

The Contribution of Molecular Diffusion in Silica Coating and Chemical Reaction in the Overall Rate of Reaction of Aluminum Hydroxide with Fluosilicic Acid

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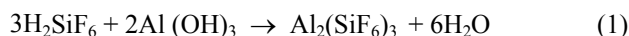
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ABSTRACT: The kinetic of the heterogeneous chemical reaction of aluminum hydroxide and fluosilicic acid was studied. It was found that the diffusion of the reactants through the porous silica coating to the aluminum hydroxide surface and the interfacial chemical reaction between the diffusing reactant and aluminum hydroxide platelets control the overall reaction rate. These two phenomena were studied and their contributions to the overall reaction rate were derived using experimental data. By combining these terms a relation for the overall reaction rate was obtained. The activation energy of the chemical reaction was calculated to be 12 kcal/mol and the activation energy of the diffusion into the silica coating was found as 28 kcal/mol. A numerical procedure was adjusted to determine the variation of the specific surface area of un-reacted core, its average particle size and the specific surface area for mass transfer.

KEY WORDS: Heterogeneous reaction, Aluminum hydroxide, Fluosilicic acid, Aluminum fluoride, Silica, Effective diffusion coefficient, Aggregation, Kinetics.

INTRODUCTION

The reaction of fluosilicic acid with aluminum hydroxide is a heterogeneous one in which an aqueous solution of fluosilicic acid reacts with aluminum hydroxide powder and leads to a solution of aluminum fluoride and silica precipitates.



According to a mechanism, proposed by Skrylev [1],

at first the water-soluble aluminum fluosilicate is formed, which is then hydrolyzed to aluminum fluoride, silica precipitates and fluoridric acid.

Grobelny [3] studied the kinetics of this reaction and proposed an empirical first-order rate equation(Eq.3) for the overall reaction, in which the individual contributions of the above mentioned phenomena, was not taken into account.

$$r = k C_L \quad (3)$$

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1021-9986/05/4/15

10/\$/3.00

$$\log k = 9.1 - 3500/T - \log(a) \quad (4)$$

In the authors previous paper [2] have presented the filtration rate of the silica precipitates as related to their morphology. It has been found that in the course of reaction the produced silica particles adsorb on aluminum hydroxide platelets in an aggregated state. The morphology of the aggregates, which has a profound influence on the filtration rate of the silica precipitates, is influenced by the reaction conditions. On the other hand, at every stage of the reaction, the overall reaction rate is influenced by the morphology of the silica coating. In the other words, the reaction conditions dictate the morphology of the silica coating and this factor influences the overall reaction rate in turn. In this paper, the results of the experimental study of the overall reaction kinetics are presented. This reaction is a complex one in which, two phenomena, the chemical reaction and the molecular diffusion of the mobile reactant in the silica coating are controlling the overall reaction rate.

The contribution of the above-mentioned phenomena in the overall reaction rate has been considered. The overall reaction rate is necessary for reactor design which is comprised of determining the reactor size, the type and size of propeller, rotational speed of agitator and operating conditions of reaction.

EXPERIMENTAL

Chemicals

Fluosilicic acid was prepared by the reaction of the analytical grade silica gel and the technical grade fluoridric acid. Aluminum hydroxide was of technical grade having a purity of 99% and an average particle size of 25 microns. All of the reactants were used as supplied and without any further purification.

Apparatus

According to Fig.1 the 500 mL reaction mixture was mixed using a digitally-controlled mechanical stirrer in a 2000 mL reactor. The reactor was heated by a hot water bath equipped with an accurate thermoregulation system. A platinum crucible was used for the alkali fusion reactions. The electron micrographs were taken using a Topcon SR50 scanning electron microscope. Particle size micro analyzer A22 Fritch has been used for size distribution measuring of $\text{Al}(\text{OH})_3$ powder.

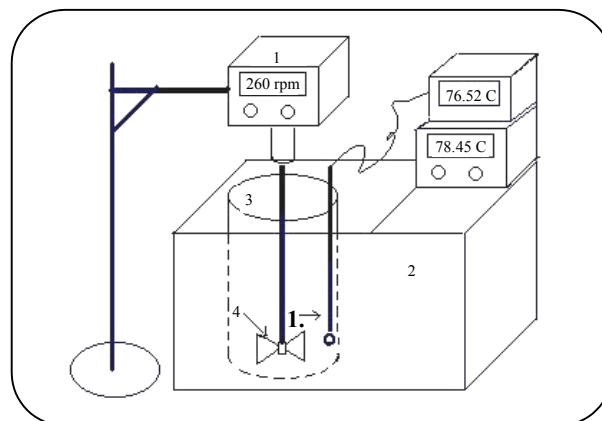


Fig. 1: Experimental Setup. 1) Digitally-controlled mechanical Stirrer (heidolph RZR2021), 2) Digitally-Controlled Hot Water Bath (Falk Sb15), 3) Reactor (Diameter = 12 cm & Volume = 2000 mL), 4) Teflon Propeller (Diameter = 6 cm & Type = Four turbine Blade), 5) Digitally Thermometer.

Experimental Procedure

In each run, the first sample was taken after 30 seconds and the next ones in 2 minutes intervals. The volume of each sample was nearly 10 mL. Each sample was filtered and the filtrate was analyzed for aluminum concentration. In order to determine the concentration of aluminum in the filtrate, a 2 ml sample was drawn from the filtrate and evaporated in a platinum crucible under gentle heating for 20 minutes. The aluminum fluoride dried completely and was exposed to alkali fusion. The aluminum content was then determined by reverse titration using EDTA [4]. Final prepared cakes of several experiments have been used for SEM studies.

Each experiment repeated three times and the experimental error was calculated to be less than 10%.

RESULTS AND DISCUSSION

The reactions were performed at 60, 70 and 80 °C. The initial concentration of fluosilicic acid was selected 0.76 and 1.08 mol/l. The initial concentrations of aluminum hydroxide were 120 and 180 g/l. The stirrer speed was set at various speed 140, 190, 260 and 320 rpm. In all experimental runs, reactants were used in the stoichiometric ratio and only in some runs one of them (fluosilicic acid of Aluminum hydroxide) was 60% excess. The reaction time was depended on the reaction temperature and varied 15 to 60 minutes.

Figs. 2 and 3 show the SEM results of the aluminum hydroxide platelets before the reaction and after 2

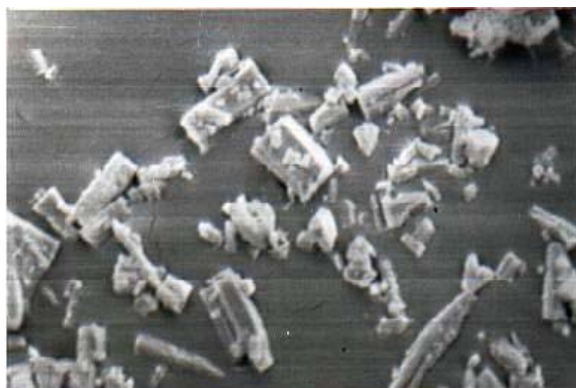


Fig. 2 : SEM micrograph of aluminum hydroxide particles.

minutes of the reaction. A silica coating is formed on the aluminum hydroxide platelets after the start of the reaction (shown in Fig.3). The reaction of aluminum hydroxide with fluosilicic acid proceeds to form the unstable aluminum fluosilicate intermediate, which is immediately hydrolyzed to aluminum fluoride, silica and fluoridric acid. Because the intermediate product is unstable, it has not enough time to diffuse backward to the outer surface of the silica coating, and hence the reaction proceeds at the surface of the aluminum hydroxide core. The latter phenomena is similar to the unreacted-core model theory [5]. The mass- transfer rate in the particle boundary layer, using equations (5) and (6) [6], has been calculated to be 13.68 mol/L.s [7](with emphasis on $\Delta C = C_L$), while by using the experimental data, the overall reaction rate has been measured about 3×10^{-3} mol/L.s.

$$Sh = 2 + 0.5 Re^{0.52} Sc^{1/3} \quad (5)$$

$$r_{b,l} = k_m a \Delta C \quad (6)$$

Therefore the mass-transfer rate in the particle boundary layer is about 4000 times greater than the overall reaction rate. It may be deduced that the molecular diffusion of the reactant in the silica coating and the interfacial chemical reaction control the overall reaction rate.

To determine the contribution of the above-mentioned phenomena in the overall reaction rate, it may be proposed that the overall reaction rate is the resultant of the rates of the individual phenomena. The rate of the reaction at every stage was determined by fitting to the experimental data.

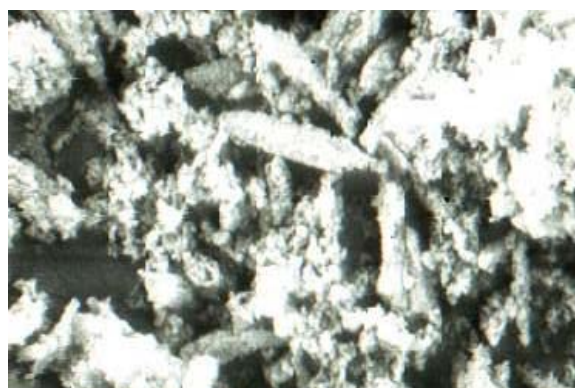


Fig. 3: SEM micrograph of Coated particles of aluminum hydroxide after 2 minutes of reaction onset.

Rate of the Chemical Reaction

The rate of the chemical reaction can be measured at the start of the reaction only, when no silica coating has been formed on the aluminum hydroxide particles. Sampling through the first 30-second of reaction startup may help to determine the accurate slope of the rate curve at the initiation of reaction. The rate equation of the chemical reaction was considered to be as follows:

$$r_{ch} = k_0 \exp(-Ea/RT) C_S^\alpha a^\beta \quad (7)$$

The coefficients of this equation can be determined from the exp. values of the reaction rate at the start of the reaction. To determine the exponents of Eq. (7), we studied the variation of the reaction rate by varying one of the parameters each time only. Fig. 4 shows the variation of the concentration of aluminum fluoride versus time at 60, 70 and 80 °C. Based on these exp. results the activation energy of the reaction has been calculated to be 12 kcal/mol while *Grobelny* [3] suggested a value of 16 kcal/mol. This value corresponds to the activation energy of the reaction obtained from the mid points of the curves in Fig. 4. In other words, *Grobelny* [3] was reported an overall activation energy, which is not a reliable value for the chemical reaction.

Fig. 5 shows the variation of aluminum fluoride concentration versus time at two different fluosilicic acid concentrations. Again based on the slope of the curves at $t = 0$, the exponent α was calculated to be 0.864. For the sake of simplicity the reaction order was supposed to be 1 (as in *Grobelny's* equation (Eq.3)).

Fig. 6 shows the variation of the concentration of aluminum fluoride versus time for two different aluminum hydroxide concentrations. For the determine the exponent β , the slope of the curves at $t = 0$ is necessary. The problem in this case is to find the specific surface area of the aluminum hydroxide at the course of reaction. We have used a numerical model to relate the variation of the specific surface area to the concentration of aluminum hydroxide [7]. The algorithm of the calculations is presented in Appendix A. since the specific surface area has been obtained as a function of aluminum hydroxide concentration, it is defined by surface area of the particles in unit volume of the slurry (m^2/m^3). The correlation equations for two initial concentrations of 120 and 180 g/L are given below:

$$a = 1103.15 \exp(0.031073 C_{\text{Al(OH)}_3}) @ \quad (8)$$

$$C_{\text{Al(OH)}_3}^0 = 120 \text{ g/L}$$

$$a = 1648.31 \exp(0.020758 C_{\text{Al(OH)}_3}) @ \quad (9)$$

$$C_{\text{Al(OH)}_3}^0 = 180 \text{ g/L}$$

Regarding the values, the exponent β was determined to be 0.35 and the rate constant (k_0) to be 10,000. Therefore, the rate equation of the chemical reaction is obtained as follows:

$$r_{\text{ch}} = 10^4 \exp(-6040/T) C_S a^{0.35} \quad (10)$$

Effective Diffusion Coefficient in Silica Coating

The silica coating formed during the chemical reaction is composed of submicron silica particles. So, this coating can be considered as a porous layer. The porosity of the latter depends on the chemical reaction parameters and hydrodynamic conditions. In other words, as reported in a previous study [2] the formed silica particles may stick to each other and form layers of different compactness. Therefore the diffusion in the silica coating may obey the equations of the diffusion in a porous solid. In a porous solid, the solid itself is completely enriched by the liquid and the molecular diffusion in the trapped liquid (through the pores) should be the mechanism of the mass transfer in the pores of the solid [8]. Because the diffusion surface and diffusion path length can not be exactly determined, an equivalent diffusion surface and path length of diffusion are defined, where an effective diffusion coefficient is obtainable [8]. It is normally to suppose the outer surface of the solid as

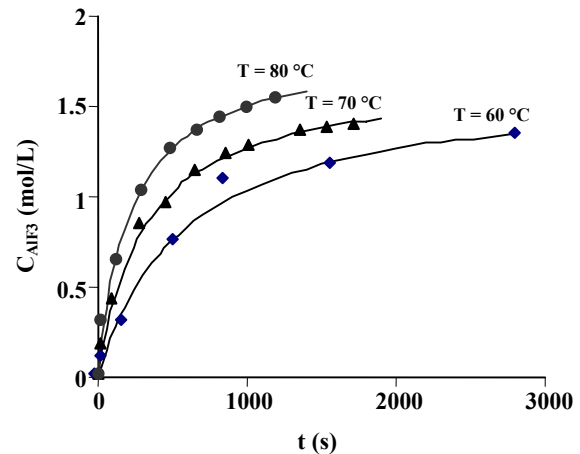


Fig. 4: Effect of temperature on the reaction rate of aluminum hydroxide with fluosilicic acid $[\text{H}_2\text{SiF}_6] = 0.76 \text{ mol/L}$, $[\text{Al(OH)}_3] = 120 \text{ g/L}$, $N = 120 \text{ rpm}$.

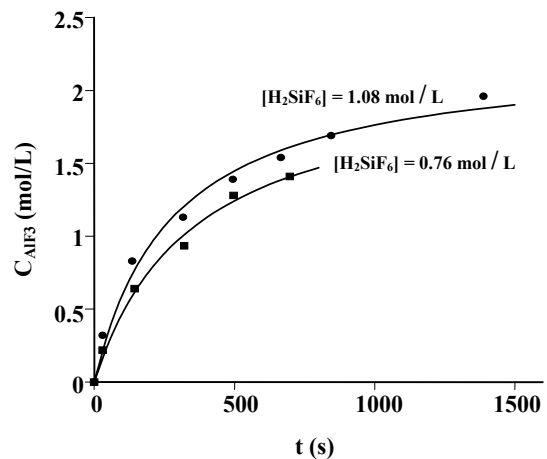


Fig. 5: Effect of Fluosilicic acid concentration on the reaction rate of aluminum hydroxide with fluosilicic acid $[\text{Al(OH)}_3] = 180 \text{ g/L}$, $T = 70 \text{ }^\circ\text{C}$, $N = 260 \text{ rpm}$.

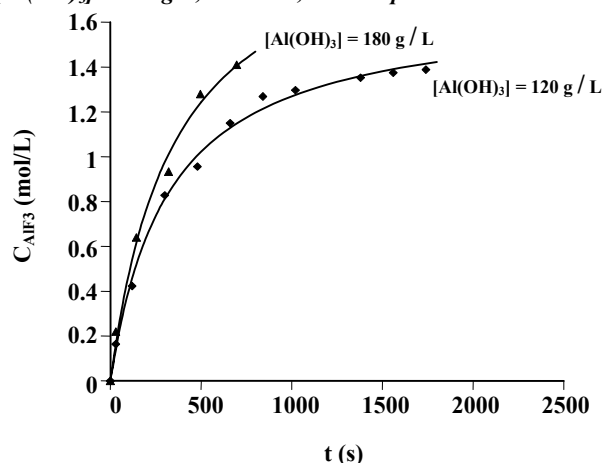


Fig. 6: Effect of aluminum hydroxide concentration on the reaction rate of aluminum hydroxide with fluosilicic acid $[\text{H}_2\text{SiF}_6] = 0.76 \text{ mol/L}$, $T = 70 \text{ }^\circ\text{C}$, $N = 260 \text{ rpm}$.

the equivalent diffusion surface and the porous film thickness as the equivalent diffusion path length [8]. In the case the mass transfer rate in the silica coating may be defined by Eq.(11) [8].

$$r_{m,t} = \frac{D_{eff}}{R_p - r_c} a_0 (C_L - C_S) \quad (11)$$

To determine the values of the effective diffusion coefficient from the experimental data, by supposing the steady state conditions, the chemical reaction and mass transfer rates for any thickness of silica coating may be equalized.

$$r = r_{ch} = r_{m,t} \quad (12)$$

$$r = \frac{D_{eff}}{R_p - r_c} a_0 (C_L - C_S) = 10^4 \exp\left(\frac{-6040}{T}\right) C_S a^{0.35} \quad (13)$$

By eliminating the C_S , the overall reaction rate is given by Eq.(14).

$$r = \frac{C_L}{\frac{(R_p - r_c)}{D_{eff} a_0} + \frac{1}{10^4 \exp\left(\frac{-6040}{T}\right) a^{0.35}}} \quad (14)$$

Using the experimental data of the overall reaction rate, the value of the effective diffusion coefficient was calculated. The values of the r_c , a_0 and a were obtained using a numerical model given in Appendix A. In the latter the best-fit equation to the obtained values is presented for the initial concentrations of aluminum hydroxide of 120 and 180 g/L. R_p is the initial average particle size of $Al(OH)_3$ powder. According to the unreacted core model, R_p was assumed to be constant during the course of reaction.

The values of the effective diffusion coefficient may be obtained using the experimental reaction rate (r) values as follows.

$$D_{eff} = \frac{10^4 \exp\left(\frac{-6040}{T}\right) a^{0.35} r}{\frac{a_0}{R_p - r_c} \left(10^4 \exp\left(\frac{-6040}{T}\right) a^{0.35} C_L - r\right)} \quad (15)$$

Normally, the effective diffusion coefficient is the same at all points of the porous layer. However in this case it has different values at different positions along the film. This can be attributed to the in-homogeneity of the density of porous film along its thickness. in-turn, the

in-homogeneity in density is caused by the in-homogeneity in the fractal dimension of the silica aggregates of which the porous layer is composed. This is because the aggregates formed during the chemical reaction are formed in different chemical conditions, since the fluosilicic acid is consumed during the reaction and the pH value of the solution rises too. At the start of the reaction the concentration of the fluosilicic acid is high and therefore the pH of the reacting liquid is very low (pH = 0.5). During the reaction the acid is consumed and the pH value rises to 3.0-3.5. Comparing these values with the iso-electric point of silica and aluminum hydroxide surfaces (2.0 and 9.3 respectively) it can be deduced that at the start of the reaction both silica and aluminum hydroxide surfaces are positively charged. During the chemical reaction as the pH value increases, there will be a transition point (pH=2.0), at which the net surface charge of the silica particles changes from positive to negative. As can be seen in Fig. 7, the variation of the effective diffusion coefficient (calculated by Eq. (15)) is not so sharp at pH = 2.0. Therefore it can be concluded that the aggregation of the particles at pH < 2 is of the same character of the aggregation at pH > 2. In other words the aggregation at pH < 2 is a hetero-aggregation induced by difference between charge density of the aluminum hydroxide and silica particles and the aggregation at pH > 2 is a hetero-aggregation induced by difference in the net charge of the surfaces [9]. Fig. 7 shows that the effective diffusion coefficient or in other words, the permeability of silica coating is increased in the course of reaction by increasing pH. From this curve and the above discussion one can conclude that the aggregation of the particles has a more RLCA nature at the start of the reaction and it changes gradually to a more DLCA nature at the end of the reaction. In general, the aggregation may cause to the formation of aggregates having two extreme fractal dimensions, 1.7 for DLCA and 2.1 for RLCA [10]. *Xiao-Yan and Logan* [11], *Gmachowski* [12] and *Romm* [13] have studied the permeability of the fractal objects. As a general conclusion a power law relationship was found between the density or packing factor of the fractal object and the ratio of the size of the primary particles and the aggregates. The exponent of the relationship depends on the fractal dimension. As the fractal dimension decreases (a more DLCA nature), the permeability of the aggregates increases. In Fig. 7 we observe a continuous increase in

the effective diffusion coefficient as the reaction proceeds. In other words, the silica coating is a film the density of which decreases as the distance to the aluminum hydroxide surface decreases.

The next step is to derive a general equation for the effective diffusion coefficient which may show the dependency of this parameter on the temperature, fluosilicic acid concentration (pH), the number of particles in the slurry (the initial concentration of aluminum hydroxide), and the dimensionless stirrer speed (the ratio of the stirrer speed to the critical stirrer speed for complete suspension). This equation may be given by:

$$D_{\text{eff}} = D_0 \exp(-E_a/RT) C_L^\delta n_t^\gamma (N/N_c)^\eta \quad (16)$$

The experimental data presented in Figs. 4,5,6 and 8 within the aluminum fluoride concentration range of 0.3 to 0.9 mol/L were used to determine the exponents of Eq. (16). This is because at concentrations less than 0.3 mol/L the silica coating formed is not enough thick and it has not any considerable effect on the overall reaction rate. At concentrations greater than 0.9 mol/L, the high film thickness of the silica coating may cause the film to crack. In order to determine the exponents of Eq. (16), the variation of the effective diffusion coefficient was considered by varying one of the parameters while other parameters were fixed.

Effect of Temperature

As may be observed from Fig.4, one can find a profound effect of temperature on the effective diffusion coefficient. According to Table 1 the average activation energy of diffusion has been obtained to be 28 kcal/mol, which is more than 2 times of the activation energy of the chemical reaction. This is the outcome of both increasing the diffusion coefficient of the reactants in the media and to a much more extent, increasing of the porosity of silica coating due to higher reaction rate. When temperature and hence the reaction rate increases, the rate of production of silica particles increases and so the latter have little time to experience different positions for sticking to each other. On the other hand, the increased rate of the chemical reaction can cause a faster pH change and so the sticking probability increases. This can cause the formation of the aggregates having a more porous structure (more DLCA nature) and so a higher effective diffusion coefficient.

Table 1: The effective diffusion coefficient used for Calculation of activation energy at different temperatures ($C_L=0.76$ mol/L, $C_{Al(OH)_3}=120$ g/L, $N=260$ rpm).

C_{AlF_3} mol/L	T_1 (°C)	T_2 (°C)	$D_{\text{eff}1} \times 10^{13}$ (m ² /s)	$D_{\text{eff}2} \times 10^{13}$ (m ² /s)	E_a kcal/mol
0.3	68.02	76.5	3.22	8.8	28.1
0.4	69.8	77.55	3.75	12.5	37.1
0.5	71.08	78.78	4.89	16.1	37.2
0.5	61.9	78.78	1.82	16.1	30.3
0.7	71.6	81	10	28.3	26
0.7	61.8	81	3.94	28.3	24.2

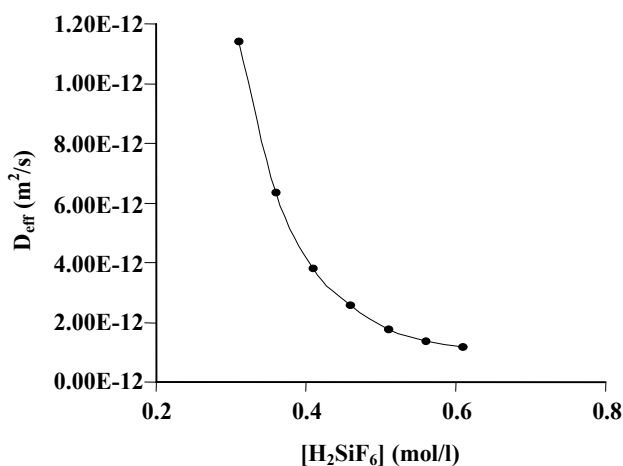


Fig. 7: Variation of effective diffusion coefficient (calculated by eq. (15)) versus fluosilicic acid concentration.

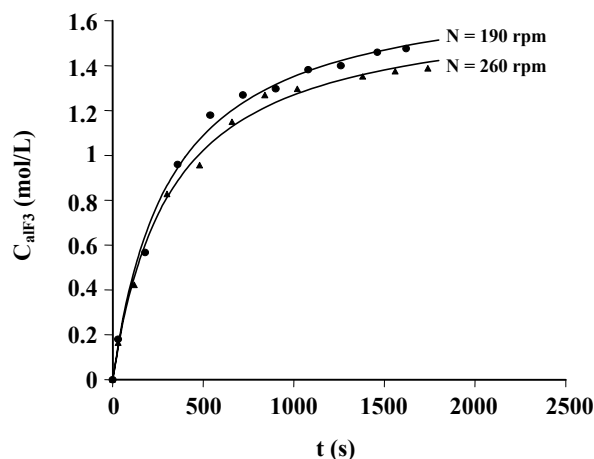


Fig. 8: Effect of stirrer speed on the reaction rate of fluosilicic acid with aluminum hydroxide. $[H_2SiF_6] = 0.76$ mol/L, $[Al(OH)_3] = 120$ g/L, $T = 70$ °C.

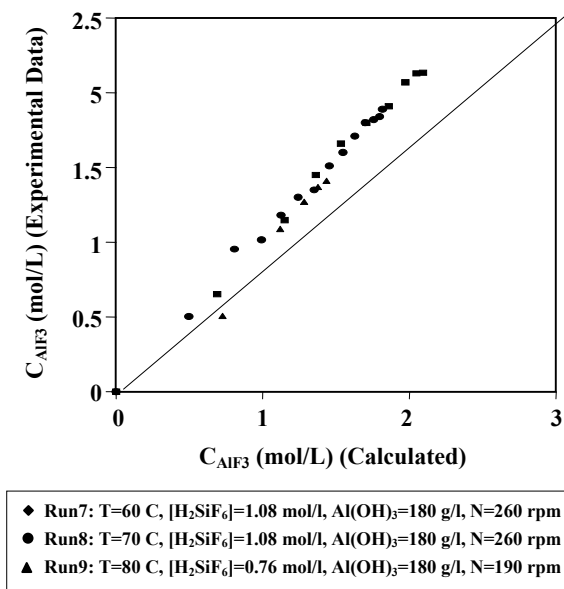


Fig. 9: Exp. vs. calculated of concentration of AlF₃ for runs 7,8,9.

Effect of Fluosilicic Acid Concentration (pH)

As mentioned earlier, the concentration of the fluosilicic acid has a pronounced effect on the porosity of the silica coating. Regarding the Exp. data presented in Fig. 5 the mean value for the exponent of the fluosilicic acid concentration term (δ) is -2.2 (Eq. (16)).

Effect of the Number of Particles in the Slurry (Aluminum Hydroxide Concentration)

Regarding the Exp. data presented in Fig. 6 it can be concluded that by increasing the concentration of the aluminum hydroxide in the slurry, the effective diffusion coefficient decreases. Eq. (17) relates the number of the dispersed particles to their concentration.

$$n_t = \frac{C_{\text{Al(OH)}_3}}{1 - \frac{\pi}{6} \bar{d}_p^3 \rho_s} \times 10^{-3} \quad (17)$$

As a outcome of increasing the concentration of the particles in the slurry, the number of inter-particle impacts increases. This may cause the silica coating to rearrange and become more compact. An increase in the compactness of the silica coating leads to a decrease in the effective diffusion coefficient. Regarding the Exp. data presented in Fig. 6, the exponent γ was determined to be -2.0 (Eq. (16)).

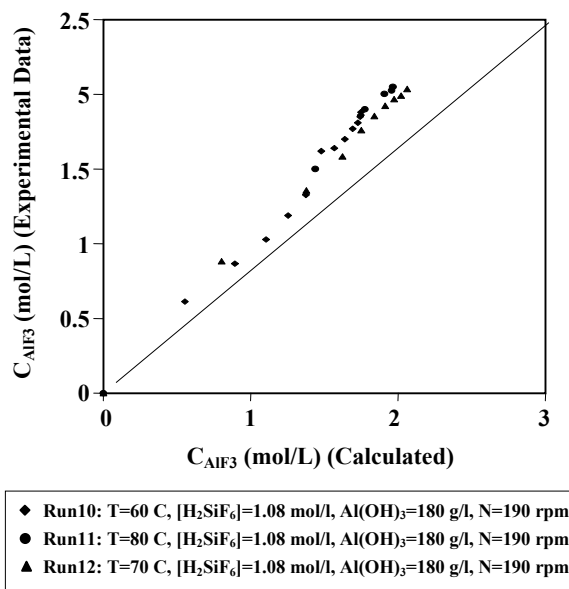


Fig. 10: Exp. vs. calculated of concentration of AlF₃ for runs 10,11,12.

Effect of Stirrer Speed

To generalize the stirrer speed term in Eq. (14), a dimensionless term, which is the ratio of the stirrer speed to the critical stirrer speed was defined [14]. The latter has the benefit of taking into account the effect of the distance of the propeller to the bottom of the reactor and the ratio of the diameter of the propeller to the diameter of the container. Otherwise by using the Reynolds number it will loss this benefit.

Regarding the Exp. data presented in Fig. 8, it may be seen that an increase in the stirrer speed, causes a decrease in the effective diffusion coefficient. Because the stirrer speed does not influence the rate of chemical reaction, the negative effect of this parameter on the mass transfer rate is obvious in the overall reaction rate. Regarding the Exp. data presented in Fig. 8, the exponent η is determined to be -2.3 . From the experimental data presented in Figs. 4-6 and 8, one can obtain the equation constant D_0 as 4.7×10^{20} . Regarding to the above-mentioned values, Eq. (16) becomes:

$$D_{\text{eff}} = 4.7 \times 10^{20} \exp(-14000/T) C_L^{-2.2} n_t^{-2} (N/N_c)^{-2.3} \quad (18)$$

To check the validity of the relations obtained using the previous data, a number of experimental runs were performed, from which the results of 6 experimental runs are presented in Figs. 9 and 10. Using Eq. (14) and the

initial conditions of the 6 experimental runs, the overall reaction rate was calculated and its value was used to predict the concentration of aluminum fluoride versus time. The obtained values were compared with the experimental data. where the derived relation fits the experimental data satisfactorily. The small deviations from the model at the end of the reaction may be attributed to the formation of cracks in the silica coating.

CONCLUSIONS

A physical model for the heterogeneous reaction of aluminum hydroxide and fluosilicic acid was proposed. Regarding the model, the controlling mechanism at the early stages (first 20 seconds) of the reaction is the chemical reaction itself. After that porous silica coating starts to form and the diffusion of the fluosilicic acid into the coating becomes important. The porosity of the silica coating increases as the chemical reaction proceeds and the pH value increases. In other words, the nature of the aggregation is varied from RLCA-like at the start of the reaction to DLCA-like at the end of the reaction. The effective diffusion coefficient is influenced by the temperature and inversely by the stirrer speed, fluosilicic acid and aluminum hydroxide concentrations.

Acknowledgement

The authors thank so much from Research & Technology Company of National Iranian Petrochemical Company for financial support of the project. Also the authors thank Miss Anvary for her help in the experimental work.

APPENDIX (A)

The model used to calculate the variation of specific surface area of aluminum hydroxide particles during the chemical reaction

In order to calculate the variation of specific surface area of aluminum hydroxide particles during the chemical reaction the whole particle size range was divided into 53 subgroups. The division is the same as the output of the particle size analyzer LMS. Using an iterative algorithm, the diameter of the largest (53rd.) particle was decreased by 0.01 microns stepwise. A "reactivity ratio" was defined which is:

$$\frac{\Delta V_i}{\Delta V_{53}} = \frac{A_i}{A_{53}} \quad (\text{A.1})$$

This ratio confirms that the amount of decrease in the volume of the other 52 particles is proportional to the ratio of their surface area to the surface area of the reference particle. By rearranging equation (A.1), equation (A.2) is obtained:

$$\frac{d_{1(i)}^3 - d_{2(i)}^3}{d_{1(53)}^3 - d_{2(53)}^3} = \left(\frac{\bar{d}_i}{\bar{d}_{53}} \right)^2 \quad (\text{A.2})$$

The following algorithm has been used for calculating specific surface area (a), specific surface area for mass transfer (a_0) and mean diameter of $\text{Al}(\text{OH})_3$ powder (d_p):

The number of each of 53 groups of particles is calculated by Eq. (A.3).

for $I=1$ to 53

$$n_i = \frac{6 * C_{\text{Al}(\text{OH})_3}^0 * x_i}{\rho_s * \pi * d_{0(i)}^3} \quad (\text{A.3})$$

In each stage 0.01 micrometer is subtracted from the biggest particle (particle group 53) and then by use of Eqs. (A.5) and (A.6), the new diameter of other 52 groups of particles and the new specific surface area have been calculated.

$$d_{2(53)} = d_{1(53)} - 1 * 10^{-6} \quad (\text{A.4})$$

for $I=1$ to 52

$$d_{2(i)} = (d_{1(i)}^3 - \left(\frac{\bar{d}_i}{\bar{d}_{53}}\right)^2 * (d_{1(53)}^3 - d_{2(53)}^3))^{1/3} \quad (\text{A.5})$$

$$a = \sum_{i=1}^{53} n_i * \pi * d_{2(i)}^2 \quad (\text{A.6})$$

To calculate the specific surface area for mass transfer, the "unshrinking particle model" was applied, in which the radius of the particle is considered to be constant during the reaction due to the formation of the silica coating. But it should be noted that it's just applicable until the un-reacted core has not been consumed completely.

$$a_0 = \sum_{i:d_{2(i)}=0} n_i * \pi * d_{0(i)}^2 \quad (\text{A.7})$$

Also the new concentration of aluminum hydroxide is calculated by Eq.(A.8)

$$C_{\text{Al(OH)}_3} = \sum_{i=1}^{53} n_i * \rho_s * \pi * d_{2(i)}^3 / 6 \quad (\text{A.8})$$

The new concentration of aluminum hydroxide has been calculated by this method for any new diameter of particles,.

The procedure continued until the diameter of the biggest particle was equal to zero. The above-mentioned calculation have been done for two initial concentrations 120 and 180 g/L of Al(OH)_3 .

The calculated values of a, a_0 and d_p in any stages have been drawn versus $C_{\text{Al(OH)}_3}$ and are fitted to equations presented as follow:

for $C_{\text{Al(OH)}_3}^0 = 120\text{g/l}$

$$a = 1103.1518 \exp(0.031073 C_{\text{Al(OH)}_3}) \quad (\text{A.9})$$

$$\bar{d}_p = 4.258 \times 10^{-6} (0.997)^{C_{\text{Al(OH)}_3}} (C_{\text{Al(OH)}_3}) \quad (\text{A.10})$$

$$a_0 = 1538 + 191 C_{\text{Al(OH)}_3} + 1.79 (C_{\text{Al(OH)}_3})^2 \quad (\text{A.11})$$

for $C_{\text{Al(OH)}_3}^0 = 180\text{g/l}$

$$a = 1648.3109 \exp(0.0207585 C_{\text{Al(OH)}_3}) \quad (\text{A.12})$$

$$\bar{d}_p = 3.5837 \times 10^{-6} (0.99799)^{C_{\text{Al(OH)}_3}} (C_{\text{Al(OH)}_3})^{0.44349} \quad (\text{A.13})$$

$$a_0 = 2326 + 184 C_{\text{Al(OH)}_3} + 1.27 (C_{\text{Al(OH)}_3})^2 \quad (\text{A.14})$$

Notations

a	Surface area of aluminum hydroxide cores per unit volume of the slurry, (m^2/m^3)
a_0	Surface area of coated aluminum hydroxide particles per unit volume of the slurry, (m^2/m^3)
A_i	Surface area of <i>ith</i> particle, (m^2)
A_{53}	Surface area of 53rd particle, (m^2)
$C_{\text{Al(OH)}_3}$	Aluminum hydroxide concentration, (g/l)
$C_{\text{Al(OH)}_3}^0$	Initial concentration of aluminum hydroxide, (g/l)
C_L^0	Initial concentration of fluosilicic acid
C_L	Fluosilicic acid concentration in the bulk of solution, (mol/l)
C_S	Fluosilicic acid concentration at the surface of aluminum hydroxide particle, (mol/l)
ΔC	Different concentrations of fluosilicic acid over boundary layer of particles(mol/l)

$d_{0(i)}$	Initial diameter of <i>ith</i> particle
$d_{1(i)}$	Diameter of <i>ith</i> particle of aluminum hydroxide at every time, (m)
$d_{1(53)}$	Diameter of 53rd particle of aluminum hydroxide at every time, (m)
$d_{2(i)}$	Diameter of <i>ith</i> particle of aluminum hydroxide after Δt , (m)
$d_{2(53)}$	Diameter of 53rd particle of aluminum hydroxide after Δt , (m)
\bar{d}_i	Mean diameter of <i>ith</i> particle, (m)
\bar{d}_{53}	Mean diameter of 53rd particle, (m)
\bar{d}_p	Mean diameter of aluminum hydroxide particles, (m)
D	Diffusion coefficient, (m^2/s)
D_a	Propeller diameter, (m)
D_0	Effective diffusion coefficient pre-factor, $\text{m}^2/\text{s} \cdot (\text{mol/l})^{2.2} \cdot (\text{particle/l})^2$
D_{eff}	Effective diffusion coefficient, (m^2/s)
D_t	Reactor diameter, (m)
E_a	Activation energy, (cal/mol)
k	Reaction rate coefficient, (1/s)
k_0	Constant of chemical reaction rate, ($\text{m}^{0.35}/\text{s}$)
k_m	Mass transfer coefficient, (m/s)
n_i	Number of <i>ith</i> group of particles, ($\text{particles}/\text{m}^3$)
n_t	Number of particles in unit volume of the slurry, ($\text{particles}/\text{l}$)
N	Stirrer speed, (rpm)
N_c	Critical stirrer speed, (rpm)
r	Overall reaction rate, ($\text{mol}/\text{l} \cdot \text{s}$)
$r_{b,l}$	Mass transfer rate in boundary layer of particles, ($\text{mol}/\text{L} \cdot \text{s}$)
r_c	Average radius of unreacted cores of aluminum hydroxide, (m)
r_{ch}	Chemical reaction rate, ($\text{mol}/\text{l} \cdot \text{s}$)
$r_{m,t}$	Mass transfer rate, ($\text{mol}/\text{l} \cdot \text{s}$)
R	Gas constant, (1.9872 cal/mol. K)
Re	Reynolds Number, ($\rho \times \varepsilon^{1/3} \times \bar{d}_p^{3/4} / \mu \mu$)
R_p	Average radius of coated aluminum hydroxide particles, (m)
Sc	Schmidt Number, ($\mu/\rho D$)
Sh	Sherwood Number, ($k_m \times \bar{d}_p / D$)
T	Temperature, (K)
ΔV_i	Volume change of the <i>ith</i> particle, (m^3)
ΔV_{53}	Volume change of the 53 rd particle, (m^3)

Greek Symbols

α	Exponent of fluosilicic acid concentration in equation of chemical reaction rate
β	Exponent of specific surface area in equation of chemical reaction rate
δ	Exponent of fluosilicic acid concentration in equation of effective diffusion coefficient, Eq.(16)
γ	Exponent of particles rampancy in equation of effective diffusion coefficient, Eq.(16)
η	Exponent of stirrer speed in equation of effective diffusion coefficient, Eq.(16)
ρ	Fluid Density, (kg/m ³)
ρ_s	Density of aluminum hydroxide, (kg/m ³)
μ	Viscosity, (kg/m.s)
ε	Agitation power, (N/60) ³ ×D _a ⁵ /D _t ³ , (w/kg)

Abbreviation

AFT	Aluminum Fluoride Trihydrate
DLCA	Diffusion Limited Colloid Aggregation
RLCA	Reaction Limited Colloid Aggregation

Received : 22th October 2003 ; Accepted : 18th April 2005

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