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Red Mud Disposal and Utilization

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IMPROVED EFFICIENCY OF RED MUD PROCESSING THROUGH SCANDIUM OXIDE RECOVERY

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Abstract

Bayer process of alumina production involves generation of considerable mud tonnage (1.5 – 3 t of red mud per 1 ton of alumina) with high content of scandium and rare earth metals up to 120 g/t and 1500 g/t respectively. Scandium is difficult-to-obtain and expensive element (oxide price – 99.9-99.99% is between USD 4 000 – 5000 per kg). The main applications are the high quality alloys, high temperature ceramics, luminescent materials, dielectrics.

In frames of creation of ecologically friendly technology to utilize red mud, RUSAL is developing process of scandium concentrate recovery based on the carbonization leaching of scandium. This process allows improvement of the efficiency of red mud processing by scandium recovery and partial caustic removal with alkali recycling to the process. This technology excludes the acids effluents and can be easily implemented into existing process circuit. This paper presents the results of the laboratory trials of red mud processing with scandium concentrate generation, as well as the data on the pilot unit to produce scandium concentrate at one of the alumina refineries in Russia.

1. Introduction

Actually the great interest is observed to the scandium production from different mineral and anthropogenic sources and this is connected first of all with growing demand in such industrial branches like fabrication of Al- scandium alloys and ceramics based on zirconium dioxide, stabilized by scandium oxide. The aluminum alloys with scandium have unique combination of technological properties: high durability, superplasticity, self-hardening, excellent weldability, high corrosion stability. Application of aluminum alloys with scandium (scandium content in commercial aluminum alloys varies within 0.05 – 0.30%) in such industrial branches like rocket production, aircraft building, railway transport, shipbuilding, oil and gas production allows not only to improve the technical and economic parameters, but to create brand new products. The application of alloy system Al-Mg-Sc instead of conventional Al-Mg allows reducing the mass and specific metal consumption for structural design by 20-30 %. [1-3]. Other dynamically developing field of scandium application is zirconium ceramic stabilized by scandium oxide specified by higher ion conduction versus the analogs (for example zirconium oxide, stabilized by yttrium oxide) It allows to reduce the operating temperature of electrochemical equipment from 1000 to 700 °C with high conductivity of separation diaphragm increasing the service life and reliability of such electrochemical reactors like Solid Oxide Fuel Cell (SOFC), electrolytic cells, sensors [4-5].

Scandium is typical dissipated element not forming its own deposit of mineral and therefore the scandium production is connected with complex processing of non-ferrous and rare earth metals (titanium, uranium, tungsten, zirconium, aluminum, iron) [6]. According to scientists assessment 70% of scandium from total forecast reserves are located in bauxite [7]. Therefore it is not surprising that red mud, the waste product of bauxite processing in Bayer circuit is one of the most challenging sources of scandium. The advantages of those sources are high scandium content (up to 120 g/t) readiness to processing (no need to mine, crush and grind), vicinity to the developed infrastructure (operating alumina refineries), huge volume of red mud (accumulated at red mud disposal areas and formed during refineries operation) [8]. Two RUSAL refineries in Russia every year are producing more than 2 million tons of red mud with scandium content 240 g/t.

The methods of scandium recovery from red mud can conventionally be divided into 2 groups, considering the type of leaching agent using to transform scandium into liquor: acid methods and carbonate methods. The acid methods of scandium recovery from red mud are based on application of different acids (mostly sulfuric, hydrochloric or nitric) for leaching of scandium from red mud. Above methods allow to recover more than 50% of scandium into liquor with secondary recovery of rare earth elements form red mud together with accompanying products (sorbents, coagulants, pigments, etc.). The considerable disadvantages of those methods are the formation of large volume of acid/salt outflows and impossibility to use the red mud processed by acid in steel industry [9].

The method of scandium carbonate leaching from red mud is based on the scandium ability to dissolve and form anion complexes of type $(Sc(CO_3)_n)^{(2n-3)-}$ ($n \geq 2$) in presence of excess carbonates and hydro carbonates of alkaline elements. The scandium solubility in the liquors of sodium bicarbonate is much higher than in carbonates 10]. The research experts of the Chemistry of Solids Institute Of Ural Russian Academy of Science suggested to produce scandium concentrate from red mud consisting in preliminary carbonization of sodium carbonate liquor by furnace gases, multistage successive leaching of scandium from red mud by carbonate-bicarbonate liquors (7 cycles) and 3 stages retention of produced liquor with increased temperature. The third stage the liquor evaporation is conducted with volume reducing in two times. As result of the process the scandium recovery reaches 15.8 % [11]. Despite the low recovery of scandium from red mud the advantage of this method consists in the potential to use it at operating refinery to improve the integrated processing of red mud and produce maximum economic effect through production of valuable and critical scandium oxide and reclaiming of red mud after carbonization process in steel and cement industries.

RUSAL company during last several years carried out large scale studies aimed on scandium recovery from red mud to improve its integrated processing. During the investigations the methods of scandium leaching by different reagents were studied: sulfuric acid, hydrochloric acid, formic acid, sodium carbonate and bicarbonate solutions and also the methods of scandium recovery from liquor. As result the ecologically friendly technology of red mud processing was developed with production of scandium concentrate, based on carbonization leaching of scandium with yield 23%. This technology excludes acid/salt outflows and allows recycling up of 30 % of caustic from red mud [12].

2. Laboratory experiments

The study of scandium recovery from red mud with incidental partial caustic removal was carried out using red mud slurry (L:S = 1.0:3.0-3.5), produced after processing of Sredniy Timan bauxite deposit at Ural refinery (Russia) The chemical analysis of slurry solid phase is presented in Table 1.

Table 1

Chemical composition of Timan red mud.

mass %						g/t	
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	Na_2O	Sc	Zr
10.0	12.0	46.0	4.5	8.0	4.5	90.0	650.0

During the process studies of scandium carbonization leaching the following key parameters impacting the scandium (Sc^{3+}) recovery rate with accompanying elements (Ti, Zr) were studied:

- temperature;
- CO_2 pressure during gassing of mud slurry;
- sodium hydro carbonate concentration ($NaHCO_3$);
- $NaHCO_3$: Na_2CO_3 ratio in leached liquor.

The selection of process conditions for scandium recovery is based on the following principals:

1) Solubility of $Sc(OH)_3$ in bicarbonate liquor ($NaHCO_3$) is considerably higher than in liquor (Na_2CO_3), therefor it is advisable to use sodium bicarbonate for carbonization leaching. During red mud processing by sodium bicarbonate the partial decomposition of sodium bicarbonate to the sodium carbonate occurs leading to the scandium yield reduction into liquor. For intensification of scandium carbonization leaching from red mud it is advisable to provide the gassing of slurry by carbon dioxide in order to shift the balance of $Sc(OH)_3$ dissolution reactions from red mud solid phase and improve the scandium recovery into liquor:

$$Sc(OH)_3 + NaHCO_3 \rightarrow Na[Sc(CO_3)_2] + NaOH + 2H_2O \qquad (1)$$

$$NaOH + CO_2 \rightarrow NaHCO_3 \qquad (2)$$

Respectively the gassing of red mud slurry by carbon dioxide with increased pressure promotes the scandium leaching process from the liquor.

2) During desilication of mud slurry in the alumina production circuit on the surface of red mud particles, mainly on Fe- bearing minerals the fine sodium hydro Al silicate (DSP) is co-precipitated impeding the access of leaching reagent (CO_3^{2-} and/or HCO_3^-) to the $Sc(OH)_3$ surface. Hereby it is required to remove the "shading" film of DSP from the surface of red mud to avoid diffusion – kinetic limitation in the process of scandium leaching using special preliminary processing of red mud.

3. Results and discussion

Table 2 depicts the results of experiments aimed on the studies of CO_2 pressure impact during gassing of red mud slurry on the yield of polyvalent metals (Sc^{3+}, Ti^{4+} и Zr^{4+}) under other equal leaching conditions: T - 50 °C, L:S in initial mud slurry 1.0-4.0.

Table 2

Impact of pressure on scandium yield from red mud

CO_2 pressure (P), Atmosphere	Recovery, %		
	Sc	Zr	Ti
1,0	17,0	50,0	2,4
2,0	21,3	57,6	3,0
4,0	23,6	63,0	4,30
6,0	25,8	68,0	6,0

As seen from table 2 the increased CO_2 pressure in heterogeneous system "red mud $NaHCO_3$ (liquor)–CO_2" considerably augment the scandium recovery into liquor (from 17.0% to 25.8%), however at the same time the recovery of associated elements to Sc^{3+} grows: titanium and zirconium.

It was noted that high pressure scandium leaching tends to the partial caustic removal from red mud with caustic recycling to the process. The total Na_2O content in mud was reduced from 4.5 mass% to 2.5 mass% due to the interaction of caustic in red mud with carbon dioxide and generation of sodium bicarbonate and its transition into solution.

The selection of scandium leaching temperature during the trials was conditioned by following:

- Reduced temperature (t ~ 30-35 °C) promotes the CO_2 solubility in water;
- Temperature profile (50-60°C) corresponds to the stability range of scandium anion carbonate complexes $[Sc(CO_3)_n]^{(2n-3)-}$;
- The increased temperature (t ~ 70 °C) with the stability of anion complexes $[Sc(CO_3)_n]^{(2n-3)-}$ due to the transition into basic carbonates $Sc(OH)(CO_3)_2$ with the low solubility in water, that apparently will reduce the scandium yield from red mud [13].

The study's results of the temperature impact on the scandium recovery are presented on figure 1.

When the carbonization leaching is conducted under the temperature = 30-40 °C, with other equal conditions, the rate of scandium recovery from red mud does not exceed 15.0% with P_{CO2}=4.0 atm and 17.5% with P_{CO2} = 6.0 atm. The optimum leaching temperature with other equal conditions is 60 °C, when the yield of scandium is 22.5 % (P_{CO2} = 4.0 atm) and 26.5 % (P_{CO2}=6.0 atm). The temperature increase to ~ 80°C reduces the scandium recovery (under other equal conditions).

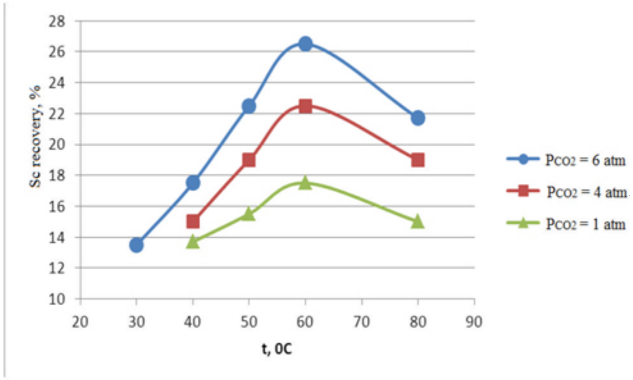

Figure 1. Impact of temperature on the recovery yield from red mud (%).

Figure 2 presents the results of studies on the impact of sodium hydro carbonate ($NaHCO_3$) concentration in initial leaching liquor on the Sc recovery yield under other equal conditions (Temperature 60 °C, S:L=1.0:4.0).

As seen from figure 2, the required and sufficient concentration of sodium hydro carbonate in leaching liquor is 125.0 g/l^3 $NaHCO_3$; and the scandium recovery yield was 22.5 % (P_{CO2} = 4.0atm) and 26.5 % (P_{CO2} = 6.0 atm) respectively.

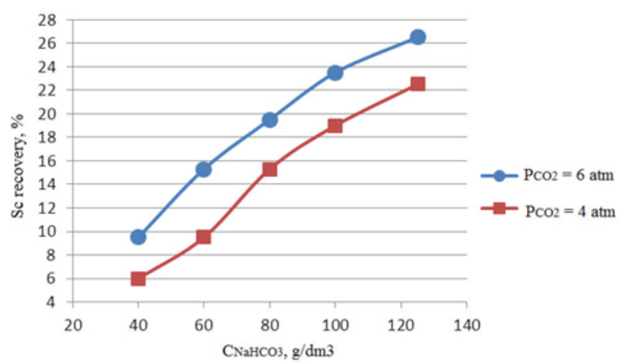

Figure 2. Impact of NaHCO3 concentration of the scandium recovery yield

The considerable concentration reduction of complexing (HCO_3^-) ions substantially reduces the scandium recovery from red mud – up to ~15.0 % $NaHCO_3$ concentration in leaching liquor 60.0 g/l (P CO_2=6.0 atm).

It is connected with the following factors:

- Interaction concurrence with complexing (HCO_3^-) ion from the side of polyvalent metals (Ti^{4+}, Zr^{4+}, Fe^{2+}, rare earth elements);
- Considerable chemical interaction of HCO_3^- ions with calcium carbonate in the red mud with formation of soluble calcium hydro carbonate considerably reducing the "proportion" of HCO_3^- ion on the complexing interaction with scandium components.

4. Pilot industrial unit for production of scandium concentrate from red mud

In the first half of 2014 UC RUSAL implemented the pilot unit for scandium concentrate production from red mud at Kamensk Uralsky Alumina Refinery (Russia) with production rate 200 kg/month. The block flow diagram of the pilot unit is presented in figure 3 and includes the carbonization leaching and 2 stages hydrolytic precipitation of scandium concentrate with removal of main impurities (Fe, Ti, Zr).

The pilot unit was commissioned in August 2014 (Figure 4).

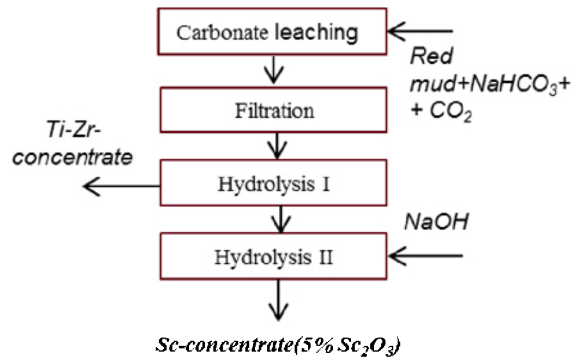

Figure 3. Block process diagram of the pilot unit to produce scandium concentrate from red mud.

Figure 4. Pilot unit to produce scandium concentrate from red mud.

Actually the pilot industrial trials are conducted to specify the regimes and technical and economic parameters of the process.

5. Conclusions

1. The ecologically friendly technology of red mud processing was developed with recovery of scandium concentrate, based on the method of scandium carbonization leaching. The technology allows improving the red mud processing efficiency due to the scandium yield as well as due to partial removal of caustic soda from red mud and its recycling to the Bayer process.

2. The laboratory trials of scandium recovery from red mud of Kamensk Uralsky Alumina Refinery were conducted with study of impact of process temperature, concentration of the leaching agent and carbon dioxide pressure on the scandium recovery yield.

3. Based on the lab research results, a pilot unit for production of scandium concentrate from red mud was constructed and commissioned at the refinery.

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