Indicators and regularities of hydrolytic decomposition of metastable aluminate solutions in the $Na_2O - K_2O - Al_2O_3 - H_2O$ system

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Introduction

Targeted processing of aluminum ores with increased potassium content is well known in the world practice and at different stages of development of alumina production technology was associated with the use of the most available and preferable raw materials, including leucites, alunites, nepheline syenites and close to them urite minerals [1–6]. This allowed not only to create a number of large industrial productions, but also to significantly develop the fundamental and scientific-technological basis for the processing of such raw materials from the perspective of the implementation of key technological operations [7–17]. Currently, we can talk about a renaissance of interest in potassium-containing raw materials due to the gradual depletion of reserves and the impoverishment of traditional aluminum-containing raw materials against the high demand for and cost of the soda-potash products, potassium fertilizers, aluminum hydroxide, alumina, and materials based on them. At the same time, new deposits of urite rocks and nepheline ores, as well as ultrapotassium rich schist and syenitic rocks confined to the Khibiny mountain massif, deposits of Eastern Siberia and the Far East region come to the fore [18–23]. In this regard, fundamental ideas about the ionic nature and properties of the key physical and chemical $Na_2O - K_2O - Al_2O_3 - H_2O$ system, which determines the performance of leading technological processes of alumina production, yield and quality of the final product against the background of limited information about this technically significant system, are of particular importance [24–29]. The purpose of the study is to determine the indicators and to establish regularities of decomposition of aluminate solutions in the $Na_2O - K_2O - Al_2O_3 - H_2O$ system and their assessment from a perspective of modern concepts of the structure of aluminate solutions and the processes of mass crystallization from solutions during chemical interaction.
Methodology

The current understanding of the ionic composition of aluminate solutions and its change in the Na₂O – K₂O – Al₂O₃ – H₂O system suggests the existence of a number of phase equilibria with the participation of three-water aluminum hydroxide and the following aluminum ionic forms Al(OH)₄⁻, Al₂O(OH)₆²⁻, AlO₂⁻, which are essential to the decomposition process. At the same time, both the ratio of aluminum ions and the equilibrium concentration of Al₂O₃ in alkaline solutions of mixed sodium-potassium composition remain the subject of further research. Therefore, to quantify the supersaturation of the initial aluminate solutions and determine the degree of precipitation of Al₂O₃ in % of the theoretically possible value, we calculated the equilibrium concentration of Al₂O₃ in the Na₂O – K₂O – Al₂O₃ – H₂O system using the known data on the equilibrium in the particular systems Na₂O – Al₂O₃ – H₂O and K₂O – Al₂O₃ – H₂O systems, respectively; N₁, K₂, A₁, A₂ are the concentrations of Na₂O, K₂O and Al₂O₃, respectively, g/l; V₁ is the amount of diluted aluminate solution required to perform research, l; 120 is the concentration of Al₂O₃ in this solution, g/l.

According to a separate methodology, the preparation of seed aluminate hydroxide was performed, the task of which was to ensure the stability of its physical characteristics related to the consistency of moisture, particle size distribution and morphology. For this purpose, a sample of factory aluminum hydroxide, obtained by decomposition method, was dried to a constant mass at a temperature not exceeding 70 °C, and subjected to separation of the fraction (−60+40) μm by vibratory sieve grading, which ensured the stability of these properties and consistency of the initial value of the specific surface of the seed per unit volume of the liquid phase.

As the main instrumental base for experimental studies was used an AutoLAB single reactor system (HEL, Great Britain). A 2-liter stainless steel reactor equipped with mechanical stirring, condensate return system and reaction volume temperature maintenance system with accuracy not less than ±0.1 deg was used, using an AZ50 HE oil circulating thermostat (Julabo, Germany) with supply of coolant (silicone oil) to the reactor heat loop. Control system consists of a personal computer, WinISO software and interface cards assembled in the control module.

For analytical control of the aluminate solution composition we used well-known methods of chemical analysis based on acid-base titration in determining the concentration of total and caustic alkali, as well as the reverse complexometric titration method in determining the aluminum oxide concentration. The hydroxide seed moisture content control was carried out using a MOC-120H weight analyzer (Shimadzu, Japan). To determine the aluminum hydroxide sludge particle size distribution and average median particle diameter as its average characteristic a Mastersizer-2000 laser analyzer (Malvern, Great Britain) was used.

Results and discussion

Experimental study of spontaneous hydrolysis of solutions in the Na₂O – K₂O – Al₂O₃ – H₂O system was performed for solutions of the previously indicated composition, which was refined by the results of analytical control. The amount of hydroxide seed was constant and amounted
to 100 g/l of aluminate solution regardless of the mole fraction of K₂O in the mixture of alkaline components. The decomposition process duration was 24 hours, with sampling for analysis at zero time and then after 1.5; 3; 6; 9; 12 and 24 hours from the beginning of the experiment. The solid hydrolysis products at the end of the process were filtered, washed and analyzed to determine the fractional composition and average median particle size. Decomposition indices of solutions with mole fraction of K₂O: 0; 0.1; 0.25; 0.33; 0.5; 0.75 and 1.0 are shown in Fig. 1 and Table 1. In this case, the calculation of the practical (η) and theoretical (ηₜ) decomposition degree, as well as the degree of decomposition in percentage of the theoretical value (ηₜ), was performed using simplified formulas that do not take into account the partial change in the solution volume during the process:

\[ \eta = 100\left(\frac{A_0 - A_i}{A_0}\right) ; \quad \eta_t = 100\left(\frac{A_0 - [A_k]}{A_0}\right) ; \quad \eta_r = 100\eta_t/\eta_t ; \]

where \( A_i \) and \( A_t \) are the concentrations of \( \text{Al}_2\text{O}_3 \) by the results of analytical control at zero point in time and at the moment of sampling, g/l, respectively; \([A_k]\) is the calculated value of equilibrium concentration of \( \text{Al}_2\text{O}_3 \) in solutions with weighted average molecular weight of alkali metals in terms of oxides \( M_k \).

The results obtained do not have a simple physical and chemical explanation, since the violation of the monotonicity of the indicators has no correlation with such properties of solutions as their density and viscosity, which are characterized by a monotonic change in properties with a change in \( n_k \), which fully obeys the principle of continuity, provided that the number and nature of phases are conserved. In this case, the appearance of the special point for \( n_k = 0.33 \) can be associated with a factor having an influence on the kinetic indicators of mass crystallization and, consequently, changes in the morphology and particle size distribution of the hydrolysis products. This assumption is fully confirmed by the results of the analysis of the fractional composition of aluminum hydroxide precipitation for 24 hours precipitation time which allows to establish a close correlation between the degree of solution decomposition and the value of the average median particle size depending on the mole fraction of potassium in the solution, Fig. 2.

![Fig. 1. Indicators of hydrolytic decomposition of aluminate solutions in the Na₂O – K₂O – Al₂O₃ – H₂O system depending on the mole fraction of K₂O for the process duration specified in the legend: 1.5; 3; 6; 9; 12 and 24 hours.](image1)

![Fig. 2. Degree of decomposition of aluminate solutions and average median particle diameter of stage for hydrolysis duration of 24 hours as a function of the mole fraction of K₂O in the aluminate solution: 1 – decomposition degree; 2 – average particle diameter.](image2)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Kinetics of hydrolytic decomposition of aluminate solutions according to the ( \text{Al}_2\text{O}_3 ) concentration in aluminate alkaline solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process duration, hours</td>
<td>Concentration of ( \text{Al}_2\text{O}_3 ) in solution according to the results of analytical control in the hydrolytic decomposition of solutions with different mole fraction K₂O (n_k), g/l</td>
</tr>
<tr>
<td></td>
<td>( n_k = 0.2 )</td>
</tr>
<tr>
<td>0</td>
<td>123</td>
</tr>
<tr>
<td>1.5</td>
<td>107.1</td>
</tr>
<tr>
<td>3</td>
<td>97.41</td>
</tr>
<tr>
<td>6</td>
<td>83.5</td>
</tr>
<tr>
<td>9</td>
<td>78.54</td>
</tr>
<tr>
<td>12</td>
<td>72.54</td>
</tr>
<tr>
<td>24</td>
<td>66.3</td>
</tr>
</tbody>
</table>
Table 2
Initial conditions and indicators of hydrolytic decomposition on aluminode solutions (decomposition) in the Na$_2$O – K$_2$O – Al$_2$O$_3$ – H$_2$O system at a process temperature of 60 °C and its duration of 24 hours

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial conditions for the hydrolysis process</th>
<th>Hydrolysis indices for the process duration of 24 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n_A$</td>
<td>$[A_{33}]$, g/l</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>58.15</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>59.89</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>61.61</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>62.45</td>
</tr>
<tr>
<td>5</td>
<td>0.33</td>
<td>62.74</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>64.17</td>
</tr>
<tr>
<td>7</td>
<td>0.75</td>
<td>63.86</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>62.40</td>
</tr>
</tbody>
</table>

$(A_0 - A_{24})$ is an index of Al$_2$O$_3$ yield (precipitate removal) from a unit volume of liquid phase; $(A_{24} - [A_{33}])$ is the degree of divergence of solution composition from solubility isotherm.

Since particle size during mass crystallization is primarily determined by growth processes that depend on the value of specific supersaturation of the system per unit of the bare surface, to assess the significance of this factor, we calculated the equilibrium composition of aluminode solutions in the Na$_2$O – K$_2$O – Al$_2$O$_3$ – H$_2$O system using equation (1). The results of the calculations are shown in Fig. 3, which allow to establish the value of absolute supersaturation ($\alpha = A_0 - [A_{33}]$) and the degree of supersaturation ($\gamma = \eta_{\%}$), which determine the mechanism of growth processes, as well as to give a comparative characteristic of the decomposition process indicators depending on the mole fraction of potassium in solution, Table 2. In this case, the lines 6–10 in Fig. 3 represent compositions with a constant caustic ratio, satisfying the following condition for solutions with different mole fraction of K$_2$O:

$$(v_k + v_N)/(v_A) = (102R_0)/(M_AR_0) = 1.6;$$

where $R_0$ is $R_O$ concentration in aluminode alkaline solution for zero time in a mixture with weighted average molecular weight of alkali metals in terms of oxides $M_A$.

Then, for the calculated or experimentally determined composition of the initial solutions, it makes possible to establish the value of supersaturation of solutions, relative to the solubility isotherm for the system with the appropriate mole fraction of K$_2$O. For example, in Fig. 3, the intersection of the dashed line and the corresponding rays (rows of lines 6–10) set the initial compositions of aluminode solutions depending on $n_A$, which allows to determine their supersaturation relative to the corresponding isotherm at the same concentration of $R_O$, Table 2. The results obtained establish sufficiently close initial values of absolute supersaturation and the degree (coefficient) of supersaturation with changes in the mole fraction of K$_2$O, which suggests their sufficiently high relevance from the position of influence on the crystallization kinetics and the intensity of nucleation. Thus, the most likely violation of the monotonicity of changes in the degree of decomposition of aluminode solutions from the molar K$_2$O value can be associated with the mechanism of the process and its change as a result of changes in the ionic composition of the aluminode solution in the transition from the Na$_2$O – Al$_2$O$_3$ – H$_2$O to K$_2$O – Al$_2$O$_3$ – H$_2$O system. This assumption has numerous indirect confirmations, but needs final verification on the basis of determining the ionic composition of aluminode solutions [29].

A noteworthy fact is the change in the state of the aluminode solution for the decomposition duration of 24 hours relative to the solubility isotherm, Table 2. At the same time, there is a transition of solutions from the supersaturation region to equilibrium and even unsaturated solutions due to the growth of K$_2$O mole fraction, which is of known interest from the position of understanding the decomposition mechanism and creation of potassium or mixed sodium-potassium cycle for processing of aluminum-containing raw materials with increased potassium content.

**Conclusion**

1. It was found that the decomposition degree of aluminode solutions in the Na$_2$O – K$_2$O – Al$_2$O$_3$ – H$_2$O system has a violation in the monotonicity of its change with
the appearance of a special point at the mole fraction of $K_2O$ equal to 0.33, which can be explained by a change in the process mechanism due to a change in the ionic composition of aluminate solution.

2. The correlation between the decomposition degree of aluminate solutions and the average median particle diameter value of the resulting aluminum hydroxide precipitate is shown, which indicates a close relationship between the growth processes of crystallization and hydrolysis mechanism in general, as well as their dependence on the ionic composition of aluminate solutions.

3. The effect of transition of supersaturated (meta-stable) aluminate solutions into the area of unsaturated compositions has been established, which is of theoretical significance for understanding the mechanism of decomposition of potassium-bearing aluminate solutions and of practical importance from a perspective of creating an effective technological cycle of aluminum-containing raw materials processing based on the $Na_2O - K_2O - Al_2O_3 - H_2O$ system.

Acknowledgements

The work was carried out with the financial support of the Russian Science Foundation under the Agreement No. 18-19-00577-II of April 28 2021 of grant for fundamental scientific research and exploratory scientific research.

References


