Research Results and Prospects for Acid-Salt Processing of Low Quality Bauxites and Other Alumina-Containing Raw Materials in a Closed Circuit

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Abstract

Acid technologies seem to be attractive for processing of low quality bauxites and alumina silicates, but the main difficulties of their application are connected to the problems of organization of circular schemes with low consumption of chemicals and energy. Acid-salt technology based on using ammonium bisulfate in full cycle can be used, but the economics of the corresponding processes proposed earlier loses as compared with the classical alkaline method. Besides, the most in demand are the processes, which fully or partially can be "inscribed" in modern equipment design and process conditions corresponding to the standard Bayer method or its industrial modifications. The results obtained in the course of long-term systematic laboratory and bench studies carried out in the "NewChem Technology" Company are presented, and they display the prospects for the creation of new efficient technology for the production of alumina from the low-grade raw in circular process with the recovery and consumption of the same amount of salt reagent in each cycle. One of the distinctive features of the proposed scheme is the use of special Acid–retardation (Newchem) technique for separating in nano-porous media the residual amounts of acid and salt to be returned to the process head. It allows significant reduction in energy and reagent consumption. A comparison with other processes is given for leaching and alumina insulation stages in terms of the completeness of reagent recycling and energy consumption.

Keywords: high-silica bauxite, nepheline, alumina, leaching, salt method.

1. Introduction

In connection with the gradual decrease in the availability of high-quality bauxites, well fit to processing by standard alkaline methods, there is resumed an interest in creating commercial technologies based on acid and salt methods of processing high-silica alumina-containing raw materials. A distinctive feature of these methods is the possibility of separating silica at the stage of digestion of raw materials, and this can significantly expand the range of such materials that are potentially interesting for industrial processing. At the same time, the lack of acid and salt methods is the need to use additional technological stages for deep purification from iron leached into productive solutions along with aluminum. In addition, there is another limitation of acid methods, more related to sulfuric or nitric acids, namely, the difficulties in organizing closed circuits with the recovery of these reagents in technological chain and their return to the head of

the process. From this point of view, two technological directions can be considered, as the most promising today: 1) hydrochloric acid processing of alumina-containing raw materials with high-temperature recuperation of hydrogen chloride [1-3] and 2) different versions of the method of using ammonium bisulfate [4-6].

Ammonium hydro-sulfate (bisulfate) process was invented by Max Buchner in Hanover-Kleefeld in 1921, piloted in Germany in the 1920s and in Oregon in 1944. Now this method is included in the list of named processes in chemical technology and is called "Aloton" or "Buchner" [7,8]. The technique consists in implementing circular process comprising the steps of thermal decomposition of ammonium sulfate into ammonia and ammonium bisulfate, dissolving the latter to treat the aluminum-containing feedstock in an autoclave, filtration of solution of alum and precipitating aluminum hydroxide with ammonia, isolation of ammonium sulfate from the mother liquor to return it to the head of circuit. Subsequently, embodiments of the Buchner method appear under which the digestion stage is carried out not by the "wet" process, but by the way of sintering the ammonium sulfate with the raw material [9-11] The process was not commercialized, and it can be assumed that in those days, in the case of good access to high quality raw bauxite materials the Buchner process could not withstand competition with the Bayer one. Moreover, it turned out that the method is more suitable for processing readily degradable clay materials and other aluminosilicates, than applicable to bauxites [12]. Last decade, the researches of Chinese specialists on the production of alumina from fly ash [13] have shown the possibility of commercial realization of combined technologies based on the first stage of sintering ash with ammonium sulfate or hydrosulfate.

Today, in the new circumstances, it seems appropriate to return to the classic Buchner process for analyzing its weaknesses and assessing the prospects. This article is devoted to an attempt to solve this problem (yet, at the laboratory level) by combining the capabilities of acid and salt methods and by introducing new separation methods, particularly, acid retardation in nano-porous media and its variant called as the "NewChem", which greatly facilitates the creation of real closed-circular schemes for processing high-silica bauxites and alumino-silicate materials [5,14,15].

2. Experimental

Three types of alumina-containing raw materials from different deposits of Russia were used: Timan bauxite of hematite-boehmite type; Kaichak kaolin clay and Kola nepheline concentrate. Table 1 shows the contents of macro-components in these materials (bauxite and kaolin work samples, as well as the analytical data on their composition, have been presented by the "Rusal – Vami" Company, S.-Petersburg, Russia; nepheline concentrate has been presented by the NIUIF Institute of the FOSAGRO Co., Moscow, Russia)

Table 1. Chemical composition of raw materials (mass %).

	Al_2O_3	Fe_2O_3	SiO_2	TiO_2	K_2O	MgO	Na_2O	P_2O_5	SO_3	CaO	SrO	MnO	H_2O
Bauxite	47.7	28.3	8.0	2.8	0.63	0.39	0.23	0.22	0.20	0.17	-	0.04	11.5
Kaolin clay	18.3	2.7	64.2	1.7	2.0	0.89	2.1	0.15	-	0.87	-	1.0	7.0
Nepheline	28.0	2.4	44.0	0.55	7.6	0.45	12.5	0.17	-	1.75	0.11	0.08	1.5

For the preparation of the reagent for leaching at processing of alumina-containing raw materials, ammonium sulfate and sulfuric acid qualification "Technical grade" were used. Leaching experiments were performed in thermostatically controlled glassware at atmospheric pressure or in a laboratory autoclave. Suspension filtration operations were performed on a Buchner filter with thermostatic system and with using a vacuum pump. To carry out the processes of separation and concentration of dissolved components at various stages of processing intermediate solutions,

technologies for the use of flue gases would make the process even more promising, ensuring the simultaneous solution of the environmental problem of sequestering CO_2.

Table 3. Comparison of the potential characteristics of the proposed process for raw materials and products with industrial technology per 1 ton of alumina produced.

	Raw material			By-products		
	NC	CO_2 ($CaCO_3$)	H_2SO_4	Na_2CO_3	K_2CO_3 (K_2SO_4)	Sludge
Industrial	4.6	- (3.6)	-	0.75	0.25	6.2
Proposed method	4.6	0.37 (0.7)	0.3	0.75	- (0.5)	3.0 (3.4)

In the case of bauxite processing (with the composition shown in Table 1), 45 kg of sulfuric acid are consumed to produce 1 ton of alumina. The consumption of ammonium bisulfate is significantly less and is associated only with the replacement of losses in a circular closed process.
The main energy costs in the proposed process (similarly to the Bayer one) are related to the need to use evaporators. The process for Timan bauxite according to the proposed scheme will require 7.2 tons of steam per 1 ton of alumina produced. It can be used equipment for autoclave leaching well known for the classic Bayer method, supplemented by apparatus for the decomposition of ammonium sulfate and the distribution of ammonia.

4. Conclusions

A circular process is proposed for processing alumina-containing raw materials using ammonium bisulfate with an admixture of sulfuric acid as a leaching reagent, which implements a closed cycle for ammonium bisulfate.

It is shown that is rational to carry out the processing of bauxite in the autoclave mode in temperature range of 120 – 130 ^{0}C, while nepheline concentrate and kaolin clay can be processed at atmospheric pressure at 190 – 100 ^{0}C

A modified acid retardation method (MAR-process) is proposed, based on the separation of acids and salts in a nano-porous reactor. Its use for the separation of components in iron-containing circulating working solutions can significantly reduce the consumption of reagents and energy for the separation of iron from these solutions.

A sorption method is proposed for deep cleaning of solutions of ammonium alum from iron to obtain a final product that meets the requirements for metallurgical alumina.

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