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, ion exchange resins were used: a strong basic anion exchanger AB-17x8 (Tokem, Russia) with quaternary ammonium groups and a chelating sorbent – polyampholite IOX C500 ("Axion", Perm city, Russia) with aminomethylene phosphonic functional groups. Operations with resins were performed using glass columns equipped with a filtering bottom and a thermostatic jacket.

3. Results and Discussion

3.1. The Composition of the Reagent to Provide a Closed Loop on Ammonium Bisulfate

Alumina-containing raw materials, along with other components, contain alkaline and alkaline earth elements. In the leaching process using ammonium bisulfate, simple and double sulfates of various components are formed, which, at subsequent stages when exposed to ammonia or in the processes of thermal hydrolysis, are converted into the corresponding hydroxides with ammonium sulfate recovery. However, the chemical transformation of ammonium sulfates with calcium, strontium, sodium and potassium with the recovery of the reagent is almost impossible. To organize a closed ammonium process, it is necessary to use an acid-salt reagent, which is ammonium hydrosulfate mixed with sulfuric acid consumed in the process, the amount of which is determined by the composition of the raw material, namely, the presence of alkali and alkaline earth elements. The advantage of using such a reagent is not only the ability to keep in circulation ammonium hydrosulfate, but also the high leaching efficiency of the target component from various types of alumina-containing raw materials [5,14].

For any alumina-containing raw materials with the general formula of the molar composition: $xAl_2O_3 \cdot yFe_2O_3 \cdot zSiO_2 \cdot \alpha Na_2O \cdot \beta K_2O \cdot \gamma CaO$, the bisulfate cycle with reagent regeneration can be schematically represented as the following sequence of chemical reactions:

$$xAl_2O_3 \cdot yFe_2O_3 \cdot zSiO_2 \cdot \alpha Na_2O \cdot \beta K_2O \cdot \gamma CaO + 6(x+y)NH_4HSO_4 + (\alpha+\beta+\gamma)\,H_2SO_4 = zH_2SiO_3\downarrow + \quad + \\ 2x\,NH_4Al(SO_4)_2 + 2yNH_4Fe(SO_4)_2 + 2(x+y)(NH_4)_2SO_4 + \alpha Na_2SO_4 + \beta K_2SO_4 + \gamma CaSO_4\downarrow + \quad + \\ [3(x+y) + z\ \alpha+\beta+\gamma]H_2O \qquad (1)$$

$$2y\,NH_4Fe(SO_4)_2 + 6y\,NH_3\uparrow + 6y\,H_2O = 2y\,Fe(OH)_3\downarrow + 4y\,(NH_4)_2SO_4 \qquad (2)$$

$$2x\,NH_4Al(SO_4)_2 + 6x\,NH_3\uparrow + 6x\,H_2O = 2x\,Al(OH)_3\downarrow + 4x\,(NH_4)_2SO_4 \qquad (3)$$

$$6(x+y)\,(NH_4)_2SO_4 = 6(x+y)NH_4HSO_4 + 6(x+y)NH_3\uparrow \qquad (4)$$

Reaction (1) is a leaching performed at elevated temperature; (2) and (3) — precipitation of iron and aluminum hydroxides by ammonia, which must be carried out separately at different stages of the process. The ammonium sulfate solution obtained in processes (1) - (3) is subjected to evaporation, crystallization and decomposition at temperatures 250 – 300 ^{0}C according to the reaction (4) with the recovery of ammonium bisulfate, as well as ammonia.

The theoretical molar ratio of ammonium bisulfate and sulfuric acid in acid salt reagent is: $6(x+y) / (\alpha+\beta+\gamma)$, and mass ratio is $115\ x\ 6(x+y)/\ 98x(\alpha+\beta+\gamma)$. For example, for bauxite with the molar composition formula: $0.57Al_2O_3 \cdot 0.23Fe_2O_3 \cdot 0.12SiO_2 \cdot 0.01K_2O \cdot 0.005Na_2O \cdot 0.005CaO$ (in accordance with the data in Table 1) the mass ratio of ammonium bisulfate and sulfuric acid is approximately 278: 1. This means that when using 40% ammonium bisulfate solution for leaching, it should also contain less than 0.2 % free sulfuric acid. It is obvious that a more rigorous calculation of the optimal composition of the reagent is carried out according to the same logic, but taking into account the content of all components in the feedstock, as well as the real degree of their extraction under the leaching at the conditions used. For nepheline concentrate with an approximate formula of raw materials: $0.47Al_2O_3 \cdot 0.03Fe_2O_3 \cdot 0.83SiO_2 \cdot 0.14Na_2O \cdot 0.07K_2O \cdot 0.02CaO$, the ratio of bisulfate and sulfuric acid in the leach solution should be about 15: 1, however, there are various options for organizing the process of extracting the associated components, which can significantly reduce the consumption of sulfuric acid while ensuring a closed cycle for ammonium bisulfate. This option is presented in Figure 1, which shows a schematic diagram, developed by us, for the alumina-containing raw material processing, consisting of two cycles.

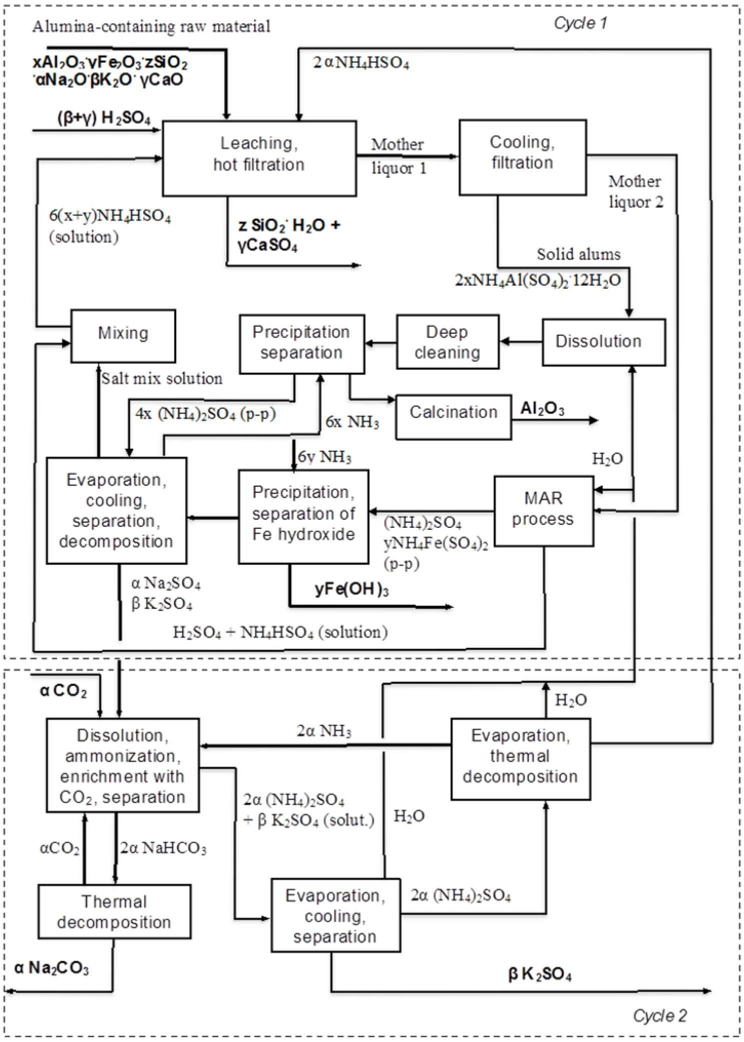

Figure 1. Schematic diagram of the bisulfate cyclic process of processing alumina-containing raw materials using a modified method of acid retention (MAR-process).

Cycle 1 is common for all types of alumina-containing raw materials, it includes the following stages: leaching at elevated temperature (80 – 130 ^{0}C depending on the type of raw material, including autoclave leaching), hot filtration with separation of silica and undecomposed residues from mother liquor 1, cooling mother liquor 1 to obtain a suspension of alum, separating the latter from the mother liquor 2, dissolving alum in pure water and deeply purifying them, for example, by the sorption method, precipitating aluminum hydroxide with ammonia and its calcination (600 ^{0}C) to obtain alumina. The solution after the precipitation containing ammonium sulfate mixed with soluble alkali metal sulfates is evaporated, cooled to separate potassium and sodium sulfates, further evaporated to dryness and thermally decomposed (300 ^{0}C) to the bisulfate returned to the head of the process for preparation of the leaching reagent and ammonia used in the processes precipitation of aluminum hydroxide (as well as iron, titanium, magnesium and other impurities). The mother liquor 2, as a rule, enriched with iron, is subjected to a special method of purification from iron, which is described below. Depending on the type of raw material, for example, during the processing of bauxite, periodic separation of alkali metal sulfates is possible and they are "transferred" from cycle 1 to cycle 2 after their corresponding accumulation in circulating working solutions during repeated circular processes of acid-salt processing.

Unlike the cycle 1, cycle 2 can be organized according to different schemes. Figure 1 shows the scheme for aluminosilicate raw materials such as nepheline with a high content of alkali metals. Here, the process is organized according to the type of soda production process according to the Solvay method. In accordance with this scheme, the total balance of processing aluminosilicate can be represented as follows:

$$xAl_2O_3 \cdot yFe_2O_3 \cdot zSiO_2 \cdot \alpha Na_2O \cdot \beta K_2O \cdot \gamma CaO + (\beta+\gamma)H_2SO_4 + \alpha CO_2 = xAl_2O_3 + yFe_2O_3 + \\ + zSiO_2 \cdot \beta H_2O \cdot \gamma CaSO_4 + \alpha Na_2CO_3 + \beta K_2SO_4 \qquad (5)$$

Taking into account the above formula for nepheline raw materials, the theoretical mass ratio of ammonium bisulfate and sulfuric acid in the leaching reagent is 32: 1. For example, at using 40% ammonium bisulfate solution for leaching, it should also contain up to 1.5% of free sulfuric acid.

3.2. Stages of Leaching and Alum Extraction

Table 2 shows the results of experiments on leaching of aluminum and iron from alumina-containing raw materials of various types. From these data, it follows that in general, as the temperature rises, the degree of extraction of the components increases. But this increase is complex. It follows from the data obtained that is advisable to carry out the processing of nepheline and clay at atmospheric pressure and temperature range 90 – 980 C, while the processing of bauxite should be carried out in an autoclave at a temperatures of 120 – 1300 C.

Table 2. The degree of leaching of the main components from various sources of alumina using 40% solution of ammonium bisulfate mixed with sulfuric acid. S / L = 1:10, leaching time - 4 hours).

Temperature, ^{0}C	Nepheline 40% NH_4HSO_4 + 1% H_2SO4		Kaolin 40% NH_4HSO_4 + 1% H_2SO4		Bauxite 40% NH_4HSO_4 + 0.2% H_2SO4	
	Al	Fe	Al	Fe	Al	Fe
70	41	42	44	45	19	24
82	66	48	-	-	34	45
90	81	72	74	61	44	50
98	85	81	79	59	59	52
120	87	90	84	66	81	63
130	-	-	84	69	78	65
150	-	-	-	-	83	86

The results obtained using a 40 % ammonium bisulfate solution are not optimal and are given as an example. The concentration of the main leaching agent significantly affects another important factor - the distribution of components in different phases after the precipitation of alum. Figure 2 presents some data for the processing of nepheline concentrate, namely, the dependence of the distribution coefficients components between the crystalline alum and the solution from the content in the leaching agent sulfate. These data were obtained by analyzing mother liquor and the solid phase after separation and drying of alum under the same conditions after separation of alum. It follows from the presented results that it is rational to use a higher concentration of ammonium bisulfate solution (60 %) in the initial solution. Under these conditions, the distribution coefficient of aluminum is more than 500, which indicates its quantitative extraction of alum in the solid phase.

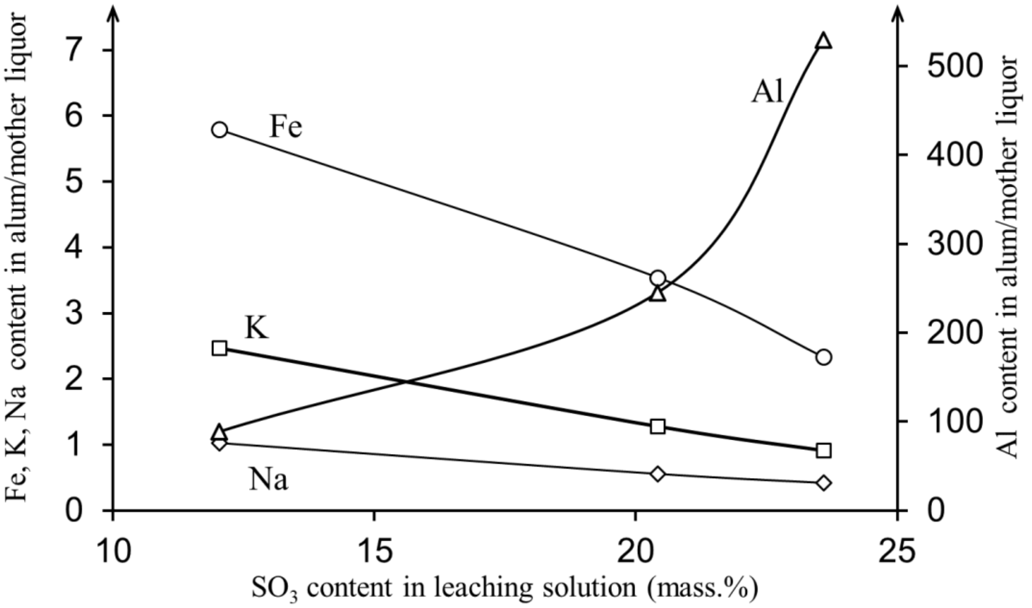

Figure 2. Distribution coefficients of the components between alum and mother liquor depending on the concentration of sulfate in leaching solution.

3.3. Partial Removal of Iron from Circulating Solutions

To increase the degree of extraction of the target component and reduce the leaching time in the bisulfate process, a significant excess of the reagent is used, which is in circulation and returns to the process head as the component of the mother liquor 2 and the acidic waters of precipitate washing after leaching (not shown in Figure 1). They are these two solutions that accumulate the main amount of iron in the form of double sulfate salts. Iron is removed by precipitating its hydroxide with ammonia below pH 5.5. However, direct isolation from highly acidic solutions requires a large amount of ammonia, ultimately the irrational expenditure of additional reagent and energy to decompose the ammonium sulfate obtained from it after the separation of $Fe(OH)_3$. To solve the indicated problem of excess expenditures in a cyclic bisulfate process, the possibility of preliminary separation of ammonium bisulfate in solution into sulfate and acid was first shown using the previously proposed modified acid retardation method (MAR -process) [16,17]. Separation is carried out due to the sieve effect - differences in the sizes of hydrated ion pairs of salts and acid molecules from concentrated solutions on nanoporous sorbents: gel anion exchangers or super-linked polystyrene. The separation stage is included in the overall cyclic process as shown in Figure1. An example of separation in a column with a gel anion exchange resin on a laboratory scale is shown in Figure 3. A strong base anion exchanger in the sulfate form is used to exclude any ion exchange processes. In essence, a sieve nano-porous reactor is used, in which there are no chemical reactions. In the first stage (I), the processed solution containing ammonium bisulfate is passed through the column, from bottom to top, while the acid is retained, and the ammonium sulfate solution with a small amount of acid (pH = 3) passes through the resin bed. In the second stage (II), a highly dilute solution of sulfuric acid (pH = 2) is passed through from the top downwards, displacing a substantially more concentrated solution of sulfuric acid mixed with ammonium bisulfate. The figure shows an example of a repeated cyclical process of separation of components during the processing of

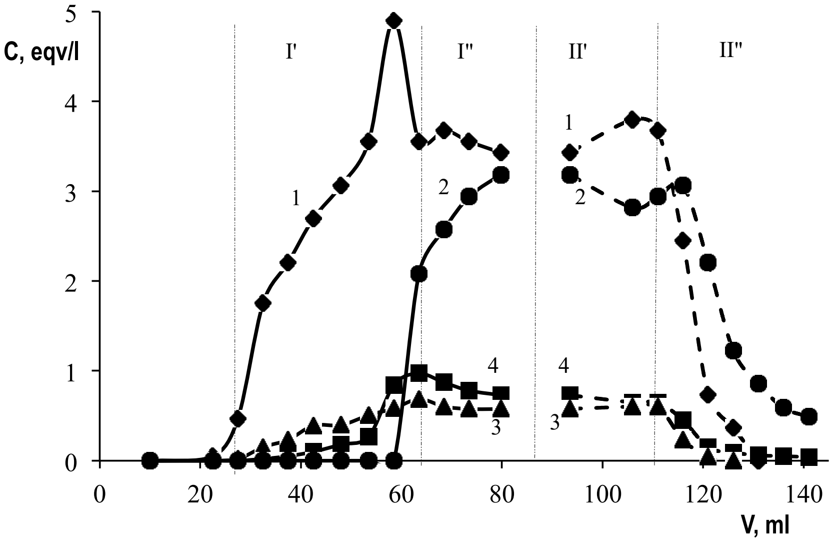

Figure 3. Separation of components by the modified method of acid retardation (MAR) at the treatment of wash water of bauxite solid residues. T = 65 ° C. (1) - (NH4) 2SO4, (2) - H2SO4. (3) - Al, (4) - Fe.

wash water after the decomposition of bauxite. First, a very dilute solution of sulfuric acid (pH = 2) is left from the column from the previous cycle and returned for use in the next cycle, then ammonium sulfate solution (I ') leaves for the precipitation of iron with ammonia, then mixed solutions leave (I' ') and (II') with a composition close to the original processed solution, in connection with which they are returned to the entrance to the column. On the last stage, we obtain a highly acidic mixture of sulfuric acid and ammonium bisulfate solution, which are returned to the head of the process shown in Figure 1 to prepare a leaching agent for the next cycle.

3.4. Deep Cleaning of Aluminum from Iron Impurities Remained in Alum

The ammonium alum after their separation has a composition characterized by the ratio of the mass content of the components: Al: Fe = (40-60): 1, depending on the raw material used. For further purification, alum is dissolved in pure water (condensate after evaporators), as shown in Figure 1. Among the possible options for deep cleaning of such a solution, we chose a sorption method for the selective isolation of iron on a chelating ion-exchange resin with aminomethylene phosphonic functional groups. Figure 4 shows the corresponding output sorption curves, from which it is clear that aluminum, despite ts excess concentration is not absorbed by the sorbent. The figure shows the breakthrough curves (concentration histories) of the complete (brought to an equilibrium) sorption process. In real technology, the sorption process is stopped after the "breakthrough" of iron at a certain level that meets the requirements for purity of the final product - alumina. Desorption of iron from the sorbent for its reuse is carried out with a solution of sulfuric acid. An example of the output desorption curves is shown in Figure 5.

Using the proposed sorption method allows to obtain a solution from which, when exposed to ammonia at pH > 6, high-purity aluminum hydroxide is released. The calcination of the latter at 600 ^{0}C makes it possible to obtain the final product (γ-Al2O3), which meets the requirements for alumina qualification G00.

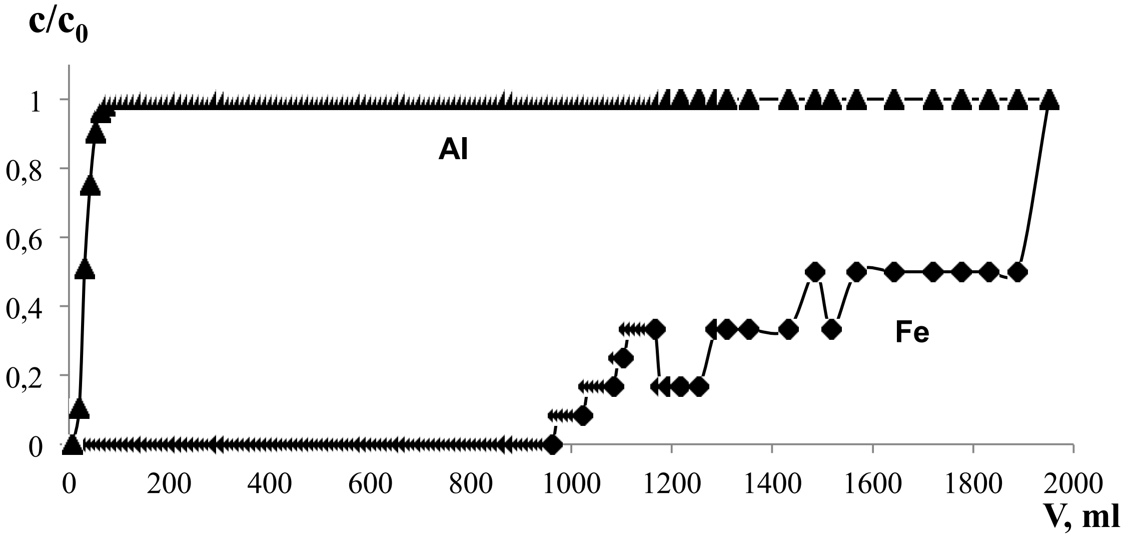

Figure 4. Sorption of iron with a chelating resin IOX C-500 (Vbed = 38 ml) from an aqueous solution of alum with concentrations of elements: c(Fe) = 0.3 g/l and C (Al) = 16.42 g/l.

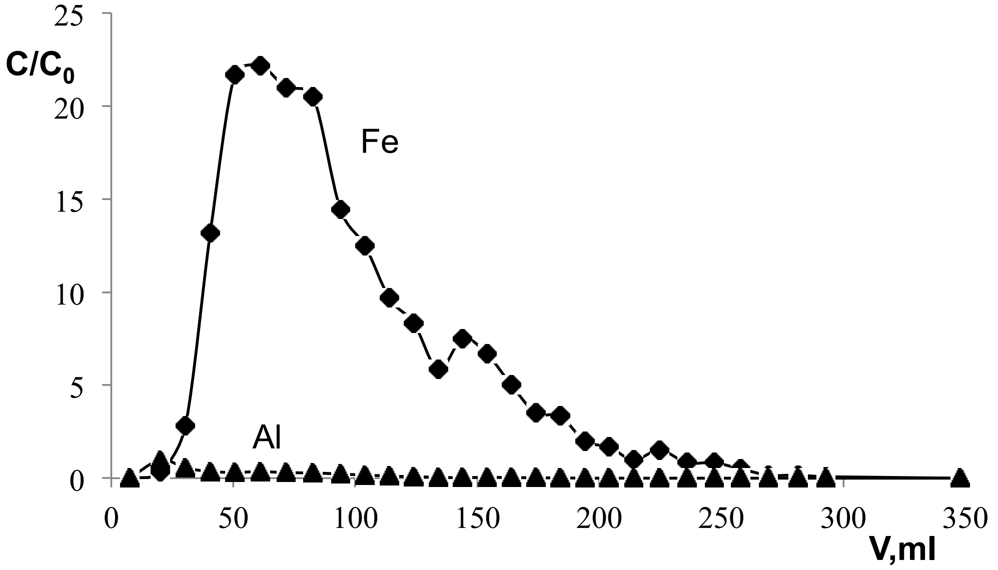

Figure 5. Desorption of components with 1N solution of sulfuric acid after the sorbent loading with iron.

3.5. Some (calculated) Technical Indicators of the Proposed Bisulfate Process

The capabilities of the proposed process can be demonstrated (Table 3) by comparing the parameters for products and raw materials with one of the industrial enterprises to which nepheline concentrate (NC) is delivered to a distance of more than 1000 km. The proposed process may be promising for implementation at the place of production of oil and gas, which would reduce the transport by 4.6 - 7 times, depending on how it is organized. The use of modern 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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