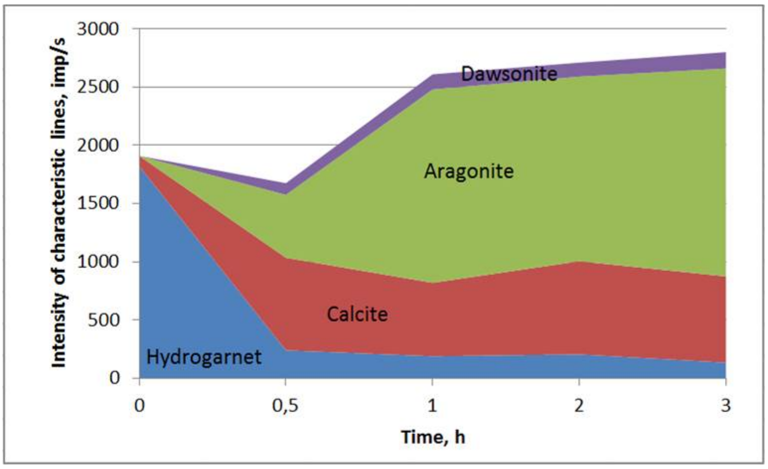

Figure 3. Results of semiquantitative X-ray diffraction analysis on TCA dissolution and formation of new phases in sodium bicarbonate solution depending on the time (see Table 7 Conditions: 85 °C, with resin).

During TCA dissolution greater part of scandium, titan and zirconium is removed from the solution (Table 3).

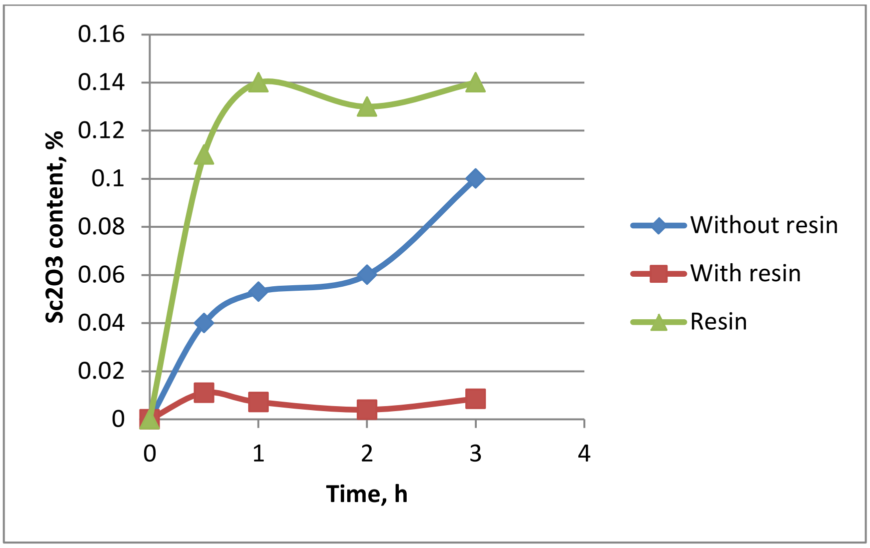

Figure 4. Scandium content in the precipitation during TCA decomposition by Sc - containing sodium bicarbonate solution depending on the residence time (without and with resin) (data from Table 7).

Figure 4 clearly shows that 70 % of scandium is absorbed on the resin for 30 minutes and after one hour sorption process is almost complete. In the absence of resin in the slurry scandium precipitation from the solution is a more complicated and longer process but over 60 % Sc is removed from the solution.

Dependence of Ca hydrogarnet quantity in red mud on scandium extraction.

To perform experiments the homogeneous slurry was prepared by adding sodium bicarbonate solution (76 g/dm^3 Na_2O_{titr}) to the weighted amount of initial red mud, and the slurry was bubbled to achieve pH ≤ 9. After that glass reactor with the slurry was placed to the thermostat heated to the certain temperature and synthetic TCA was added. After experiment completion the slurry was filtered using Buchner funnel under vacuum and washed with 10 cm^3 of hot water. Process water was mixed with the filtrate. The filtrate was analyzed for Na_2O_{total}, Na_2O_{carb}, $Na_2O_{bicarbonate}$, Al_2O_3, Sc_2O_3. The mud was analyzed by XSA, XRD, ICP AS methods. The results are specified in Table 7.

Conditions of experiment on red mud digestion with TCA:

- red mud weighted amount (ICP 243, KB 315) – 50 (on dry basis);
- L : S = 4.5 : 1**;**
- TCA amount – 1, 3, and 5 mass. % by dry red mud weight;
- experiment temperature – 85 °C;
- residence time at reaction temperature – 3 hours;
- pH = 8.8÷9.0.

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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