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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Fluoride Processing of Non-Bauxite Ores

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Abstract—Integrated processing of non-bauxite ores using ammonium hydrogen difluoride was studied. The kinetics of sintering of the raw material, sublimation of ammonium hexafluorosilicate, and formation of aluminum fluoride and alumina were described. The rate constants and activation energies of the reactions were determined.

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Today alumina is mainly produced from high-quality low-silica bauxites by the widely used Bayer method. The resources of high-quality bauxites in the Russian Federation are limited, and the demand of the Russia's aluminum industry for alumina is met by domestic resources to only 40–45% [1]. At the same time, in Russia there are inexhaustible resources of various non-bauxite ores: kaolin rocks, high-alumina shales, anorthosites, alkaline aluminosilicates, etc. [2]. Much promise is shown by kaolin and kyanite concentrates whose alumina content reaches 62.6%, and in this respect they are comparable with high-quality bauxites.

The goal of this study was to examine fluoride processing of non-bauxite ores and develop an alumina recovery procedure that would be comparable in profitability with the alumina recovery from high-quality bauxites. In so doing, we performed integrated processing of non-bauxite ores with the preparation of ammonium hexafluorosilicate, aluminum fluoride, and other valuable products.

EXPERIMENTAL

As starting non-bauxite ore we used kaolin concentrates of KN-73 (50.28, Al_2O_3 33.88, Fe_2O_3 0.71, TiO_2 0.47, Na_2O 0.14, K_2O 1.20, calcination loss 12.86%) and KM-1 (SiO_2 46.83, Al_2O_3 37.00, Fe_2O_3 0.96, TiO_2 0.66, Na_2O 0.16, K_2O 1.33, calcination loss 12.83%) grades (Chalgan deposit of kaolin-containing sands, Amur oblast). The alumina content of the dehydrated kaolin concentrates reaches 39.09 and 42.60%, respectively, but the cost of recovery of these concentrates from kaolin-containing sands is considerably lower than the cost of production of kyanite concentrates from high-alumina shales and gneisses with a massive texture.

As fluorinating agent we used ammonium hydrogen difluoride (NH_4HF_2) of analytically pure grade, produced by Galogen Joint-Stock Company (Perm). Under normal conditions, NH_4HF_2 is a relatively inert crystalline powder which is considerably safer environmentally than fluorine and hydrofluoric acid. However, at elevated temperatures it becomes a powerful fluorinating agent. The melting point of ammonium hydrogen difluoride is 126.8, and the decomposition point, 238°C.

The starting components taken in stochiometric ratios were thoroughly ground and placed in Teflon, glassy carbon, or platinum cups or crucibles. The sample weight was 5–40 g. Experiments were performed in a nickel or nickel-lined steel reactor. The initial charges were heated at 50–550°C for 0.25–4.5 h, with condensation of volatile products. The volatile products were collected with a two-zone condenser. Argon was used as carrier gas.

The initial samples, intermediate phases, and final products were studied by X-ray phase analysis (DRON-3, CuK_α radiation), emission spectrum analysis (STE-1 spectrograph), and chemical methods. The content of ammonia and fluorine in volatile products was determined by titration of the resulting aqueous solutions with sulfuric acid and thorium nitrate, respectively. Thermal

gravimetric analysis was performed with a Q-1000 derivatograph in platinum crucibles with lids at a heating rate of 2–5 deg min^{-1} (initial sample weight 150 mg).

The kinetic parameters of the processes (rate constants and activation energies) were calculated from the sample weight loss in definite time intervals at given temperatures and from the results of elemental analysis of the reaction products. The degree of formation of the reaction products, required for further calculations, was determined by the formula

$$\alpha = m_a/m_{calc},$$

where m_a is the weight of the product formed and m_{calc}, theoretically possible amount of the product.

The calculations were performed using two procedures: by the generalized Erofeev topochemical equation and by the Emanuel'–Knorre method.

Fluoride processing was performed in two steps: sintering of the initial ore with ammonium hydrogen difluoride at 50–200°C and heat treatment of the resulting solid precipitate in the temperature range 350–550°C. The sintering involves the following reaction:

$$1/2\ Al_4[Si_4O_{10}](OH)_8 + 12\ NH_4HF_2 = 2\ (NH_4)_2SiF_6 + Kaolin + 2\ (NH_4)_3AlF_6 + 2\ NH_3\uparrow + 9\ H_2O\uparrow. \quad (1)$$

Thermodynamic calculations were performed using data from [3, 4]. These results show that the Gibbs energy of reaction (1) under normal conditions is –2197.0, and at 200°C, –2684.2 kJ.

On mixing kaolin concentrates with NH_4HF_2, a viscous mass is formed owing to the release of water, and the reaction actually starts at room temperature. Figure 1 shows the time dependences of the amount of ammonia released in the course of sintering at various temperatures. As follows from the rate constants and activation energy, the process is kinetically controlled (Table 1), and it can be accelerated by increasing temperature. In an NH_4HF_2 melt, the reaction occurs at the maximal rate, and under the optimal conditions (200°C, 3 h) the amount of the released ammonia exceeds 98% of the theoretical value.

According to X-ray phase analysis, the solid precipitate obtained after sintering is a white powder consisting of a mixture of $(NH_4)_3AlF_6$ and $(NH_4)_2SiF_6$.

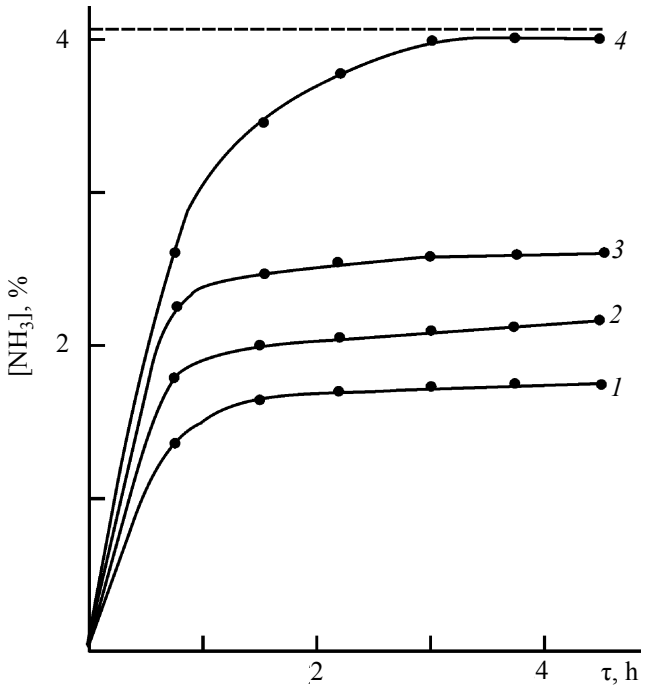

Fig. 1. Amount of ammonia [NH_3] released in the course of sintering of kaolin concentrate with ammonium hydrogen difluoride at various temperatures, as a function of the process time τ. Dashed line denotes the theoretically possible amount of the released ammonia. Temperature, °C: (*1*) 50, (*2*) 100, (*3*) 150, and (*4*) 200.

Heat treatment under reducing conditions of the solid precipitate obtained after sintering yields aluminum fluoride, and treatment under oxidizing conditions with steam purging yields alumina. The reactions involved are as follows:

$$(NH_4)_3AlF_6 + (NH_4)_2SiF_6 = AlF_3 + (NH_4)_2SiF_6\uparrow + 3\ NH_3\uparrow + 3\ HF\uparrow, \quad (2)$$

$$2\ (NH_4)_3AlF_6 + (NH_4)_2SiF6 + 3\ H_2O = Al_2O_3 + (NH_4)_2SiF_6\uparrow + 6\ NH_3\uparrow + 12\ HF\uparrow. \quad (3)$$

Thermodynamic calculations show that the reactions start at temperatures exceeding 320°C: ΔG_{320} = –28.6 (2), ΔG_{320} = –7.8 kJ (3). With increasing temperature, the Gibbs energy decreases, and the reaction equilibrium is shifted toward formation of the final products.

Heat treatment is accompanied by sublimation of $(NH_4)_2SiF_6$ at temperatures exceeding 320°C, in agreement with the previous data [5]. Figure 2 shows the kinetic curves calculated from the weight loss of the nonvolatile residue under reducing conditions with the

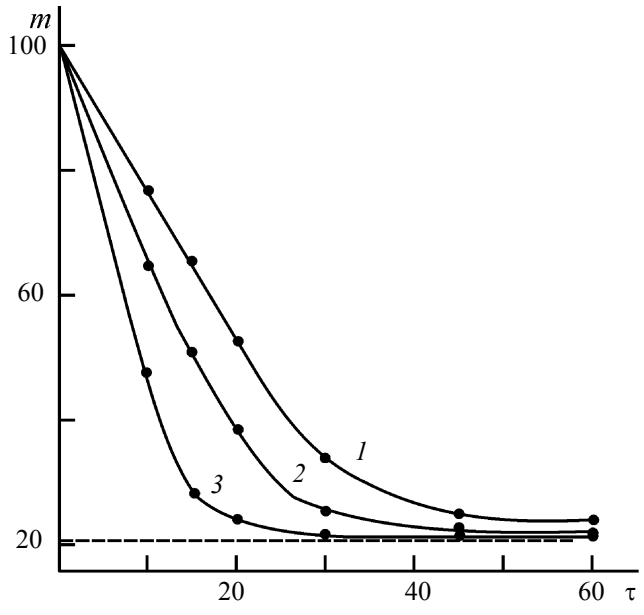

Fig. 2. Kinetic curves of silicon removal from the nonvolatile residue under reducing conditions at various temperatures, with the formation of aluminum fluoride. (*m*) Sample weight (the initial weight is taken as 100%) and (τ) sublimation time. The dashed line denotes the theoretically possible amount of the nonvolatile residue. Temperature, °C: (*1*) 350, (*2*) 450, and (*3*) 550; the same for Fig. 4.

formation of ammonium fluoride, at various temperatures and times of heat treatment. It can be seen that the temperature of 550°C is the most favorable for the removal of silicon from the concentrates: The calculated theoretical amount of the nonvolatile residue is attained in 30–45 min.

Figure 3 shows a thermogram of the reaction of the kaolin concentrate with NH_4HF_2. It can be seen that the reaction becomes active at 100°C, after which the reactants start to decompose with sublimation of the fluorinated components. In the DTA curve, there are endothermic peaks at 190, 320, and 410°C. The peak at 320°C is the broadest and the deepest, which is due to simultaneous occurrence of two processes: sublimation of $(NH_4)_2SiF_6$ and decomposition of $(NH_4)_3AlF_6$. According to X-ray phase analysis, the nonvolatile residue contains γ-AlF3.

The impurities of Fe, Na, and K compounds in the course of sublimation under reducing conditions form simple fluorides which remain in the nonvolatile residue. Soluble alkali metal fluorides (NaF, KF) are removed by treatment of the nonvolatile residue with water, and with respect to the main component (AlF_3) content aluminum fluoride meets the extra grade requirements [GOST (State Standard) 19181–78]. Off-grade iron impurity (FeF_3) is removed by repeated fluoride and aqueous acid processing of the nonvolatile residue. Aluminum fluoride is widely used for preparing cryolite, fluxes, enamels, glasses, and other materials.

From the experimental data on the degree of formation of volatile $(NH_4)_2SiF_6$, we calculated the rate constants and activation energies (Table 1). The process is

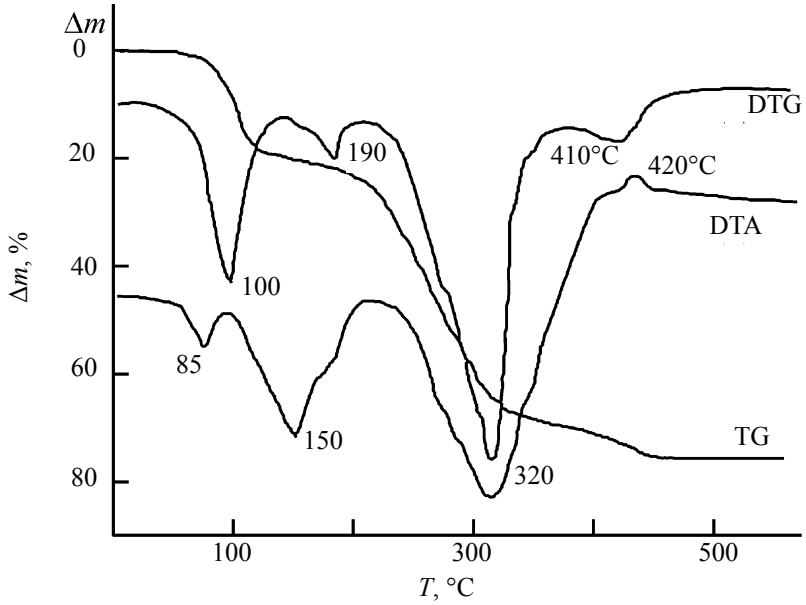

Fig. 3. TG, DTG, and DTA curves of the reaction of kaolin concentrate with NH_4HF_2 (weight ratio 1 : 2.6). Platinum crucible with a cup, heating rate 2–5 deg min^{-1}. (Δ*m*) Weight loss and (*T*) temperature.

characterized by low activation energy and high reaction rate constants. Sublimation of volatile $(NH_4)_2SiF_6$ occurs within a short time, and at 550°C the degree of formation of this product in 30 min exceeds 98%.

According to emission spectrum analysis, volatile ammonium hexafluorosilicate is of high purity: The content of metal impurities (Al, Fe, Mn, Mg, Cu) does not exceed 10–3–10–5%.

Ammonium hexafluorosilicate is widely used in chemical, woodworking, food, and other industries. In aqueous solution in the presence of ammonia, ammonium hexafluorosilicate undergoes hydrolysis with the precipitation of finely dispersed amorphous silica of high chemical purity, with large specific surface area and good filterability [6].

Volatile (NH4)2SiF6 is trapped in a special condenser, and NH3 and HF vapors released in the course of decomposition of fluoroammonium salts again react with each other in the condenser trap to form ammonium fluoride. Evaporation of an aqueous solution of NH4F results in crystallization of ammonium hydrogen difluoride, which is returned to the step of sintering of the starting raw material.

Pyrohydrolysis of the solid precipitate obtained after sintering was performed with overheated steam fed to the reactor under argon pressure. It is common knowledge that inorganic fluorides are highly resistant to oxygen but readily decompose under the action of steam. Ammonium fluorometallates are also prone to pyrohydrolysis and undergo it at lower temperatures compared to simple fluorides.

Figure 4 shows how the degree of conversion of ammonium fluoroaluminate into alumina depends on the temperature and time. Data on the rate constants and activation energies are given in Table 1. Analysis of the kinetic curves shows that the optimal temperature at which the rate of alumina formation is maximal is 550°C. In this case, the degree of recovery exceeds 99%

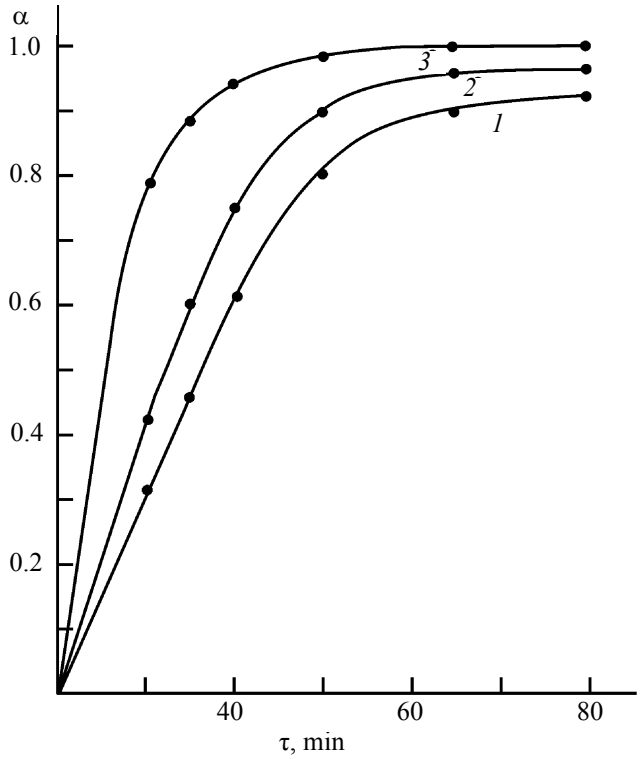

Fig. 4. Degree of conversion α of ammonium fluoroaluminate into alumina under oxidizing conditions at various temperatures as a function of heating time τ.

in 45 min. Higher temperatures are not appropriate, because contamination of the nonvolatile residue with the apparatus material drastically increases.

The nonvolatile residue after pyrohydrolysis contains aluminum and iron oxides and readily water-soluble sodium and potassium fluorides. Iron oxide readily dissolves in 5–10% HCl. Volatile ammonium hexafluorosilicate does not undergo pyrohydrolysis with steam and is separated by the known procedure described in [7] for ammonium hexafluorotitanate hydrolyzate.

The nonvolatile residue obtained is placed in 5–10% HCl. The undissolved precipitate is filtered off and washed with water to remove soluble impurities. Then

Table 1. Rate constants k_r and activation energies E_a of processes described by reactions (1)–(3)

$T_{(1)}$, °C	k_r, min^{-1}	$T_{(2)}$, °C	k_r, min^{-1}	$T_{(3)}$, °C	k_r, min^{-1}
Reaction (1)		Reaction (2)		Reaction (3)	
50	0.004122	350	0.06593	350	0.06572
100	0.005312	450	0.09571	450	0.08983
150	0.01123	550	0.1798	550	0.017
200	0.02781				
E_a, kJ mol^{-1}	31.0	8.0		9.1	

Table 2. Interplanar spacings of the Al_2O_3 phase obtained from kaolin concentrate (d_{exp}) and of reference compounds α-Al_2O_3 (no. 10-173 [8]) and γ-Al_2O_3 (no. 29-63 [8]) (d_{tab})

R-652 sample		α-Al_2O_3		γ-Al_2O_3	
d_{exp}, nm	J/J_1, %	d_{tab}, nm	J/J_1, %	d_{tab}, nm	J/J_1, %
4.801	16.3	–	–	–	–
4.332	11.5	–	–	4.33	35
3.47	80.6	3.479	75	–	–
2.78	20.5	–	–	2.8	45
2.55	100	2.552	90	–	–
2.376	42.8	2.379	40	2.39	65
–	–	2.165	<1	–	–
–	–	–	–	2.28	40
2.08	92.1	2.085	100	–	–
1.99	13	1.964	1	1.98	80
1.736	37.5	1.74	45	–	–
1.595	66.3	1.601	80	–	–
–	–	1.546	3	1.53	10
–	–	1.514	5	–	–
–	–	1.51	7	–	–
1.41	26.8	1.40	30	–	–
1.388	14	–	–	1.4	100
1.374	32.6	1.374	50	–	–

the solid precipitate is dried and calcined at temperatures exceeding 800°C. According to X-ray phase analysis, the solid residue is a white crystalline powder consisting of α- and γ-alumina (Table 2). Its chemical composition (%) determined by chemical analysis was as follows: Al_2O_3 99.8, SiO_2 0.03, Fe_2O_3 0.04, TiO_2 traces, CaO not detected, Na_2O not detected, and K_2O traces. The degree of recovery of alumina is 98.7%.

The resulting alumina corresponds to G-1 grade and can be used for production of primary alumina by the electrolytic procedure and of special kinds of ceramics and electroceramics.

As a result of studying fluoride processing of non-bauxite ores, we developed a procedure that can be implemented on standard equipment produced in Russia. In integrated processing of kaolin concentrates, the procedure can compete with the widely used process of alumina recovery from high-quality bauxite ores by Bayer's procedure [9]. The procedure we developed can be used for recovering alumina from low-grade high-silica bauxites, high-alumina shales, and aluminosilicate rocks: anorthosites, nepheline syenites, synnyrites, etc. [10]. Industrial mastering of this procedure can be important for expanding the sources of raw materials for alumina and aluminum industry of the Russian Federation.

CONCLUSION

A procedure was developed for preparing alumina from various non-bauxite ores, with simultaneous recovery of other valuable components.

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