MATHEMATICAL DESCRIPTION OF THE ALUMINATE SOLUTION DESILICONIZING PROCESS

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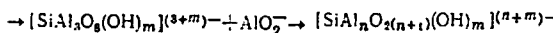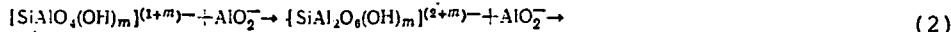I. Z. Pevzner, A. S. Dvorkin, M. Ya. Fiterman, N. I. Eremin, and Ya. B. Rozen

A great deal of attention has recently been given to the optimization of technological processes using mathematical descriptions. In spite of the abundance of experimental material, a sufficiently complete mathematical model of the aluminate solution desiliconizing process has not been available up to the present. The existing work [1-3] is far from complete and does not extend to all the aspects of this complex process in chemical technology.

Published findings and our own researches are used in the present work as a basis for mathematical description of the physical and chemical processes which take place in the first stage of aluminate solution desiliconizing and involve the evolution of silica from solution in the form of sodium hydroaluminosilicate.
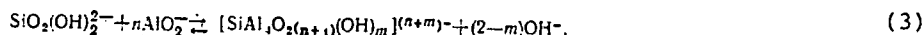
According to [4,5], the process of aluminosilicon complex formation in the solution is in accordance with the following reaction equations:

$$SiO_2(OH)_2^{2-} + AlO_2^- \rightleftharpoons [SiAlO_4(OH)_m]^{(1+m)} + (2-m)OH^-. \tag{1}$$
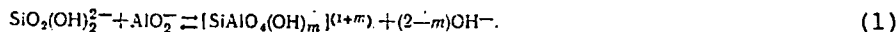
With an increase in the aluminum ion concentration, new complexes are formed according to the following system:

$$[SiAlO_4(OH)_m]^{(1+m)-} + AlO_2^- \rightarrow \{SiAl_2O_6(OH)_m]^{(2+m)-} + AlO_2^- \rightarrow$$
$$\rightarrow [SiAl_3O_8(OH)_m]^{(3+m)-} + AlO_2^- \rightarrow [SiAl_nO_{2(n+1)}(OH)_m]^{(n+m)-} \tag{2}$$

or in total

$$SiO_2(OH)_2^{2-} + nAlO_2^- \rightleftharpoons [SiAl_nO_{2(n+1)}(OH)_m]^{(n+m)-} + (2-m)OH^-. \tag{3}$$
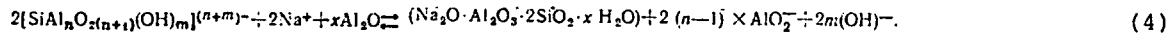
where n = 1, 2, 3, 4.

The formation of sodium hydroaluminosilicate from these complexes can be described by the following reaction equation:

$$2[SiAl_nO_{2(n+1)}(OH)_m]^{(n+m)-} + 2Na^+ + xAl_2O_3 \rightleftharpoons (Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot xH_2O) + 2(n-1) \times AlO_2^- + 2m(OH)^-. \tag{4}$$

The sodium hydroaluminosilicate which forms initially is amorphous in structure; it subsequently crystallizes into a structure which is thermodynamically stable in the given conditions.

We adopt the following well-known propositions and assumptions for the mathematical description of the kinetics of elementary processes in desiliconizing.

1. The kinetics of chemical reaction (4) and the diffusion of aluminosilicon complexes to the surface of the solid phase are the limiting stages in the formation of sodium hydroaluminosilicate.

2. The law of mass action written in concentrations holds good for reactions (3) and (4).

3. The concentration of aluminum and sodium in the liquid phase is much higher than the silica concentration.

The following notations were adopted for the mathematical description: C_{Al}, C_{Na}, C_{OH}, and C_{Si} are the respective concentrations of AlO_2^-, Na^+, OH^-, and $SiO_2(OH)_2^{2-}$ ions in the solution, $kmole/m^3$; C_{cp} is the concentration of aluminosilicon complexes $[SiAl_nO_{2(n+1)}(OH)_m]^{(n+m)-}$ in the solution, $kmole/m^3$; C is the solution total silica content, $kmole/m^3$; C^e is the equilibrium SiO_2 concentration in the $Na_2O - Al_2O_3 - SiO_2 - H_2O$ system, $kmole/m^3$; C_d is the total silica concentration in the diffusion layer, $kmole/m^3$; C_{cdp} is the concentration of aluminosilicon complexes $[SiAl_nO_{2(n+1)}(OH)_m]^{(n+m)}$ in the diffusion layer, $kmole/m^3$; G is the specific amount of solid phase (in a unit of solution volume), kg/m^3; β_p and β_{cp} are the chemical reaction equilibrium constants, $kmole/m^3$; K_1 and K_2 are the normalized constants for the speed of the sodium hydroaluminosilicate formation reaction, $1/sec$, $m^3/(kmole \cdot sec)$; K_d is the diffusion speed constant, m/sec; δ is the thickness of the diffusion layer, m; d_e is the sodium hydroaluminosilicate particle equivalent diameter, m; S is the total specific surface of the sodium hydroaluminosilicate particles, $1/m$; and ρ is the density of the solid phase, kg/m^3.

The structure of the mathematical model is a system of algebraic and ordinary differential equations, based on the material balances for sodium hydroaluminosilicate, silicon, and the aluminosilicon complexes.

Let us find the relationship between the principal parameters governing formation of aluminosilicon complexes and sodium hydroaluminosilicate in the solution in accordance with the assumed process mechanism.

Formation of Aluminosilicon Complexes. Aluminosilicon complexes are formed in the liquid phase as a result of instantaneous chemical reactions (3). The equilibrium conditions for these reactions will be written in the form

$$\beta_{cp} = \frac{C_{cp}C_{OH}^{2-m}}{C_{Si}C_{Al}^{n}}. \tag{5}$$

The ionic balance can be written as follows, on the basis of the electrical neutrality conditions for the solution:

$$C_{Al} + C_{OH} + 2C_{Si} + \sum_{n=1}^{4}(n+m)C_{cp} = C_{Na}.$$

Since C_{Si}, $C_{cp} \ll C_{Al}$, C_{Na} in the solution, the ionic balance will be

$$C_{Al} + C_{OH} \approx C_{Na}$$

or

$$C_{OH} \approx C_{Na} - C_{Al}. \tag{6}$$

The material balance for silica in the liquid phase is shown thus:

$$C_{Si} + \sum_{n=1}^{4} C_{cp} = C;$$

for C_{Si} we obtain

$$C_{Si} = C - \sum_{n=1}^{4} C_{cp}. \tag{7}$$

Then by substituting (7) and (6) into (5) we find

$$\beta_{cp} = \frac{C_{cp}(C_{OH} - C_{Al})^{2-m}}{\left(C - \sum_{i=1}^{4} C_{ki}\right) C_{Al}^{n}}$$

or we obtain the following by way of the caustic modulus $\alpha = C_{Na}/C_{Al}$:

$$\beta_{cp} = \frac{C_{cp}(\alpha - 1)^{2-m}}{\left(C - \sum_{i=1}^{4} C_{ki}\right) C^{n-2+m}}. \tag{8}$$

To find C_{cp} (n = 1, 2, 3, 4) from the system of equations we multiply each equation (8) by C_{Al}^{n-2+m} and integrate for n:

$$\sum_{i=1}^{4} \beta_{ki} C_{Al}^{i-2+m} = \frac{(\alpha-1)^{2-m} \sum_{i=1}^{4} C_{ki}}{C - \sum_{i=1}^{4} C_{ki}}.$$

Hence we find

$$\sum_{i=1}^{4} C_{ki} = C \frac{\sum_{i=1}^{4} \beta_{ki} C_{Al}^{i-2+m}}{(\alpha-1)^{2-m} + \sum_{i=1}^{4} \beta_{ki} C_{Al}^{i-2+m}}$$

and obtain the following by substituting into (8):

$$C_{cp} = C \frac{\beta_{cp} C_{Al}^{n-2+m}}{(\alpha-1)^{2-m} + \sum_{i=1}^{4} \beta_{ki} C_{Al}^{i-2+m}}. \tag{9}$$

Formation of Crystalline Sodium Hydroaluminosilicate. Crystalline sodium hydro-aluminosilicate is formed as a result of heterogeneous chemical reactions (4), the formation being accompanied by diffusion of aluminosilicon complexes to the particle reaction surfaces.

We find the expressions for the speeds of reactions (4) in accordance with the law of formal kinetics:

speeds of forward reactions ω_{fr_n} :

$$\omega_{sr_n} = K_n C_{cdp}^2 C_{Na}^2$$ (10)

speeds of reverse reactions ω_{rr_n} :

$$\omega_{rr_n} = K_n' C_{Al}^{2(n-1)} C_{OH}^{2m}$$ (11)

resultant reaction speeds ω_{r_n} :

$$\omega_{r_n} = \omega_{fr_n} - \omega_{rr_n} = K_n C_{Na}^2 (C_{cdp}^2 - C_{cp}^{e2})$$ (12)

where K_n and K_n' are the forward and reverse speed constants of reactions (4) and C_{cp}^e are the equilibrium aluminosilicon complex concentrations obtained from (10) and (11) for $\omega_{fr_n} = \omega_{rr_n}$ and $C_{cdp} = C_{cp}^e$:

$$C_{cp}^e = \beta_n \frac{C_{Al}^{n-1} C_{OH}^m}{C_{Na}},$$ (13)

where

$$\beta_n = \sqrt{\frac{K_n'}{K_n}}.$$

Since expression (9) obviously holds good for the diffusion layer also, C_{cdp} and C_{cp}^e can be obtained from (9) by assuming $C = C_d$ and $C = C^e$ in it respectively. We then obtain the following instead of (12), taking account of ionic balance (6):

$$\omega_{rp} = K_n Z_n^2 (C_d^2 - C^{e2}).$$ (14)

where

$$Z_n = \frac{\beta_{cp} C_{Al}^{n-1+m} \alpha}{(\alpha - 1)^{2-m} + \sum_{i=1}^{4} \beta_{ki} C_{Al}^{i-2+m}}.$$

By equating (9) and (13) for $C = C^e$ and $C_{cp} = C_{cp}^e$ we find the expression for the equilibrium concentration of SiO_2 is the system taking account of the ionic balance (6):

$$C^e = \frac{\beta_p}{\beta_{cp}} \frac{(\alpha - 1)^2}{\alpha} + \frac{\beta_p}{\beta_{cp}} \frac{(\alpha - 1)^2}{\alpha} \cdot \sum_{i=1}^{4} \beta_{ki} C_{Al}^{i-2+m}.$$

It follows from this expression that

$$\frac{\beta_p}{\beta_{cp}} = const = \beta.$$

therefore

$$C^e = \beta \frac{(\alpha - 1)^2}{\alpha} \left[(\alpha - 1)^{2-m} + \sum_{i=1}^{4} \beta_{ki} C_{Al}^{i-2+m} \right].$$ (15)

Having regard to the fact that the total speed of the reverse reactions of sodium hydroaluminosilicate solution is determined mainly by the driving force $C_d^2 - C^{e2}$ [see equation (14)], it may be regarded as independent of C_{Al} and α, i.e., it is possible to assume $\sum_{i=1}^{4} K_i Z_i^2 = const = K$; then we find the total resultant speed of sodium hydro-aluminosilicate formation ω_r by integrating (14) for n = 1, 2, 3, 4:

$$\omega_r = \sum_{i=1}^{4} \omega_{pi} = K'(C_d^2 - C^{e2}).$$ (16)

We can now compile instantaneous material balances for SiO_2 in the body of the solution and in the diffusion layer. Assuming, as is customary, that the speed of diffusion is proportional to the drop in concentrations on the diffusion region boundaries we have:

the balance in the body of the solution

$$\frac{dC}{dt} = -K_d(C - C_d)S;\qquad(17)$$

the balance in the diffusion region, taking account of the fact that the volume of the diffusion layer for all particles is $S\delta V$

$$\delta\frac{dC_d}{dt} = K_d(C - C_d) - K(C_d^2 - C^{e_1}),$$

or, after dividing by δ

$$\frac{dC_d}{dt} = K_1(C - C_d) - K_2(C_d^2 - C^{e_1}).\qquad(18)$$

It is convenient to express the specific surface S of the particles in terms of the concentration G and the equivalent diameter d_e of the solid phase particles. We have

$$S = S_1 N, \quad G = V_1 \rho N,$$

where S_1 and V_1 are the surface and the volume of one particle and N is the concentration of the solid phase part.

The total specific surface of the sodium hydroaluminosilicate is

$$S = \frac{S_1}{V_1}\frac{G}{\rho},$$

or, expressing S_1/V_1 in terms of the equivalent particle diameter d_e

$$\frac{S_1}{V_1} = \frac{6\pi d_e^2}{\pi d_e^3} = \frac{6}{d_e},$$

we obtain

$$S = \frac{6G}{\rho d_e}.\qquad(19)$$

Equations (15), (17), and (18) taking account of (19) form a complete mathematical model of the aluminate solution desiliconizing process.

Identification of the Mathematical Model. The unknowns in the mathematical model are the equilibrium constants β, $\beta_n (n = 1, 2, 3, 4)$, the diffusion speed constant K_d and chemical reaction speed constants K_1 and K_2, and also the stoichiometric integral coefficient m in the formula for the complex aluminosilicon ions. The coefficients enumerated were found by identification of the mathematical model, the equilibrium constants β and β_n and coefficient m being found by statistical processing of the equilibrium states of the system $Na_2O - Al_2O_3 - SiO_2 - H_2O$ according to formula (15) and constants K_d, K_1, and K_2 by statistical processing of the kinetics in that system according to equations (17) and (18). The file of experimental values of C^e, C_{Al}, and α obtained in experiments with 100 – 170-hr desiliconizing of synthetic solutions is given in Table 1.

The file of experimental values of C(t) obtained in 8-hr kinetic experiments on desiliconizing synthetic aluminate solutions with addition of solid phase in the form of slime from Turgaisk bauxite leaching is given in Table 2.

Expression (15) was equalized as follows:

$$Y = \beta + aX,$$

where

$$Y = \frac{C^e \alpha}{(\alpha - 1)^2}; \quad X = (\alpha - 1)^{m-2}; \quad a = \sum_{i=1}^{4}\beta_i C_{Al}^{i-2+m}.$$

Table 1
File of Experimental Values of C^e, $C_{Al_2O_3}$, and α (T = 98° C)

α	$C_{Al_2O_3}$, kg/m³				
	80	100	120	140	160
1,75	0,30	0,35	0,44	0,63	0,80
2,00	0,29	0,38	0,54	0,73	0,84
2,25	0,32	0,41	0,56	0,84	0,94
2,50	0,32	0,44	0,64	0,86	1,01

Note: The data are averaged from four series of parallel experiments.

Table 2
File of Experimental Values of C(t), G, and d_e (T = 98° C, $C_{Al_2O_3}$ = 120 g/liter, α = 1.8)

t, min	C, kg/m³		
	G=20 kg/m³ d_e=50 μm	G=40 kg/m³ d_e=65 μm	G=60 kg/m³ d_e=55 μm
0	3,63	3,61	3,62
10	3,45	3,30	3,30
30	3,00	2,44	2,40
60	2,40	1,65	1,40
90	1,80	1,15	1,00
120	1,41	0,90	0,73
150	1,00	0,65	0,55
180	0,85	0,60	0,54
240	0,85	0,49	0,47
360	0,60	0,50	0,48
480	0,52	0,45	0,44

Note: The data are averaged from four series of parallel experiments

The file of experimental values of C^e and α for C_{Al} = const (and consequently a = const) was then plotted in a Y-X system of coordinates for various values of m (see Fig.). It is apparent from the Figure that the optimum value of m = 1.
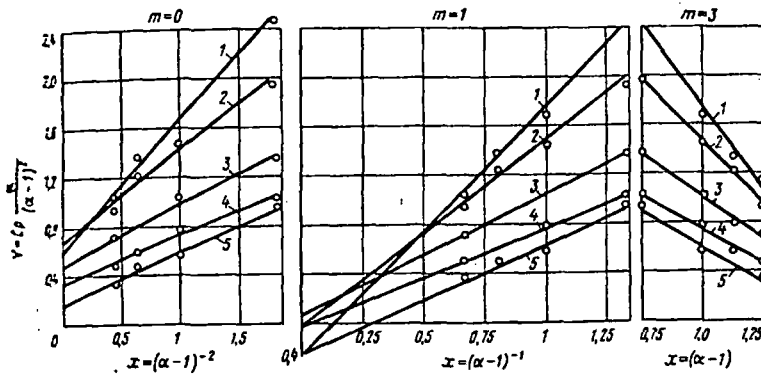
Finding coefficient m for the following Al_2O_3 contents, g/liter: 1) 160; 2) 140; 3) 120; 4) 100; 5) 80.

The values of equilibrium constants β and β_n were found in the next stage of identification in the equilibrium state. Two of the β_n constants were left in (β_1 and β_3 proved to be the most suitable for this), because the accuracy of the experiments did not permit reliable determination of all four of the β_n constants (n = 1, 2, 3, 4) in equation (15).

Expression (15) was equalized as follows:

$$Y = \beta X_1 + \beta_1 + \beta_3 X_2, \qquad (20)$$

where

$$Y = \frac{Ce\,\alpha}{\alpha - 1}; \quad X_1 = \alpha - 1; \quad X_3 = C^2_{Al}.$$

Statistical processing of formula (20) gave the following result: $\beta = 0$; $\beta_1 = 0.224 \times 10^{-2}$ kmole/m^3; $\beta_3 = 0.293 \times 10^{-2}$ kmole/m^3; the maximum relative error in formula (15) was 7.2% and the mean-square error was 5%.

The zero value of coefficient β, which is equal to β_n/β_{cp} according to the notation, provides practical evidence of the high values of the β_{cp} equilibrium constants, i.e., of the fact that almost all of the silica in the solution is present in the form of aluminosilicon complexes. This is also confirmed by the published findings [4].

After identification, formula (15 takes the following form:

$$C^e = \frac{\alpha - 1}{\alpha} (0.224 \cdot 10^{-3} + 0.293 \cdot 10^{-2} C^2_{Al}). \qquad (21)$$

The kinetic constants K_d, K_1, and K_2 were found by the method of least squares by minimizing the sum of the squares of the deviations of SiO_2 concentration experimental values from the calculated values:

$$K_d = 0.251 \times 10^{-6} \text{ m/sec}; \quad K_1 = 0.606 \times 10^{-4} \text{ 1/sec};$$

$$K_2 = 0.166 \times 10^{-10} \text{ m}^3/(\text{kmole.sec}).$$

The mean-square error of formulas (17) and (18) is 5.4%.

Thus the mathematical model obtained may be regarded as adequate for the physical and chemical processes which take place during desiliconizing of aluminate solutions.

REFERENCES

1. S. I. Kuznetsov, V. A. Derevyankin, I. P. Kraus, and T. P. Porotnikova. In the book: Theory and Practice of Desiliconizing Aluminate Solutions. Moscow. Tsvetmetinformatsiya, 1971, pp. 42-47.
2. N. F. Balabai, A. Ashimov, and V. D. Ponomarev. Theory and Technology of Alumina Production. No. 35. Alma-Ata, IMO AN KazSSR, 1969, pp. 23-25.
3. N. F. Pecherskaya and L. P. Ni. New Processes in Alumina Production. No. 47. Alma-Ata, IMO Kaz SSR, 1972, pp. 34-37.
4. I. Z. Pevzner, N. I. Eremin, Ya. B. Rozen, et al. ZhPKh, 1974, vol. 47, No. 12, pp. 2758-2760.
5. I. Z. Pevzner, A. S. Dvorkin, M. Ya. Fiterman, and Ya. B. Rozen. Alumina Production. Collection No. 85, Leningrad, VAMI, 1974, pp. 61-65.
6. I. Z. Pevzner, A. S. Dvorkin, M. Ya. Fiterman, et al. In the book: Materials of the Vth Anniversary Scientific-Technical Session of MISiS Dedicated to the 50th Anniversary of the USSR. Moscow, MISiS, 1972, pp. 159-160.