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Hydrolysis of Aluminum Sulfates in the Presence of Ammonium Sulfite

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Abstract—Hydrolysis of aluminum sulfate and potash alum in the presence of an ammonium sulfite additive in the temperature range T_{boil}–200°C was studied. A possible reaction mechanism was suggested. The composition and structure of the precipitates formed were determined and certain differences in their morphology were noted. Recommendations for practical implementation of the method of hydrolytic recovery of aluminum from solutions of its sulfate salts were given.

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Hydrolysis of aluminum sulfates is the most widespread method for recovery of aluminum(III) from solutions in sulfuric acid processing of aluminum-containing raw materials into alumina [1–5]. It has been found that aluminum sulfates can be arranged in order of increasing susceptibility to hydrolysis as follows: aluminum sulfate < ammonium alum < sodium alum < potash alum [6].

The effect of additions of ammonium, sodium, and potassium sulfates on the hydrolysis of aluminum sulfate has been studied [7, 8]. It was shown that the cations can be arranged in order of increasing effect on the degree of hydrolysis as follows: $H^+ < NH_4^+ < Na^+ < K^+$. It was noted that the ionic radii increase in the same order, which suggests that the solubility of basic aluminum salts decreases as the ionic radius of cations becomes larger.

The effect of temperature has been studied in detail. It was found that a noticeable precipitation of the basic aluminum sulfate is observed only at $T >$ 200°C. For example, according to [6], the degree of hydrolysis of potash alum $KAl(SO_4)_2$, which is the most susceptible to hydrolysis, does not exceed 84% at 240°C. The process is hindered by accumulation of sulfuric acid in solution.

High-temperature hydrolysis involves a large power expenditure and requires an intricate equipment (autoclaves working under a pressure $P > 30$ atm). This is one of the principal reasons why the hydrolytic recovery of basic aluminum salts from sulfate solutions has not been implemented in practice so far. Therefore, it is a topical task to develop procedures that would increase the degree of aluminum(III) extraction into a precipitate of a basic salt, with a simultaneous pronounced decrease in the hydrolysis temperature.

In this study, the hydrolysis of aluminum sulfate (AS) and potash alum (PA) in the presence of ammonium sulfite was examined.

Ammonium sulfite was obtained by bubbling sulfur dioxide through a concentrated solution of ammonium hydrate. As the solution was saturated, ammonium sulfite monohydrate $(NH_4)_2SO_3 \cdot H_2O$ precipitated, which was confirmed by chemical, X-ray phase, and IR spectroscopic analyses. According to [9], ammonium sulfite obtained by various methods contains up to 9–9.4% ammonium sulfate. Therefore, it was taken that the content of the main substance in the resulting salt is 95 wt %. The solution containing 10 wt % ammonium sulfite had pH = 8.2–8.4.

For the experiments, we prepared AS and PA (analytical grade) solutions containing 80 g l^{-1} of Al_2O_3, which is characteristic of solutions obtained by processing aluminosilicate raw materials. The expenditure of ammonium sulfite varied from 0.5 to 2 mol per mole of Al_2O_3. The experimental temperature range was from T_{boil} to 200°C (the boiling points of AS and PA solutions were 103 and 105°C, respectively). The duration of the process at the boiling points of the solutions was 4 h. Hydrolysis at 125, 150, 175, and

Parameters of hydrolysis of aluminum sulfate and potash alum

T, °C	Expenditure of ammonium sulfite, mol mol^{-1} Al_2O_3	Degree of salt hydrolysis, %	
		AS	PA
T_{boil}	–	–	–
	0.5	15.5	46.7
	1.0	42.7	74.9
	1.5	54.9	84.5
	2.0	61.9	88.3
125	–	–	39.5
	0.5	17.2	78.4
	1.0	44.9	86.3
	1.5	58.0	90.7
	2.0	67.9	94.1
150	–	–	58.3
	0.5	22.9	87.5
	1.0	57.1	97.4
	1.5	79.8	98.1
	2.0	85.9	98.8
175	–	–	70.7
	0.5	37.7	92.4
	1.0	61.2	98.2
	1.5	83.6	99.0
	2.0	90.8	99.2
200	–	–	76.9
	0.5	43.7	93.9
	1.0	72.8	99.1
	1.5	87.7	99.3
	2.0	93.0	100.0

200°C was carried out in autoclave bombs, into which 40 ml of a solution was charged and a necessary amount of ammonium sulfite was added. Then the bombs were kept at a prescribed temperature for 1.5 h. The solutions were agitated by tumbling rotation of the bombs. After the process was complete, the autoclave was cooled and the precipitate formed was filtered off, thoroughly washed, and dried to constant weight at 105°C. The precipitates and solutions were analyzed for the content of Al_2O_3. The experimental data listed in the table clearly demonstrate that ammonium sulfite most strongly affects the hydrolysis of aluminum sulfates. No basic aluminum sulfate was precipitated on heating an aluminum sulfate solution up to 200°C.

The addition of ammonium sulfite results in a sharp shift of the reaction equilibrium toward hydrolysis. At the minimum expenditure of the sulfite (0.5 mol per mole of Al_2O_3), a precipitate is formed even at the boiling point of the solutions. At the same temperature, an increase in the expenditure of ammonium sulfite from 0.5 to 2.0 mol per mole of Al_2O_3 results in that the degree of hydrolysis grows by a factor of 2.1–4. At the boiling point (103°C) and an expenditure of ammonium sulfite equal to 1.0 mol per mole of Al_2O_3, a higher degree of hydrolysis (42.7%) is reached, compared with the case of hydrolysis of aluminum sulfate at 230°C, but in the absence of ammonium sulfite (23.2%) [7]. The fullest and technologically acceptable recovery of aluminum(III) into a precipitate of the basic sulfate salt (90.8–93.0%) occurs at an expenditure of ammonium sulfite equal to 2.0 mol per mole of Al_2O_3 and 175–200°C. It is apparent that a virtually complete hydrolysis of aluminum sulfate can be achieved by further raising the temperature.

It is seen from the data obtained that the effect of ammonium sulfite on the PA hydrolysis is more clearly pronounced than that in hydrolysis of aluminum sulfate. At the boiling point (expenditure of ammonium sulfite equal to 1–2 mol per mole of Al_2O_3), the recovery of aluminum(III) into a precipitate of the basic salt reaches 75–88%; the degree of hydrolysis is 86–94% at 125°C and a virtually complete recovery of aluminum(III) into a precipitate of the basic salt is reached at 150°C and higher temperatures.

The role of ammonium sulfite in the hydrolysis of aluminum sulfates is as follows. In an aqueous solution, aluminum sulfate and potash alum are hydrolyzed in accordance with the equation

$$Al_2(SO_4)_3 + 2nH_2O \rightleftarrows Al_2(OH)_{2n}(SO_4)_{3-n} + nH_2SO_4, \qquad (1)$$

where $0 < n \le 3$.

The forming sulfuric acid reacts with ammonium sulfite introduced into a solution in accordance with the equation

$$nH_2SO_4 + n(NH_4)_2SO_3 \rightarrow n(NH_4)_2SO_4 + nH_2O + nSO_2\uparrow, \qquad (2)$$

with the weaker sulfurous acid displaced and ammonium sulfate formed. Being unstable, sulfurous acid readily decomposes into H_2O and SO_2. A part of SO_2, which corresponds to its solubility at a given temperature, remains in the solution, whereas its main part is discharged into the gas phase. As a result, the acid is not accumulated in the solution, and the equilibrium of reaction (1) is shifted toward hydrolysis of aluminum salts.

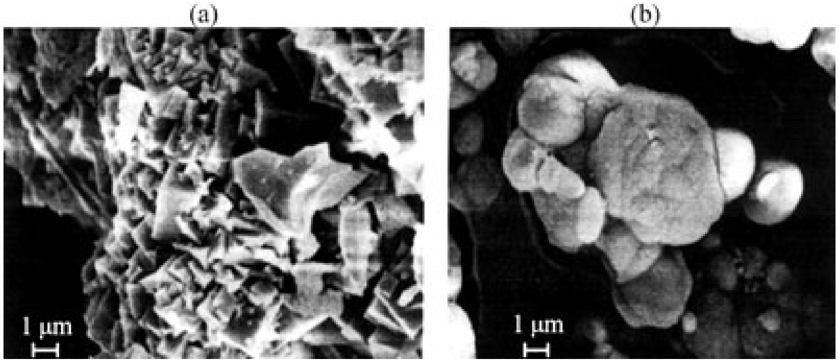

Fig 1. Micrographs (×10 000) of basic aluminum sulfates obtained in hydrolysis of potash alum; (a) in the absence of ammonium sulfite and (b) in the presence of ammonium sulfite.

Summing up the left- and right-hand parts of Eqs. (1) and (2), we obtain the following equation of the hydrolysis reaction.

$$\begin{aligned} &Al_2(SO_4)_3 + n(NH_4)_2SO_3 + nH_2O \\ &\rightarrow Al_2(OH)_{2n}(SO_4)_{3-n} + n(NH_4)_2SO_4 \\ &+ nH_2SO_3,\ (nH_2O + nSO_3), \end{aligned} \tag{3}$$

where $0 < n \leq 2$.

In this scheme, one of the conditions for a shift of the equilibrium toward hydrolysis is satisfied: the forming sulfuric acid is continuously bound into a neutral compound.

When there is no free sulfuric acid, ammonium sulfite enters into an exchange reaction directly with aluminum sulfate or potash alum in accordance with the equation (for the example of aluminum sulfate)

$$\begin{aligned} &Al_2(SO_4)_3 + n(NH_4)_2SO_3 \\ &\rightarrow Al_2(SO_4)_{3-n}(SO_3)_n + n(NH_4)_2SO_4 \end{aligned} \tag{4}$$

($0 < n \leq 2$) to form aluminum sulfate-sulfite, which is hydrolyzed by the reaction

$$\begin{aligned} &Al_2(SO_4)_{3-n}(SO_3)_n + 2nH_2O \\ &\rightarrow Al_2(OH)_{2n}(SO_4)_{3-n} + nH_2O + nSO_2\uparrow. \end{aligned} \tag{5}$$

The overall reaction equation is similar to Eq. (3):

$$\begin{aligned} &Al_2(SO_4)_3 + n(NH_4)_2SO_3 + nH_2O \\ &\rightarrow Al_2(OH)_{2n}(SO_4)_{3-n} + n(NH_4)_2SO_4 \\ &+ nH_2SO_3,\ (nH_2O + nSO_2\uparrow), \end{aligned} \tag{6}$$

where $0 < n \leq 2$.

According to this scheme, the process goes through a stage of formation of an intermediate salt that is more susceptible to hydrolysis than the starting aluminum sulfate or PA.

As the reactions of ammonium sulfite with sulfuric acid and aluminum sulfate or potash alum occur simultaneously and yield the same products, it is impossible to determine the priority of a particular reaction pathway.

The composition of the basic salts formed in hydrolysis of aluminum sulfate and potash alum in the presence of ammonium sulfite is close to the formula $(H_2O, NH_3, R_2O) \cdot 3Al_2O_3 \cdot 5SO_3 \cdot 9H_2O$, where R is Na or K. According to the X-ray phase analysis, all the basic sulfates formed have a similar structure analogous to that of natural rock alum. The basic salt produced in hydrolysis of aluminum sulfate is an isomorphous mixture of ammonium and hydrogen rock alums, and that formed in hydrolysis of potash alum is potassium rock alum with a minor admixture of ammonium rock alum.

The electron micrographs of basic aluminum sulfates formed in hydrolysis of potash alum in the absence (Fig. 1a) and presence (Fig. 1b) of ammonium sulfite show different shapes of the resulting particles. According to the crystal-optical analysis, the particles obtained in the first case are polycrystalline formations with a refractive index $N = 1.575$. A slight tendency for individual grains to have a rounded oval shape is seen. In the second case, the overwhelming part of particles are isometric (rounded) grains with $N = 1.510$.

The study performed is of technological importance. It is shown for the first time that aluminum sulfates can be hydrolyzed with virtually complete precipitation of aluminum(III) basic salts at comparatively low temperatures (150°C), which allows the process to be carried out in standard chemical apparatus working at pressures of up to 6 atm. The suggested method of hydrolysis also furnishes a real opportunity for preparation of basic aluminum sulfates with a decreased content of iron. Furthermore, there are prerequisites for regeneration of ammonium sulfite and its recycling.

CONCLUSIONS

(1) A study of the effect of ammonium sulfite on the hydrolysis of aluminum sulfate and potash alum in the temperature range from T_{boil} to 200°C demonstrated that the role of ammonium sulfite consists in that it reacts both with the forming sulfuric acid and directly with aluminum sulfate or potash alum. In the first case, sulfuric acid is bound, whereas in the second, intermediate compounds more susceptible to hydrolysis, compared with the starting salts, are formed. As a result the reaction equilibrium is shifted toward a fuller hydrolysis.

(2) Parameters of the hydrolysis process were determined: at an expenditure of ammonium sulfite equal to 1–2 mol per mole of Al_2O_3 at 150°C, potash alum is almost completely hydrolyzed. In hydrolysis of aluminum sulfate under similar conditions, the recovery of aluminum(III) into a precipitate of a basic sulfate reaches almost 86%.

(3) It was found that all the basic aluminum salts formed are similar in composition and structure to the natural mineral rock alum.

(4) The comparatively low hydrolysis temperature and the possibility of using the standard equipment create real prerequisites for implementation of the method in sulfuric acid processing of alumina-containing raw materials.

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