

MATHEMATICAL DESCRIPTION OF A FULL DESILICONIZING PROCESS FOR ALUMINATE SOLUTIONS

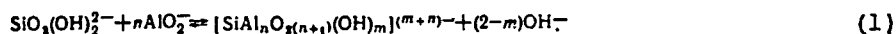
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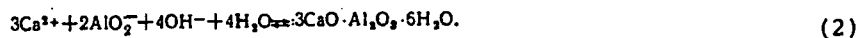
After the first stage of desiliconization, aluminate solutions contain silica at a level close to the equilibrium concentration for SiO_2 in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system. This level of SiO_2 removal from the solutions proves to be insufficient to obtain high-grade aluminum hydroxide in alumina production by the sintering method. The level of desiliconization is raised by making the silica in the solution combine to form hydrogarnet, a compound which is less soluble than sodium hydroalumosilicate.

Hydrogarnet is formed as a result of chemical reactions between lime and aluminate solution containing silica. Its composition is expressed by the formula $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot x\text{SiO}_2(6-2x)\text{H}_2\text{O}$. The formation of this compound can be expressed as follows.

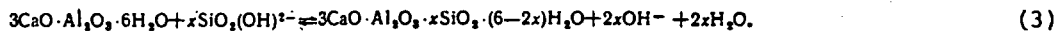
According to [1, 2], silica is present in aluminate solutions as two compounds: the simple ion $\text{SiO}_2(\text{OH})_2^{2-}$ and alumosilicon complexes $[\text{SiAl}_n\text{O}_x(\text{OH})_m]^{(m+n)-}$, $n = 1, 2, 3, 4$, which are formed by the following reaction:



When lime reacts with the aluminate solution, tricalcium hydroaluminate forms first according to the following reaction equation:



The latter reacts with silica in the solution, forming hydrogarnets by the following reaction:



Formation of hydrogarnet by this reactions shifts the equilibrium of Reaction (1) toward breakdown of the alumosilicon complexes, which do not participate directly in hydrogarnet formation.

In accordance with heterogeneous reaction (3), the formation of hydrogarnets on the phase interface must be accompanied by diffusion of $\text{SiO}_2(\text{OH})_2^{2-}$ in the liquid phase. Apart from liquid-phase diffusion there is solid-phase diffusion, causing particle saturation with silica X which decreases steadily in depth.

From the mathematical viewpoint, the formation of particles with a degree of silica saturation variable in depth is equivalent to the formation of a hydrogarnet layer of finite thickness with a constant degree of saturation with silica X around particles of tricalcium aluminate.

Thus, it may be assumed that solid-phase diffusion takes the form of growth of the hydrogarnet layer into the particles of tricalcium hydroaluminate.

According to [3], the kinetics of full desiliconization in the initial stage can be satisfactorily explained by the laws of chemical kinetics; it then apparently passes into the solid-phase diffusion region as the tricalcium hydroaluminate becomes saturated with silica. Differential equations for transfer of a substance with a discontinuous right-hand side are mathematically adequate for this physical model of the hydrogarnet formation process.

Thus, the structure of the mathematical model of physico-chemical reactions in full desiliconization takes the form of a material balance equation and differential transfer equations with a piecewise smooth right-hand side, as well as geometric relationships to describe the interface of the solid and liquid phases.

The following assumptions were made for mathematical description of the physical model formulated for full desiliconizing processes.

1. Formation of the complex alumosilicon ions (1) and tricalcium hydroaluminate (2) is instantaneous.

2. The law of mass action in concentration form is applicable to all the reactions.

3. The tricalcium hydroaluminate particles which form as a result of the chemical reaction between lime and aluminate solution are spherical in shape and with an identical diameter constant in time,

4. The diffusion layer is a thin globular layer adjacent to the particle outer surface, having an identical concentration gradient for all particle and a thickness variable in time.

The following symbols were adopted for the mathematical description:

C_{Al} , the concentration of AlO_2^- ions in the solution, kmoles/m³;

ΔC_{Al} , losses of aluminum with tricalcium hydroaluminate, kmoles/m³;

C_{Na} , the concentration of Na^+ ions in the solution, kmoles/m³;

C_{Si} , the concentration of $\text{SiO}_2(\text{OH})_2^{2-}$ ions in the solution, kmoles/m³;

C_{Si}^e , the equilibrium concentration of $\text{SiO}_2(\text{OH})_2^{2-}$ in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system kmoles/m³;

- C_c , the concentration of alumosilicon complexes $[\text{SiAl}_n\text{O}_2 (n+)(\text{OH})_m]^{(m+n)-}$ in the solution, kmoles/m³;
 C , the solution total SiO_2 content, kmoles/m³;
 C_e , the equilibrium SiO_2 concentration in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system, kmoles/m³;
 C_{Ca} , the concentration of Ca^{2+} ions in the solution, kmoles/m³;
 C_{OH} , the concentration of OH^- ions in the solution, kmoles/m³;
 $G_3\text{CAL}$, the specific amount (concentration) of tricalcium hydroaluminat $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ in a unit of solution volume, kmoles/m³;
 G_h , the specific amount of hydrogarnet $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot x\text{SiO}_2 (6-2x)\text{H}_2\text{O}$;
 D , the diffusion coefficient, m²/sec;
 δ , the thickness of the diffusion layer, m;
 d , the particle diameter, m;
 N , the particle concentration, 1/m³;
 β , the equilibrium constant of chemical reaction (3);
 $\alpha = C_{\text{Na}}/C_{\text{Al}}$, the aluminate solution ratio;
 $\mu_3\text{CA}$, μ_h , the molecular masses of tricalcium hydroaluminat and hydrogarnet, kg/(kmole);
 $\rho_3\text{CAL}$, ρ_h , the densities of tricalcium hydroaluminat and hydrogarnet, kg/m³.

Mathematical Model of Elementary Processes

In the initial stage, the process of full desilicization is governed by the speed of chemical reaction (3), which according to [3] is of the second order:

$$w_e = K(C_{\text{Si}} - C_{\text{Si}}^e)^2,$$

where K is the chemical reaction speed constant.

According to Pick's equation, the speed of diffusion $\text{SiO}_2(\text{OH})_2^{2+}$ ions through the layer of hydrogarnet which forms is:

$$w_d = \frac{D}{\delta} (C_{\text{Si}} - C_{\text{Si}}^e).$$

We will assume the point at which the speeds of the chemical reaction and of diffusion are equal to be the points of transition τ from the kinetic region to the diffusion region:

$$K [C_{\text{Si}}(\tau) - C_{\text{Si}}^e]^2 = \frac{D}{\delta(\tau)} [C_{\text{Si}}(\tau) - C_{\text{Si}}^e]$$

or

$$[C_{\text{Si}}(\tau) - C_{\text{Si}}^e] \delta(\tau) = \frac{D}{K}. \quad (4)$$

Having regard to what has been said, it follows from the material balance for $\text{SiO}_2(\text{OH})_2^{2-}$ in the solution that

$$\frac{dC_{\text{Si}}}{dt} = \begin{cases} -w_e n d^3 N & \text{where } t < \tau; \\ -w_d n d^3 N & \text{where } t > \tau \end{cases}$$

or, by substituting the w_e and w_d values:

$$\frac{dC_{\text{Si}}}{dt} = \begin{cases} -K n d^3 N (C_{\text{Si}} - C_{\text{Si}}^e)^2 & \text{where } t < \tau; \\ -\frac{D}{\delta} n d^3 N (C_{\text{Si}} - C_{\text{Si}}^e) & \text{where } t > \tau. \end{cases} \quad (5)$$

According to [4], the relationship between the total concentration of silica and the concentration of silicon ions in the solution can be expressed by the following equation:

$$C_{\text{Si}} = C \frac{\alpha - 1}{\alpha - 1 + \sum_{i=1}^n \beta_i C_{\text{Al}}^{i-1}}. \quad (6)$$

where β_{ki} are the stability constants of the corresponding alumosilicon complexes.

In the equilibrium state ($t \rightarrow \infty$), taking the ionic balance into account

we obtain, from Reaction (3)

$$C_{\text{Al}} + C_{\text{OH}} \approx C_{\text{Na}} \\ \beta^x = \frac{(C_{\text{Si}}^e)^x}{(C_{\text{Na}} - C_{\text{Al}})^{2x}}. \quad (7)$$

We obtain the following from Equations (6) and (7) for the equilibrium state of the system (where $t \rightarrow \infty$):

$$C^e = (\alpha - 1) C_{\text{Al}}^2 \left[\beta (\alpha - 1) + \sum_{i=1}^n \beta_i C_{\text{Al}}^{i-1} \right]. \quad (8)$$

where $\beta_i = \beta \beta_{ki}$.

We then find the relationship between the geometric characteristics of the particles d and δ and the concentrations of the solids formed $G_3\text{CAL}$ and G_h . Taking into account (see paragraphs 3 and 4 of the assumption) that the particle volume is $1/6\pi d^3$ and the volume of the globular hydrogarnet layer is $\pi d^2 \delta$, we may write

$$\frac{1}{6} \pi d^3 N = \frac{G_3\text{CAL} \mu_3\text{CAL}}{\rho_3\text{CAL}}, \quad \pi d^2 \delta N = \frac{G_h \mu_h}{\rho_h}.$$

Hence,

$$N = \frac{6G_3\text{CAL} \mu_3\text{CAL}}{\pi d^3 \rho_3\text{CAL}}.$$

$$\delta = \frac{G_h \mu_h \rho_{3\text{CAI}}^d}{6 G_{3\text{CAI}} \mu_{3\text{CAI}} \rho_h} \quad (9)$$

The concentrations $G_{3\text{CAI}}$ and G_h of the solids can be found from the material balances. According to equation (2), we have:

$$G_{3\text{CAI}} = \frac{1}{3} C_{\text{Ca}} \quad (10)$$

Similarly according to the equation for reaction (3) we have

$$G_h = \frac{C_{\text{Si}}(0) - C_{\text{Si}}}{x} \quad (11)$$

Using relationships (6)-(11), we write differential equation (5) relative to the total silica concentrations in solution C in explicit form:

$$\frac{dC}{dt} = -K_1 \frac{(\alpha-1)^2 C_{\text{Al}}^2 C_{\text{Ca}}}{C^2} (C - C^e) \quad \text{where } t < \tau; \quad \frac{dC}{dt} = -K_2 \frac{C^e C_{\text{Ca}}^2}{C_{\text{Al}}^2 (\alpha-1)^2} \frac{C - C^e}{C(0) - C} \quad \text{where } t > \tau \quad (12)$$

where

$$K_1 = \frac{2K\beta\mu_{3\text{CAI}}}{d\beta_{3\text{CAI}}}; \quad K_2 = \frac{D\rho_h x}{\beta\mu_h} \left(\frac{2\mu_{3\text{CAI}}}{d\rho_{3\text{CAI}}} \right)^2$$

The expression for determining τ is obtained from equations (4) or (12) and is as follows, taking into account the symbols which have been introduced:

$$[C(\tau) - C^e][C(0) - C(\tau)] = \frac{K_2}{K_1} \frac{(C^e)^2 C_{\text{Ca}}}{(\alpha-1)^4 C_{\text{Al}}^4} \quad (13)$$

Finally, the losses of aluminum ΔC_{Al} with the tricalcium hydroaluminate which forms are governed by the amount of lime added and are as follows, in accordance with the equation for reaction (2):

$$\Delta C_{\text{Al}} = \frac{2}{3} C_{\text{Ca}} \quad (14)$$

Thus, the mathematical model for elementary processes in full desiliconizing takes the following form:

$$\frac{dC}{dt} = -K_1 (C - C^e)^2 \frac{(\alpha-1)^2 C_{\text{Al}}^2 C_{\text{Ca}}}{C^2} \quad \text{where } t < \tau; \quad \frac{dC}{dt} = -K_2 \frac{C - C^e}{C(0) - C} \frac{C^e C_{\text{Ca}}^2}{C_{\text{Al}}^2 (\alpha-1)^2} \quad \text{where } t > \tau \quad (15a)$$

$$[C(\tau) - C^e][C(0) - C(\tau)] = \frac{K_2}{K_1} \frac{(C^e)^2 C_{\text{Ca}}}{(\alpha-1)^4 C_{\text{Al}}^4};$$

$$C^e = (\alpha-1) C_{\text{Al}}^2 \times \left[\beta(\alpha-1) + \sum_{i=1}^4 \beta_i C_{\text{Al}}^{i-1} \right];$$

$$\Delta C_{\text{Al}} = \frac{2}{3} C_{\text{Ca}}$$

Identification of Mathematical Model

The undefined coefficients in mathematical model (15) are K_1 , K_2 , β , and β_i . Only β and β_i affect the equilibrium state of the process; these can be found from equation (15c) by identification according to the results of experiments in the equilibrium state.

Coefficients K_1 and K_2 reflect the kinetics of the process and can be found by identification of the mathematical model according to the results of experiments on the kinetics of full desiliconizing with the β and β_i values which have been found.

The methods and results of the experiments on full desiliconizing have been set out in detail in [5].

The substantial error in measuring the SiO_2 concentration at values less than 0.1 kg/m³ prevents reliable determination of β and β_i , which prove to be close to zero within the limits of error.

$$C^e = 0 \quad (16)$$

is therefore adopted, and $K_2 C^e$ in formula (15a) is replaced by K'_2 :

$$K_2 C^e = K'_2 = \text{const.} \quad (17)$$

Statistical treatment of equation (15a) then revealed that the kinetics of full desiliconizing were well described by one equation (15a) for $t > \tau$ in the entire range of time $t > 0$:

$$\frac{dC}{dt} = -\frac{K'_2 C_{\text{Ca}}^2}{C_{\text{Al}}^2 (\alpha-1)^2} \frac{C}{C(0) - C} \quad (18)$$

Consequently, the process of full desiliconizing is limited by the diffusion stage. To find K_2 , equation (18) was balanced by the following replacement of variables:

$$x = \frac{1}{C}; \quad x_0 = \frac{1}{C(0)}. \quad (19)$$

In these variables, we have

$$\frac{dx}{dt} = K \frac{x^2 x_0}{x - x_0},$$

where

$$K = \frac{K_2 C_{Ca}^2}{C_{Al}^2 (\alpha - 1)^2},$$

and by integrating, we obtain:

$$\frac{1}{x_0} \ln \frac{x}{x_0} + \frac{1}{x} - \frac{1}{x_0} = Kt. \quad (20)$$

Consequently, it is necessary to take the following to balance (20):

$$Y = C(0) \ln \frac{C(0)}{C} + C - C(0). \quad (21)$$

We then have the following instead of (20):

$$Y(t) = K_2 \frac{C_{Ca}^2}{C_{Al}^2 (\alpha - 1)^2} t. \quad (22)$$

Identification of equation (22) by the least-squares method gives the following value for K_2 :

$$K_2 = 2.71 \cdot 10^{-4} \text{ kmoles}/(\text{m}^2 \cdot \text{sec}) \quad (23)$$

with a mean square error of 10%.

Thus, the identified mathematical model of full desiliconizing takes the following form:

$$\frac{dC}{dt} = -2.71 \cdot 10^{-4} \frac{C_{Ca}^2}{C_{Al}^2 (\alpha - 1)^2} \frac{C}{C(0) - C}; \quad (24a)$$

$$\Delta C_{Al} = \frac{2}{3} C_{Ca}. \quad (24b)$$

The equations from the mathematical model of full desiliconizing have been used with equations from the mathematical model for desiliconizing stage I [4] for optimizing the standard process of two-stage desiliconizing of aluminate solutions without auto-claves [5].

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