ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 2, pp. 193−196. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © D.R. Ruziev, U.M. Mirsaidov, Kh.S. Safiev, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 2, pp. 199−202.

INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Method for Synthesis of Sodium Aluminate by Caking Products from the Mud Storage Area of Aluminum Plant

D. R. Ruziev, U. M. Mirsaidov, and Kh. S. Safiev

Nikitin Institute of Chemistry, Academy of Sciences of the Republic of Tajikistan, Dushanbe, Tajikistan

Received September 15, 2008

Abstract—Results obtained in a study of the topographic, layer-by-layer, chemical, and mineralogical composition of products in the mud storage area of an aluminum plant and in an analysis of the kinetics and mechanism of processes occurring in synthesis of sodium aluminate by the caking method are presented. It is shown that the processing mode affects the yield of sodium aluminate in the cake and the coagulating properties of the resulting sodium aluminate.

DOI: 10.1134/S1070427209020049

Aluminum sulfate and iron chloride are for the most part used as coagulants in natural water treatment. The coagulating properties of these salts are due to the formation of poorly soluble hydroxides upon hydrolysis [1]. Solutions of these salts are corrosive to ordinary carbon steels. Therefore, special brands of stainless steels and concretes should be used in their preparation, transportation, and storage [2].

Aluminate solutions that can be used as an alkaline coagulant are less corrosive, because hydrolysis of aluminates is accompanied by release of hydroxide ions and increase in pH in the course of time.

With account of this circumstance and of the necessity for utilization of the industrial waste of Tajik aluminum plant, a method for production of an alkaline coagulant from the gas-treatment mud has been developed [1]. The method consists in high-temperature caking of the mud and leaching of sodium aluminate from the cake.

EXPERIMENTAL

A topological analysis of the mud for 48 samples taken from 8 points of the mud storage area at depths of 0 to 100 cm demonstrated that the content of its components widely fluctuates. For example, the content of water-soluble salts in the mud may vary from 5 to 40 wt %. Our present study was performed with an averaged sample containing 30 ± 1 wt % water-soluble salts. We varied the content of these salts in the mud by addition of a sulfate-containing precipitate of soluble salts, formed in evaporation and cooling of a solution from the mud storage area [4]. Depending on the composition of the starting solution, the precipitate contained (wt %): Na_2SO_4 75.0–84.0 and NaF 3.5–15.0.

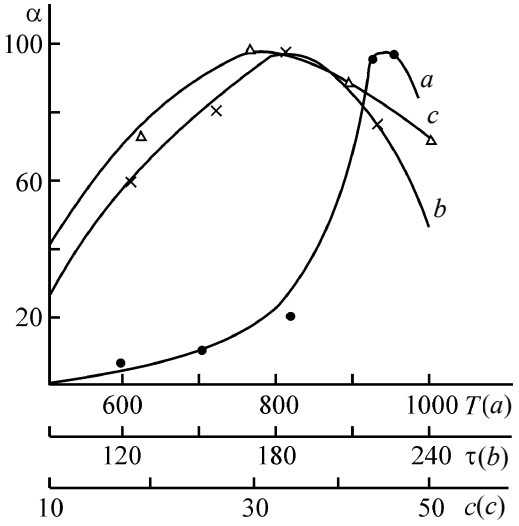

Fig. 1. Effect of (*a*) temperature *T*; (*b*) caking duration τ, min; (*c*) content c_{ws} of water-soluble salts in the mud on the yield of sodium aluminate in the cake, wt % .

In order to raise the content of sodium aluminate in the cake, we studied the effect of temperature, process duration, and content of water-soluble salts in the mud on the yield of sodium aluminate (Fig. 1). It can be seen in Figs. 1a and 1b that the maximum yield of sodium aluminate (98.9%) is obtained in the following mode: temperature 950°C; process duration 180 min; content of water-soluble salts in the mud, 30 wt %. In this case, the conversion to sodium aluminate is 98.7%. If the content of water-soluble salts in the mud decreases to below 30 wt % because of deficiency of Na_2SO_4, Na_2CO_3, and $NaHCO_3$ or the content of these salts increases to above this value because of deficiency of Na_3AlF_6 and Al_2O_3, the yield of the aluminate becomes lower (Fig. 1c).

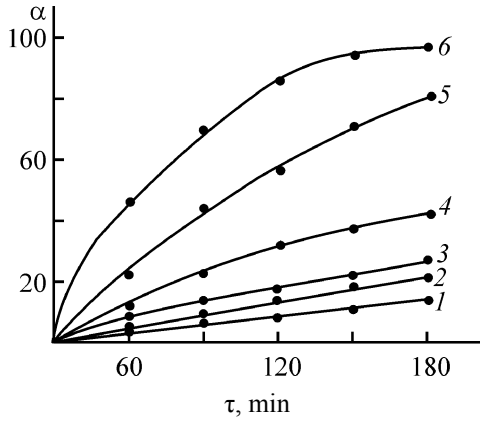

Fig. 2. Degree of $Na_2O\ Al_2O_3$ recovery, α, vs. time τ. Caking temperature (°C): (*1*) 700, (*2*) 750, (*3*) 800, (*4*) 850, (*5*) 900, and (*6*) 950.

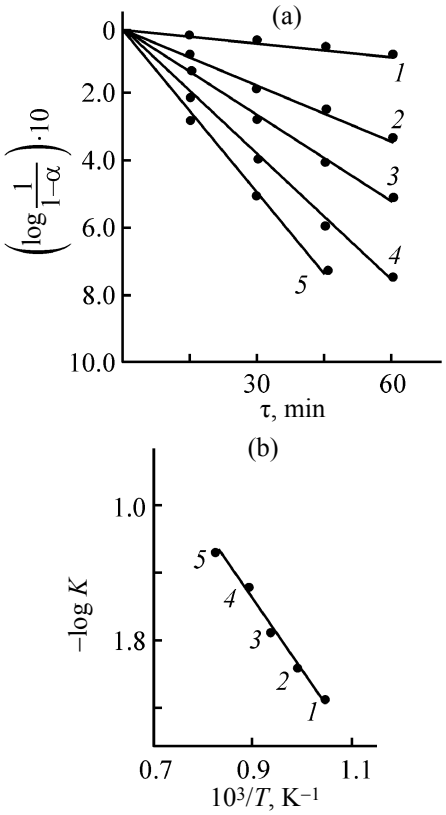

Fig. 3. (a) $\log[1/(1-\alpha)]$ vs. time τ and (b) $\log K$ vs. inverse temperature $1/T$. Caking temperature (°C): (*1*) 700, (*2*) 750, (*3*) 800, (*4*) 850, and (*5*) 900.

We examined the process kinetics at the optimal composition of the stock (c_{ws} = 30 wt %) in the temperature range 700–950°C in the isothermal mode, with the stock kept in a muffle furnace for 60–180 min and then leached with water in a thermostated reactor.

It can be seen in Fig. 2 that, as the temperature is elevated and the caking made longer, the degree of recovery of sodium aluminate increases; the kinetic curves are almost linear below 800°C, and first linear and then parabolic at 850°C.

These curves are well described by a first-order equation

$$\frac{d\alpha}{d\tau} = K(1-\alpha). \qquad (1)$$

The straight lines in the plot of the dependence of

$$\log\frac{1}{1-\alpha}$$

on time (Fig. 3a) have a negative slope equal in absolute value to K/2.303.

We found the apparent activation energy E and the pre-exponential factor K_0 graphically with the use of the Arrhenius equation

$$K = K\ e_0^{-\frac{E}{RT}}$$

and

$$\log K = \log K_0 - \frac{E}{2.303RT}. \qquad (2)$$

In the plot of the logarithm of the average rate constants against inverse temperature, points fall on a single straight line (Fig. 3b). The apparent activa-tion energy calculated by the Arrhenius equation is 114.64 kJ mol^{-1}. This indicates that the mud caking process occurs under kinetic control.

The studies we performed make it possible to determine the mechanism of the caking process and enable choice of a reasonable mode of manufacture of sodium aluminate from products in mud storage areas of aluminum plants.

Our physicochemical studies demonstrated that aluminate cakes have a complex chemical and phase composition, which includes sodium orthoaluminate ($3Na_2O\ Al_2O_3$), sodium oxide (Na_2O), gamma-alumina (γ-Al_2O_3), alpha-alumina (α-Al_2O_3), and cryolite (Na_3AlF_6).

The cake obtained under the optimal conditions from the stock was crushed to particle size of 0.1–0.5 mm and leached with water.

The degree of recovery of the cake components depends on numerous factors: chemical composition and physical properties of the cake, leaching mode, and apparatus used for this purpose.

To find the optimal mode of sodium aluminate leaching from the cake with water, we studied the effect of temperature, s : l ratio, and process duration on the degree of sodium aluminate recovery.

We examined the effect of the cake leaching temperature in the range from 20 to 96°C (Fig. 4a). It was found that, as temperature increases, the recovery of sodium aluminate varies from 25.6 to 98.7%.

As the duration of cake leaching is raised to 120 min, the degree of sodium aluminate recovery increases to 98.6% and then remains invariable (Fig. 4b).

The results we obtained in a study of the l : s ratio in the slurry on the degree of sodium aluminate recovery (Fig. 4c) indicate that the degree of sodium aluminate recovery increases at the beginning of the process to 98.7% and then remains nearly invariable.

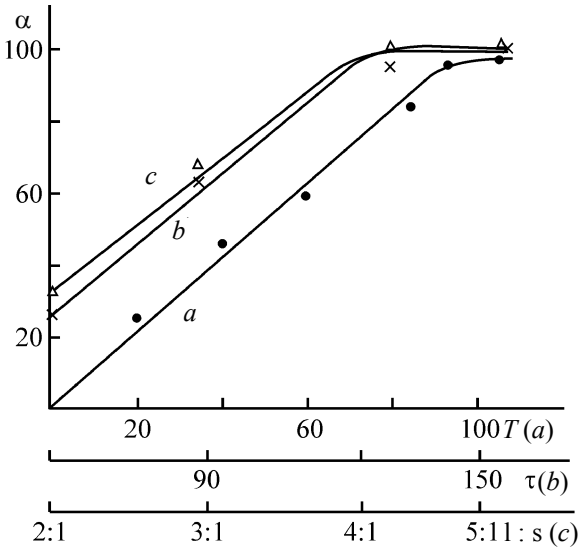

Fig. 4. Effect of (*a*) temperature *T,* °C, (*b*) process duration τ, min, and (*c*) l : s ratio on the degree of sodium aluminate recovery, α.

The aluminate solution obtained in the study contains (g l^{-1}): Na_2SO_4 2.2, Na_2O 10.7, Al_2O_3 4.0, and NaF 2.4. In view of the fact that the content of Na_2O in solution exceeds that of Al_2O_3 by more than a factor of 2.5, it can be concluded that sodium aluminate is present in solution as the hydroxo complex $Na_3[Al(OH)_6](3Na_2O\ Al_2O_3)$.

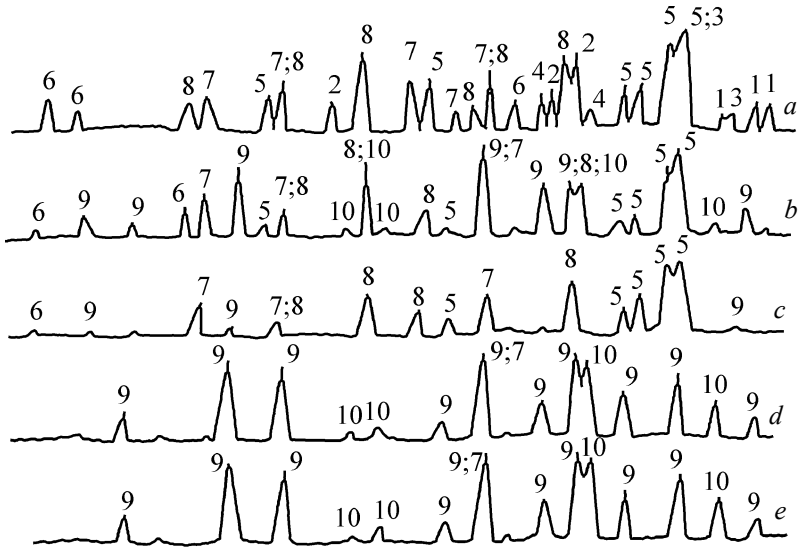

Fig. 5. X-ray diffraction patterns of (*a*) mud, (*b*) cake obtained in the optimal mode, (*c*) solid residue, (*d*) dry residue of the water-soluble component, and (*e*) dry residue of a solution of the reference mixture. (1) Schairerite (Na_2SO_4NaF), (2) thenardite (Na_2SO_4), (3) burkeite ($2NaSO_4\ Na_2CO_3$), (4) nahcolite ($NaHCO_3$), (5) graphite (C), (6) gamma-alumina (γ-Al_2O_3), (7) alpha-alumina (α-Al_2O_3), (8) cryolite (Na_3AlF_6), (9) sodium orthoaluminate ($3Na_2O\ Al_2O_3$), and (10) sodium oxide (Na_2O).

Our study demonstrated that, as the amount of the coagulant increases and the process becomes longer, the degree of coagulation reaches the maximum value and the residual content of suspended substances in water remains 21.25 mg dm^{-3} in the following coagulation mode: coagulant concentration 5 mg cm^{-3}, process duration 30 min. Thus, sodium aluminate can be used for drinking and wastewater treatment to remove suspensions.

To elucidate the mechanisms of the processes occurring in mud processing, we made and X-ray phase analysis of the starting raw material and products of its processing. Figure 5 shows X-ray diffraction patterns of the starting mud and its processing products.

As can be seen in the X-ray diffraction pattern of the starting mud (Fig. 5a), its main components are cryolite (Na_3AlF_6), alpha- and gamma-alumina (α-Al_2O_3, γ-Al_2O_3), thenardite (Na_2SO_4), and nahcolite ($NaHCO_3$).

The X-ray diffraction pattern of the cake obtained in the optimal mode contains no lines of schairerite, burkeite. thenardite, and nahcolite; the intensity of lines associated with graphite and cryolite is lowered; and line of sodium orthoaluminate and oxide are present. This is accounted for by the possibility of occurrence of high-level chemical reactions in mud caking.

CONCLUSIONS

(1) The topographic, layer-by-layer, chemical, and mineralogical composition of products in mud storage areas of Tajik aluminum plant was determined. The chemical and mineralogical composition of 48 samples taken at 20 points of the mud storage area at depths of 20 to 160 cm was found, with the content of carbon and the water-soluble component varying, respectively, from 11.8 to 34.3 wt % and from 5.1 to 47.8 wt % in terms of the dry mud mass.

(2) The kinetics of sodium aluminate production by caking of muds from mud storage areas of aluminum plants was studied. The apparent activation energy of the process is 114.64 kJ mol^{-1}, which indicates that it occurs under kinetic control.

(3) The orthoaluminate solution obtained was tested in coagulation of impurities in water. The optimal coagulation mode was found to be the following: coagulant concentration 5 mg cm^{-3}, process duration 30 min. In this case, the residual concentration of suspended substances in water becomes 21.2 mg dm^{-3}.

REFERENCES

1. Zapol'skii, A.K. and Baran, A.A., *Koagulyanty i flokulyanty v protsessakh ochistki vody* (Coagulants and Flocculants in Water Treatment Processes), Leningrad: Khimiya, 1987.
2. Raizman, V.L., Linevich, S.I., Vil'son, E.V., et al., *Tsv. Met.*, 1993, no. 3, pp. 36–37.
3. Eurasian Patent 003660.
4. Safiev, Kh.S., Azizov, B.S., and Ruziev, D.R., *Dokl. Akad. Nauk Resp. Tajikistan,* 1999, vol. 42, no. 2, pp. 46–49.