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Modern Physicochemical Equilibrium Description in Na₂O–Al₂O₃–H₂O System and Its Analogues

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Equilibrium and non-equilibrium states of systems Na₂O–Al₂O₃–H₂O and K₂O–Al₂O₃–H₂O are crucial for establishing key technological parameters in alumina production and their optimization. Due to a noticeable discrepancy between experimental results and thermodynamic calculations based on materials of individual researchers the necessity of systematization and statistical processing of equilibrium data in these systems to create a reliable base of their physicochemical state, analysis and mathematical modeling of phase equilibria is substantiated. The tendency to a decrease of the hydration degree of solid sodium aluminates with increasing temperature and the transition of systems from the steady state of gibbsite to equilibrium with boehmite is revealed. The paper contains approximating functions that provide high-precision description of equilibrium isotherms in technologically significant area of Na₂O–Al₂O₃–H₂O and K₂O–Al₂O₃–H₂O concentrations. Approximating function can be simplified by dividing the isotherm into two sections with the intervals of alkaline content 0–0.25 and 0.25–0.4 mole/100 g of solution. The differences in solubility isotherms for Na₂O–Al₂O₃–H₂O and K₂O–Al₂O₃–H₂O systems provide are associated with changes in the ionic composition solutions that depends on concentration and temperature, as well as differences connecting with alkali cation hydration, which is crucially important for thermodynamic modeling of equilibria under consideration.

Key words: alumina industry systems; aluminate solutions; gibbsite; boehmite; ionic composition; equilibrium isotherms; analysis; mathematical modeling

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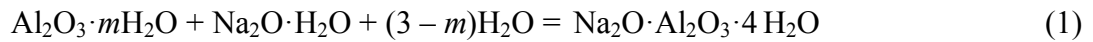
Introduction. Modern thermodynamics of alkaline alumina production has gone a long way from empirical interpretations of alkaline aluminate solutions that described in the patents of C.J. Bayer to modern thermodynamics of multicomponent systems, which allow to perform multiple optimizations of technological processes. Two independent approaches to the assessment of solution characteristics and processes, occurring in the basic system of alumina production Na₂O–Al₂O₃–H₂O, have been formed. The western scientific school traditionally utilizes such characteristics of aluminate solutions as TC (total caustic), TA (total alkaline) and A/TC, where only A (alumina) fully complies with the Russian school accepted representation of the concentration of aluminum in alkaline solutions in terms of Al₂O₃. Here TC is a volume concentration of NaOH in terms of Na₂CO₃, TA is total concentration of titrated alkalis, i.e. the sum of caustic and sodium in terms of Na₂CO₃, whereas A/TC ratio is the saturation value of alkaline solution as related to thermodynamic stability of the solid phase. The difference between these parameters and the ones historically utilized in Russia is not so big. They are equivalent to the values of caustic alkali (Na₂O_c or N_c), total alkali (Na₂O_t or N_t) and caustic module (α_c) – alumina to caustic ratio or a molar ratio of caustic alkali to Al₂O₃ in the solution. All the above mentioned parameters have strict stoichiometric links that simplify the conversion from one set of values into another:

$$N_c = TC \cdot 62/106; \quad N_t = TA \cdot 62/106; \quad \alpha_c = 102 \cdot TC/106 \cdot A,$$

where 62, 106, 102 – molar weight of Na₂O, Na₂CO₃ and Al₂O₃ respectively.



Simplicity and sufficiency of analytical control of solutions in terms of the above mentioned elements, including for the purposes of equilibrium composition estimation, usability of relative characteristics and their independency from dilution, have played a decisive role in the utilization of this set of parameters both in R&D and in alumina production. E.g., Bayer reaction equilibrium, expressed on conversion of elements' material composition to respective oxides



on a first approximation is determined by an equilibrium alumina to caustic ratio, calculated as follows

$$Q = 1/((\alpha_c)^e - 1), \quad (2)$$

where Q – concentration equilibrium constant of reaction (1); $(\alpha_c)^e$ – equilibrium value of the alumina to caustic ratio.

As it follows from equation (2), an increase of end product yield, caused by a displacement of reaction (1) equilibrium to the left or to the right, is associated with the opportunity of reaching the lowest values of alumina to caustic ratio during leaching and as high values of caustic ratio as it possible during decomposition. Under real-life industrial conditions, these parameters fall into a relatively narrow range (from 1.3 to 3.8, or even more constrained). This means that high product yield and high agent utilization rate cannot be obtained. At the same time, reversibility of the process is an obvious advantage of Bayer's method [3, 11, 12]. Decomposition level of aluminate solutions, which characterizes Al_2O_3 extraction into the solid phase, can be estimated using the following formula

$$\eta = 1 - (\alpha_c)^i / (\alpha_c)^f, \quad (3)$$

where η – solution decomposition degree; α_c^i , α_c^e – initial and final values of the alumina to caustic ratio respectively.

Absence of the term «alumina to caustic ratio» in the western scientific school implies that the calculation of decomposition level occurs as follows:

$$\eta = (A_i - A_f)/A_i, \quad (4)$$

where A_i , A_f – initial and final concentration of Al_2O_3 in the solution respectively. Inaccuracy of this expression is associated with the fact that during decomposition it does not take into account changes in solution composition as a result of binding 3 moles of water into $\text{Al}(\text{OH})_3$ and hence the results it shows are lower than the ones calculated using equation (3).

In equation (1), effective utilization rate of caustic alkali during aluminum leaching is estimated using the value of $1/\alpha_c$, which serves as a calculation basis for the effectiveness of alkali circulation in the following expression [11]:

$$E = 1.645(N_c)_r(1/(\alpha_c)_a - 1/(\alpha_c)_r), \quad (5)$$

where $(N_c)_r$ – Na_2O_c concentration in the reverse solution; $(\alpha_c)_a$ and $(\alpha_c)_r$ – respectively, alumina to caustic ratio of aluminate solution after leaching and alumina to caustic ratio of the reverse solution before leaching; 1.645 – ratio of molar weight of Al_2O_3 and Na_2O , i.e. 102/62.

Given examples allow to come to a definitive conclusion that equilibrium in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ plays a fundamentally important role of justifying optimal technological regimes of all hydrometallurgical operations forming the Bayer cycle, as well as regimes of alkali processing of high-silica bauxites and other aluminum-bearing materials [3, 11, 12]. It has determined constant interest in the investigation of the system and its comparables, appearing due to added complexity of cation and anion composition and characteristic features of technological processes and raw materials. In the general case, this added complexity corresponds to the system $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}-\text{An}^{n-}$, where the most significant role belongs to the following anions: $(\text{SO}_4)^{2-}$; Cl^- ; $(\text{CO}_3)^{2-}$; $(\text{C}_2\text{O}_4)^{2-}$; SiO_3^{2-} , including anion groups and associated complexes.



Problem statement. Development of automatic control systems in the field of alumina production, based on mathematical modeling, sparks heightened interest to digitalization of physicochemical characteristics of technological processes and systems. One of the first studies in this field provides mathematical description of experimental data on equilibrium in $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{CO}_2-\text{H}_2\text{O}$ system, which provided an adequate solution for a wide range of technological problems [12]. In mid-90s thermodynamic equilibrium model for aluminate solutions in the Bayer process has been developed, which took into account a wide range of technically significant factors affecting gibbsite solubility [1]. Development of these models uncovered a number of serious problems associated with them, e.g. credibility and accuracy of experimental data application, justified selection and usability of approximating functions, validity of physicochemical hypotheses lying at the foundations of thermodynamic models, and finally, their adequacy. This allow to give top priority to the task of collection, analysis and mathematical processing of available information on the state of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system and its closest analogue $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$, as well as creation of a database suitable for interpolation and physicochemical modeling.

Methodology. The simulation is based on the generalization, analysis and systematization of known state diagrams for $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ and $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ systems. The data on equilibrium in three-component systems plotted in rectangular coordinates by Schreinemakers method and in a concentration triangle by Roseboom method was used. Analysis of solubility isotherms served as an additional information source, which had experimental basis. In engineering practice the most conventional measuring unit is weight part, therefore all the empirical data in the study has been converted to fit Schreinemakers diagram coordinates – moles of aluminum oxide and alkali oxide in 100 g of the solution. It allows ruling out the «phantom» gap in the content of potassium and sodium alkali due to the difference in molar weight.

Experimental results have been borrowed directly from primary sources or, in case of their absence, obtained by digital processing of state diagrams and (or) solubility isotherms.

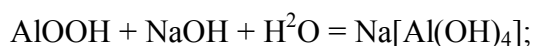
Results and discussion. From the general data set one can separate diagrams that describe solubility (crystallization) areas of aluminum oxide in the form $\text{Al}(\text{OH})_3$ or AlOOH (left area of the isotherm) and solubility (crystallization) areas of sodium and potassium aluminates (right area of the isotherm) [3, 4, 7, 8, 13-17, 21-23, 26].

Analysis of state diagrams for the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$, obtained for gibbsite under temperature 30 °C, demonstrates certain differences in maximum solubility of aluminum hydrate, which equals (in weight parts) 26 % according to [17], 24 % in [7] and 21 % basing on [23]. It should be noted that results of [17] and [7] have been calculated using Schreinemakers method, whereas the result published in [23] was experimental. By contrast with interpolation mathematical modeling, thermodynamic equilibrium models require accurate understanding of the physical condition of aluminum oxide and ionic composition of the solution, as dissolution – precipitation reactions for boehmite and gibbsite are described by different chemical and mathematical equations:



$$K = \frac{a_{\text{Al}(\text{OH})_4^-}}{a_{\text{OH}^-}} = \frac{[\text{Al}(\text{OH})_4^-] \gamma_{\text{Al}(\text{OH})_4^-}}{[\text{OH}^-] \gamma_{\text{OH}^-}} = QP_\gamma, \quad (6)$$

or for aluminum oxyhydroxide AlOOH :



$$K = \frac{a_{\text{Al}(\text{OH})_4^-}}{a_{\text{OH}^-} a_{\text{H}_2\text{O}}} = \frac{[\text{Al}(\text{OH})_4^-]}{[\text{OH}^-][\text{H}_2\text{O}]} \frac{\gamma_{\text{Al}(\text{OH})_4^-}}{\gamma_{\text{OH}^-} \gamma_{\text{H}_2\text{O}}} = Q P_\gamma, \quad (7)$$

where Q – concentration equilibrium constant; P_γ – product of activity coefficients.

Until recently the question about the physical form of aluminum oxide under temperature 95 ± 5 °C remained open. According to earlier studies, when aluminate solution decomposes, crystallization form of aluminum oxide depends on the nature of seed material or temperature mode of the process [7, 14, 15]. At the same time, results published in [7, 14, 15] for 95 and 100 °C, align with the diagram reliably describing dissolution (crystallization) of gibbsite [26]. Therefore it is possible to say that authors of previous publications have also obtained data on dissolution – crystallization of this form of aluminum oxide.

Analysis of state diagrams led to the conclusion that composition and amount of aluminates depend on temperature. Sodium aluminate $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$ – the most stable compound – forms in the temperature interval 25-180 °C [3, 8, 18, 22, 25]. Until recently it was considered that under 30 °C, apart from $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$, sodium aluminate hexahydrate could also be formed [8, 17]. Successive studies demonstrated existence of a whole range of sodium aluminate hydrates containing from 6 to 12 water molecules [23, 26]. Latest research, however, casts serious doubt on the existence of six-molecule sodium aluminate, whereas sodium aluminate of the composition $4\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ has been confirmed to form under 30 °C [23, 26]. At temperatures from 95 °C and above, existence of sodium aluminates of the following stoichiometry has been proven: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$, $4\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ and $6\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ [26]. Under 110 °C, apart from $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$, only $6\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ can be formed [26]. Boehmite state diagrams, obtained at temperatures between 130 and 180 °C, show no presence of hydrated sodium aluminates beside the stable form of $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$ [21, 22]. Thus, a clear trend can be seen that with increasing temperature and system's transition from gibbsite stable conditions to boehmite equilibrium, the hydration degree of sodium aluminates decreases.

By contrast with $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$ system, the dependency of aluminum oxide solubility from temperature is less noticeable for $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$, and solubility isotherms obtained for 30 and 40 °C are almost identical. Analysis of equilibrium diagrams for $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$ system allows to come to a conclusion that the only crystallization form of potassium aluminate in the temperature interval from 30 to 95 °C is $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, whereas at temperatures from 150 to 200 °C apparently forms a four-molecule structure [4, 13].

Chemical composition and hydration degree of alkali metal aluminates in the systems $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$ and $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$:

Temperature, °C	Forms of sodium aluminate
30-60	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$; $3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$; $4\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$
30-95	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
95	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$; $6\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$; $4\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$
110	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$; $6\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$
130-180	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$; $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$
150-200	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$

Fig.1 presents a data set with the results of an analysis of three-component state diagrams [7, 8, 14, 17, 26], satisfying an equilibrium (6) with the participation of $\text{Al}(\text{OH})_3$, complemented by the results of a study on gibbsite solubility isotherms for the solutions with alkali content no higher than 0.25 mole per 100 g of the solution [5, 15, 24].

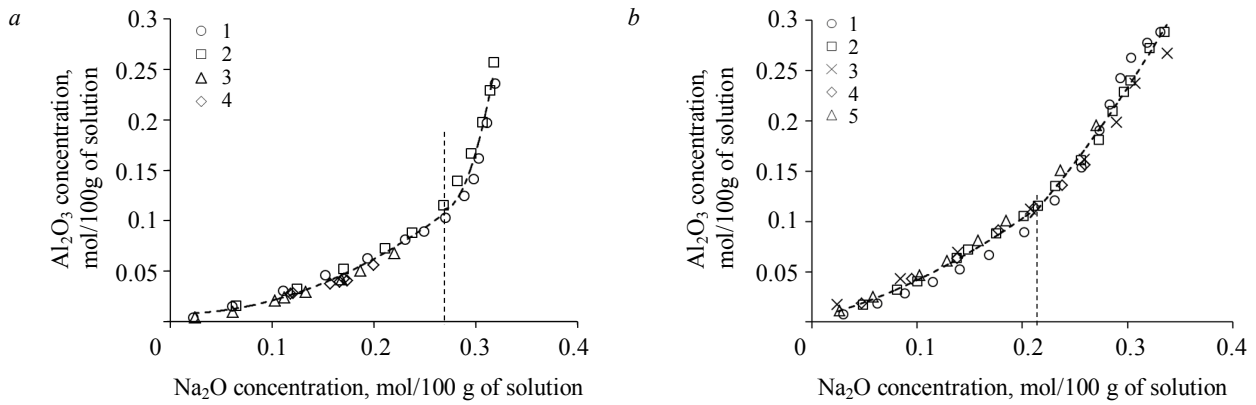


Fig. 1. Dependency of gibbsite solubility on alkali concentration and temperature in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$:
 a – $T = 60^\circ\text{C}$; 1 – [7, 8], 2 – [17], 3 – [24], 4 – [5]; b – $T = 95^\circ\text{C}$; 1 – [7, 8], 2 – [14], 3 – [26], 4 – [15], 5 – [24]
 Approximation line is shown dashed; the vertical dashed line represents approximation intervals

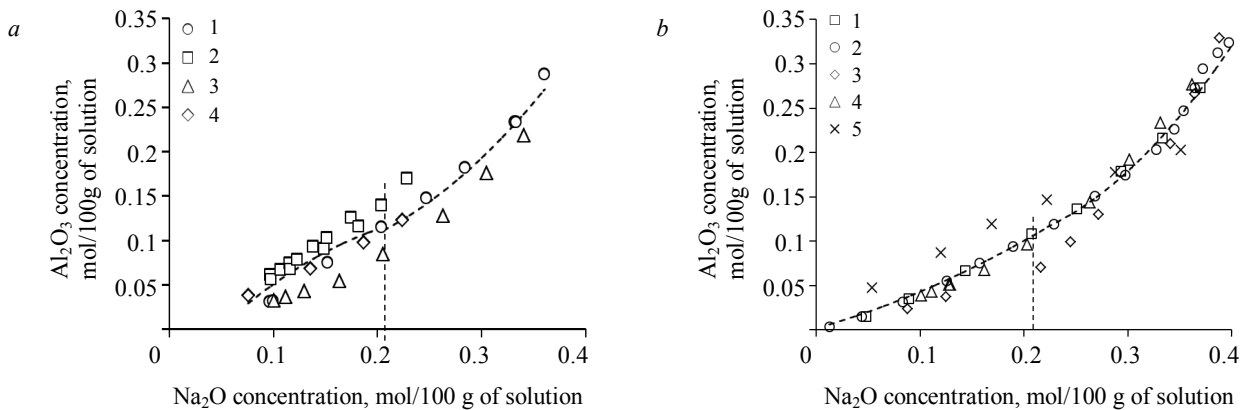


Fig. 2. Dependency of boehmite solubility on alkali concentration and temperature in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$:
 a – $T = 130^\circ\text{C}$; 1 – [21], 2 – [3], 3 – [24], 4 – [18]; b – $T = 150^\circ\text{C}$; 1 – [3], 2 – [7, 8], 3 – [22], 4 – [24], 5 – [6]
 For legend see Fig. 1

Fig. 2 presents a data set describing boehmite equilibrium with aluminate alkali solution in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$. Approximation functions for respective isotherms are presented in Table 1. On the whole, as illustrated on the example of boehmite solubility under temperature 150°C , experimental data on this equilibrium [6, 18, 24] complement dependencies obtained from equilibrium diagrams [3, 7, 8, 21, 22]. For the temperature 130°C results of later studies [3, 18, 21, 22] differ from sources [6, 24] and show higher solubility of aluminum oxide in the alkali.

Table 1

Approximation functions, describing composition of aluminate solutions in the equilibrium with $\text{Al}(\text{OH})_3$ or AlOOH in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ ($R^2 \geq 95\%$)

$T, ^\circ\text{C}$	Sodium oxide content, mole/100 g of solution		
	From 0 to 0.25	From 0.25 to 0.34	From 0.25 to 0.4
30	$n_{\text{Al}_2\text{O}_3} = 1.28n_{\text{Na}_2\text{O}}^2 - 0.16n_{\text{Na}_2\text{O}} + 0.01$	$n_{\text{Al}_2\text{O}_3} = 105n_{\text{Na}_2\text{O}}^2 - 66.34n_{\text{Na}_2\text{O}} + 10.58$	
60	$n_{\text{Al}_2\text{O}_3} = 1.39n_{\text{Na}_2\text{O}}^2 - 0.01n_{\text{Na}_2\text{O}} + 0.01$	$n_{\text{Al}_2\text{O}_3} = 53.72n_{\text{Na}_2\text{O}}^2 - 28.80n_{\text{Na}_2\text{O}} + 3.97$	
95	$n_{\text{Al}_2\text{O}_3} = 1.14n_{\text{Na}_2\text{O}}^2 + 0.27n_{\text{Na}_2\text{O}}$	$n_{\text{Al}_2\text{O}_3} = 2.15n_{\text{Na}_2\text{O}}^2 + 0.30n_{\text{Na}_2\text{O}} - 0.05$	
110	$n_{\text{Al}_2\text{O}_3} = 0.20n_{\text{Na}_2\text{O}}^2 + 0.45n_{\text{Na}_2\text{O}}$		$n_{\text{Al}_2\text{O}_3} = 3.27n_{\text{Na}_2\text{O}}^2 - 0.83n_{\text{Na}_2\text{O}} + 0.13$
130	$n_{\text{Al}_2\text{O}_3} = -2.14n_{\text{Na}_2\text{O}}^2 + 1.26n_{\text{Na}_2\text{O}} + 0.05$		$n_{\text{Al}_2\text{O}_3} = 2.67n_{\text{Na}_2\text{O}}^2 - 0.48n_{\text{Na}_2\text{O}} + 0.10$
150	$n_{\text{Al}_2\text{O}_3} = 0.82n_{\text{Na}_2\text{O}}^2 + 0.33n_{\text{Na}_2\text{O}}$		$n_{\text{Al}_2\text{O}_3} = 3.42n_{\text{Na}_2\text{O}}^2 - 0.97n_{\text{Na}_2\text{O}} + 0.16$
200	$n_{\text{Al}_2\text{O}_3} = 0.75n_{\text{Na}_2\text{O}}^2 + 0.44n_{\text{Na}_2\text{O}}$		$n_{\text{Al}_2\text{O}_3} = 2.92n_{\text{Na}_2\text{O}}^2 - 0.49n_{\text{Na}_2\text{O}} + 0.10$

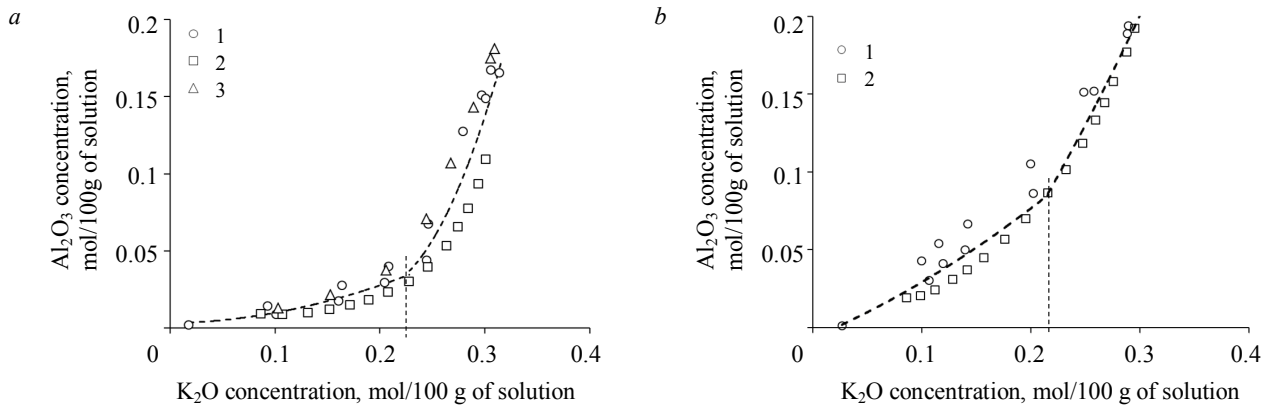


Fig.3. Dependency of gibbsite and boehmite solubility on alkali concentration and temperature in the system $K_2O-Al_2O_3-H_2O$:
 a – $T = 30\text{ }^\circ\text{C}$; 1 – [4, 13], 2 – [17], 3 – [16]; b – $T = 60\text{ }^\circ\text{C}$; 1 – [4, 13], 2 – [17]
 For legend see Fig. 1

Diagrams of dependency between Al_2O_3 solubility and alkali concentration, regardless of the substance physical state, can be divided into two areas. Isotherms in these areas differ from each other significantly, but both are approximated with a second order polynomial (Table 1).

For gibbsite dissolution these areas are 0-0.25 and 0.25-0.34 mole of alkali per 100 g of the solution. For boehmite dissolution under temperature 110-200 °C a change in Al_2O_3 solubility occurs at 0.25 mole of sodium hydroxide per 100 g of the solution, in the second area there is a shift to the region of higher alkali content – up to 0.4 mole of alkali per 100 g of the solution.

Fig. 3 demonstrates dependencies of gibbsite and boehmite solubility in potassium hydroxide [4, 13, 16, 17].

It should be noticed that there is a visible discrepancy in the data obtained by different authors for the temperature 30 °C [13, 16, 17]. Same as $Na_2O-Al_2O_3-H_2O$, the system $K_2O-Al_2O_3-H_2O$ can be divided into two areas with different isotherm characteristics, which means that the physical state of aluminum changes in the solution. Analysis and mathematical processing of equilibrium isotherms in the system $K_2O-Al_2O_3-H_2O$ for temperatures 95, 150 and 200 °C have been based on data from a single source [4], respective approximation functions are presented in Table 2.

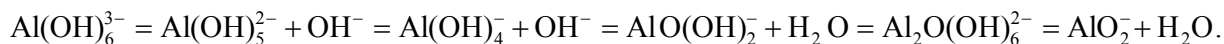
Table 2

Approximation functions, describing composition of aluminate solutions in the equilibrium with $Al(OH)_3$ or $AlOOH$ in the system $K_2O-Al_2O_3-H_2O$

$T, \text{ }^\circ\text{C}$	Potassium oxide content, mole/100 g of solution	
	From 0 to 0.23	From 0.23 to 0.3
30	$n_{Al_2O_3} = 0.54n_{Na_2O}^2 + 0.01n_{Na_2O}$	$n_{Al_2O_3} = 9.74n_{Na_2O}^2 - 3.75n_{Na_2O} + 0.39$
60	$n_{Al_2O_3} = 0.59n_{Na_2O}^2 + 0.30n_{Na_2O} + 0.01$	$n_{Al_2O_3} = 1.45n_{Na_2O}^2 + 0.61n_{Na_2O} - 0.11$
95	$n_{Al_2O_3} = 1.31n_{Na_2O}^2 + 0.41n_{Na_2O}$	$n_{Al_2O_3} = 3.53n_{Na_2O}^2 - 0.60n_{Na_2O} + 0.12$
	From 0 to 0.27	From 0.27 to 0.43
150	$n_{Al_2O_3} = 0.27n_{Na_2O}^2 + 0.50n_{Na_2O}$	$n_{Al_2O_3} = -1.70n_{Na_2O}^2 + 2.21n_{Na_2O} - 0.31$
200	$n_{Al_2O_3} = -0.09n_{Na_2O}^2 + 0.67n_{Na_2O} + 0.01$	$n_{Al_2O_3} = -1.88n_{Na_2O}^2 + 2.42n_{Na_2O} - 0.33$

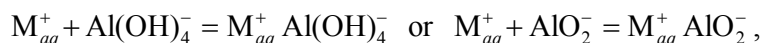
Comparison of approximation functions from Tables 1 and 2 points to some evident dependencies, related to the possibility of describing solubility isotherms in the low concentrations area for the entire temperature range, as well as in the area of high concentrations and temperatures above 95 °C. In this sense one can highlight a low-temperature interval of high-concentration aluminate-alkali solutions in the system $Na_2O-Al_2O_3-H_2O$, distinguished by its non-linearity and resulting from significant changes

in ionic structure of aluminate solutions. At the same time, the pattern of changes in Al_2O_3 solubility in the area of low alkali concentrations regardless of Al_2O_3 equilibrium form (gibbsite or boehmite) and the alkali component nature (sodium or potassium) points to uniformity of ionic composition of the solution, consistent with the equations (6) and (7). With an increase in alkali and aluminum concentrations, occurs consecutive dehydration of aluminum hydroxo-complexes with liberation of meta-aluminate ion AlO_2^- in solutions with no less than 0.3 mole of sodium oxide and no less than 0.1 mole aluminum oxide per 100 g of the solution according to the pattern [9, 10, 20]:



Comparative analysis of isotherms for Al_2O_3 solubility in sodium hydroxide and potassium hydroxide has been carried out by means of graphical plotting (Fig.4) with using of approximation functions presented in Tables 1 and 2 for the same range of alkali concentrations.

Obtained results demonstrate that with rising temperature (up to 60-95 °C) aluminum solubility in KOH increases, as compared to NaOH. At the same time, with increasing concentration of stable solutions decreases the concentration of $\text{Al}(\text{OH})_4^-$ ions and increases the concentration of partially dehydrated anions $[\text{AlO}(\text{OH})_2]^-$ or dimer forms $\text{Al}_2\text{O}(\text{OH})_6^{2-}$, as well as fully dehydrated ions AlO_2^- [9, 10, 20]. In the solutions with sodium oxide concentration above 0.3 mole and no less than 0.2 mole of aluminum oxide per 100 g of the solution, formation of «molecular» ionic pairs is likely:



where M – potassium or sodium cation, which reduces the ionic strength of the solution, and, consequently, the activity coefficient of ions and leads to a decrease in the solubility of aluminum oxide [9, 10, 20].

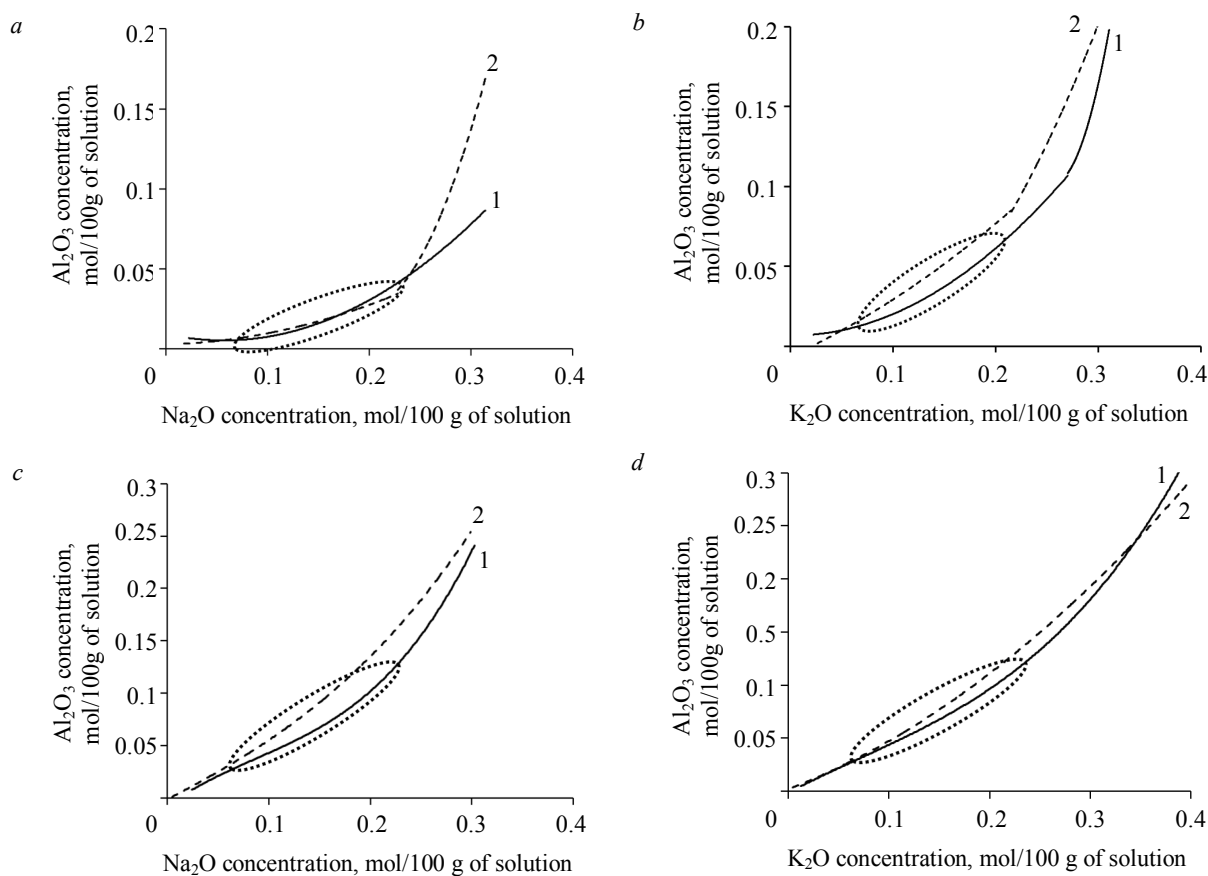


Fig.4. Comparison of solubility isotherms in the systems $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ and $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ according to approximation functions (Tables 1, 2):

$a - T = 30^\circ\text{C}$; $b - T = 60^\circ\text{C}$; $c - T = 95^\circ\text{C}$; $d - T = 50^\circ\text{C}$; 1 – Na_2O ; 2 – K_2O
 A dotted oval represents technologically significant area of concentrations

Subsequent increase of temperature up to 150 °C eliminates all differences in Al₂O₃ solubility in sodium and potassium alkalis.

Differences between sodium and potassium aluminate solutions can roughly be explained by specific hydration properties of sodium and potassium ions in water solutions. It is a stated fact that hydration of metal cation increases with the ratio z/r , where z – cation charge, r – ionic radius.

Comparative characteristic of sodium and potassium cations [19]:

Characteristic	Na ⁺	K ⁺
Ionic radius, nm	0.102	0.138
Hydrated ion radius, nm	0.276	0.232
Gibbs energy of hydrated ion formation, kJ/mol	–262	–283
Gibbs energy of hydration, kJ/mol	–371	–300
Hydration heat, kJ/mol	–423	–339

Potassium cation is hydrated less than the sodium one, which provides slightly stronger Coulomb interaction with opposite-charged ions, e.g. hydroxide, aluminate or tetrahydroxoaluminate ions. In concentrated alkali solutions, this leads to the formation of ion pairs with hydroxide anions and the formation of hydrated structures through the interaction of OH[–] groups with water molecules due to hydrogen bonds [19]. In the presence of anionic aluminum hydroxo-complexes, a similar mechanism assures formation of ionic pairs from potassium cation and aluminum hydroxo-complex anion. Formation of ionic pairs decreases ionic strength of the solution and, as a result, reduces Al₂O₃ solubility in potassium alkali, as compared to sodium hydroxide.

On the other hand, with rising temperature the ion hydration degree usually decreases [19]. In the area of low temperatures (below 60 °C), cations of alkali metals preserve their hydration sphere, which prevents the forming of ionic pairs with aluminum anions and increases Al₂O₃ solubility in the sodium alkali. As the temperature rises to 60 °C and higher, hydration sphere disintegrates. Hydration sphere of sodium cation is not as stable as potassium one, and increasing of temperature leads to more intensive dehydration of its one. This leads to a shift in the region of existence of ion pairs with a sodium cation towards lower concentrations and a decrease in the solubility of aluminum oxide. For potassium systems a small increase of temperature will not be as notable as for sodium systems, which will lead to inversion of Al₂O₃ solubility in potassium hydroxide solutions under temperatures 60 and 95 °C. If the temperature increases even further, hydration sphere ~~hydrated~~ ^{easing} disintegrates and notable differences in solubility disappear.

Nevertheless, full thermodynamic modeling of equilibria in above mentioned systems and their comparables is impossible without accurate understanding of ionic composition of the solutions and its changes under the impact of defining thermodynamic factors.

Conclusion

1. Currently available database on equilibrium in the systems Na₂O–Al₂O₃–H₂O and K₂O–Al₂O₃–H₂O for its correct application needs to be converted to a uniform dimension of concentrations and has to be statistically processed due to a visible discrepancy of experimental results with thermodynamic estimations based on materials of individual studies.

2. In the technically significant area of concentrations, approximation functions of equilibrium isotherms for the systems Na₂O–Al₂O₃–H₂O and K₂O–Al₂O₃–H₂O have a low degree of curvature and a confidence level of 95 %.

3. Identified dependencies in the nature of solubility isotherms for the systems Na₂O–Al₂O₃–H₂O and K₂O–Al₂O₃–H₂O provide satisfactory explanation from the viewpoint of changes in ionic composition of aluminate solutions depending on their concentration and temperature, as well as on differences associated with alkali cation hydration, which is critically important for thermodynamic modeling of equilibria under consideration.



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