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PROFESSIONAL PAPER

666.122.2+54-145.2:531.3:519.87

BATCH DISSOLUTION OF QUARTZ SAND IN AQUEOUS SODIUM SOLUTION – KINETIC MODELS

Silica dissolution in aqueous NaOH, corresponding to the ratio $\text{SiO}_2/\text{Na}_2\text{O} = 2$, is a complex process at elevated temperatures and high pressure. However, it is desirable to have a simple model for predictive purposes. In this study several kinetic models were developed, and compared with experimental results. As a first approximation, the silica was assumed to be smooth spheres, which decreases in size as dissolution proceeds. The influence of the particle size, the operating temperature and the hydroxide ion molality on the kinetic rate was studied. It is certain that these models can be used to correlate the experimental data on dissolution.

Production of sodium silicate in pressurized reactor using wet process is carried out according to chemical reaction: $y\text{SiO}_2(\text{sd}) + 2\text{NaOH} \rightarrow \text{Na}_2\text{Si}_y\text{O}_{2y+1} + \text{H}_2\text{O}$. This production rise in past ten years, due to the usage of sodium silicate (molar ratio $\text{SiO}_2/\text{Na}_2\text{O} = 2$), which is the important raw material in ecologically acceptable detergent zeolite industry [1–3]. For the purpose of sodium silicate processing optimization, experimental data concerning process kinetics are required, as well as data regarding reaction temperature, SiO_2 particle size, and NaOH molality. Developing of kinetic model for SiO_2 dissolution in aqueous solution of NaOH is necessary for better understanding of all process steps, and the determination of important process parameters. Model validation, i.e. dissolution mechanism, is carried out by comparing it with experimental results. Within this work, a few models will be developed: empirical model and a few modified shrinking core models (models based on particle diameter shrinking during dissolution process).

EXPERIMENTAL MEASUREMENTS

Experiments were done with sand with of average particle size, $2r$ of 250 μm , and minimal content of SiO_2 of 97%. Sodium hydroxide, NaOH, solution of 12.5 mol/kg was used during experiments, prepared by 100% NaOH dissolving in distilled water. Measured quantities of sand, m_0 and NaOH aqueous solution, in respect with molar ratio $\text{SiO}_2/\text{Na}_2\text{O} = 2$, were poured in Parr autoclave, volume 2 l, and the heater is turned on. Autoclave temperature was maintained at 220 °C using thermocouple. Autoclave is equipped

by mixer. At the end of each experiment, autoclave is cooled with cold water in order to abruptly decrease reaction temperature, T and to stop sand dissolution reaction. Reactor mixture is filtered after the end of experiment. Filter cake, consisted of undissolved sand, was washed with hot water until it becomes neutral. Filter cake (m) is dried and measured. Evaluation of process kinetics parameters such as: $\alpha(t)$, $r(t)$, S are determined by using measured parameters: m_0 , m , T , $r(0)$.

MATHEMATICAL MODELS

A few approaches used for description of SiO_2 dissolution under high pressure and temperature are shown within this article. These models are known as: empirical model, shrinking core model based on diffusion, shrinking core model based on surface chemical reaction, modified shrinking core model based on constant activation energy and modified shrinking core model based on varying activation energy.

Acquired experimental results can be expressed by different empirical relations. It is possible to write the following equation for description of dissolution kinetics:

$$\alpha(t) = \alpha [1 - \exp(-bt)] + c \quad (1)$$

where: a , b , c are adjustable parameters, which are acquired by experimental measurement, and $\alpha(t) = \frac{m_0 - m(t)}{m_0}$ is conversation rate (%), m_0 – initial weight of sand, t – reaction time, m – weight of undissolved sand.

It is assumed that there is no undissolved sand in the mixture, i. e. $c = 0$.

$$\alpha(t) = \alpha [1 - \exp(-bt)] \quad (2)$$

In Fig. 1, dashed and full lines show experimental results and model conversion rate, using eq. (2),

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Paper received: January 31, 2007.

Paper accepted: May 24, 2007.

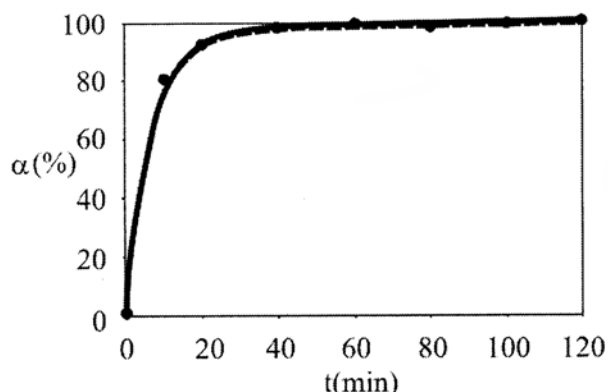


Figure 1. Conversion rate

respectively. Parameters *a* and *b* were determined by graphical analysis.

It is assumed that all sand particles in NaOH solution are of the spherical shape, with the same radius, and that radius decreases during the reaction. Using this assumption and geometrical analysis, it is possible to write the equation for particle radius change in time *t*:

$$r(t) = r_0 \cdot \sqrt[3]{1 - \alpha} \tag{3}$$

In Fig. 2, radius change calculated by eq. (3) is shown by full line and experimental results are plotted with dashed line. This diagram shows that there is a considerable discrepancy between model, eq. (3) and experimental results for the particle radius smaller than 50 μm. As can be seen, model predicts that particle remains undissolved even when degree of conversion reaches 99%, which does not represent the real nature of this process. That is why some shrinking core approach is used later on.

By differentiating eq. (2), dissolving kinetics curve can be written as:

$$\frac{d\alpha(t)}{dt} = a \cdot b \cdot \exp(-bt) \tag{4}$$

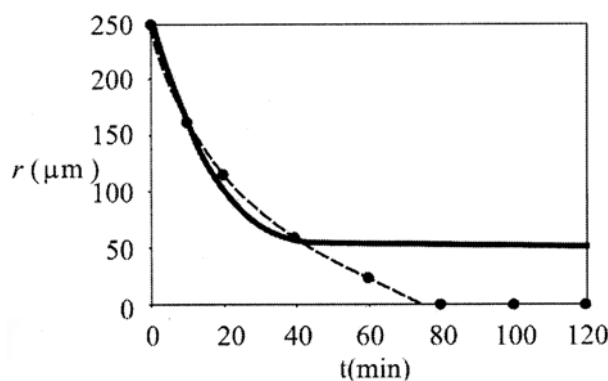


Figure 2. Sand particle size decreasing according to empirical model

In shrinking core model using diffusion expression of kinetics, the mole variation of SiO₂ with time is [1,2]:

$$\frac{dn(t)}{dt} = - \frac{D \cdot (C_m(t) - C_s)}{\delta} \cdot \frac{4\pi r^2(t)}{\sigma} \cdot N \tag{5}$$

where *D* is the diffusion coefficient of OH⁻, *C_m* – the OH⁻ concentration in the bulk of solution, and *C_s* – the OH⁻ concentration on the particle surface, *δ* – depth of diffusion layer, *σ* – ratio [OH⁻]/[SiO₂] and *N* – number of particles.

On the basis of simple geometrical analysis, it is possible to determine the number of particles involved in reaction (upon the assumption that all sand particles are spheres of uniform radius):

$$N = \frac{3 \cdot m_0}{4 \cdot \pi \cdot \rho \cdot r_0^3} \tag{6}$$

where: *m₀* is a initial weight of sand, *r₀* – initial particle radius, and *ρ* – sand particles density. Combining eqs. (5) and (6), following relation was obtained:

$$\frac{dn(t)}{dt} = - \frac{D \cdot (C_m(t) - C_s)}{\delta} \cdot \frac{r^2(t)}{\sigma} \cdot \frac{3 \cdot m_0}{\rho \cdot r_0^3} \tag{7}$$

The relation between conversion rate and number of SiO₂ moles variation in time can be expressed as:

$$\frac{d\alpha(t)}{dt} = -k_1 \cdot \frac{dn(t)}{dt} \tag{8}$$

where: *k₁* is coefficient of proportionality.

Applying equations (7) and (8), it is possible to plot the dependence of conversion rate change during reaction of dissolving (Fig. 3, full line), and by using eq. (3) it is possible to plot particle size curve (Fig. 4, full line). Dashed line in Figs. 3 and 4 represents the experimental results. Obviously, this model (eqs. (7) and (8)) does not satisfactory describe particle size reduction, i.e. large particle size of 50 μm remains even when degree of conversion reaches

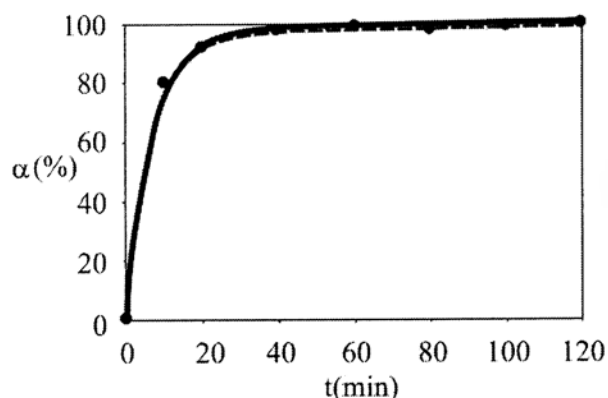


Figure 3. Conversion rate

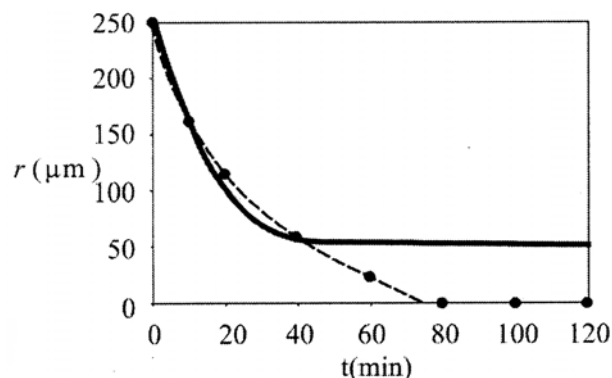


Figure 4. Sand particle size decreasing according to diffusion model

99%. So, it does not represent the real nature of this process.

In shrinking core model using assumption that at the beginning of reaction the system is controlled by chemical reaction, it is possible to write [1,2]:

$$\frac{d\alpha(t)}{dt} = k \cdot S(t) \cdot C_m(t)^\gamma \quad (9)$$

where k is the kinetic constant, γ – the reaction order with respect to OH^- , $S(t) = 4 \cdot r^2(t) \cdot \pi$ – free surface.

Modified shrinking core model has been proposed to describe the kinetic of dissolution of sand into sodium hydroxide solutions, under experimental conditions (200 °C, 16 bar), close to those in the industry of the wet-process sodium silicate production. The attention was directed to the effect of particle size on the reaction rate. The experimental kinetic data were analyzed to determine the controlling mechanisms.

When the rate limiting step is a surface reaction, the reaction rate can be expressed by the following equation [3]:

$$m_0 \cdot \frac{d\alpha}{dt} = y \cdot k^0 \cdot C_{\text{OH}^-}^b(t) \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \quad (10)$$

where: y is stoichiometric coefficient, k^0 – a constant factor, S – surface area, E_a – activation energy, C_{OH^-} – hydroxide ion molality, b – reaction order with respect to ion hydroxide, R – universal gas constant, T – absolute temperature, t – reaction time. Using eq. (10), diagram of degree of conversion can be plotted (Fig. 5, full line), and by using eq. (3) it is possible to plot particle size (Fig. 6, full line). Dashed line on Figs. 5 and 6 represents the experimental results. It is obvious that eqs (10) and (3) describe very well experimental results, hence very good agreement between model and experiment was obtained.

Considering the variable activation energy term the kinetic expression of the sand dissolution can be written as [3]:

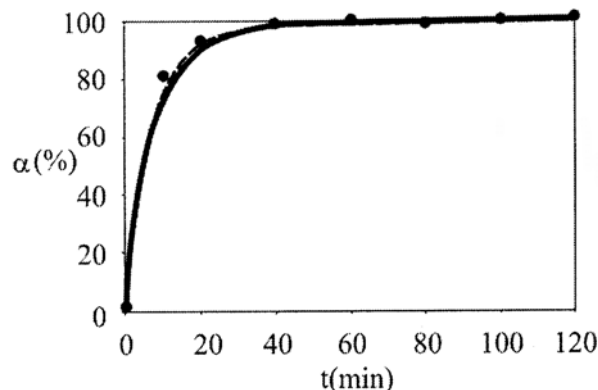


Figure 5. Conversion rate

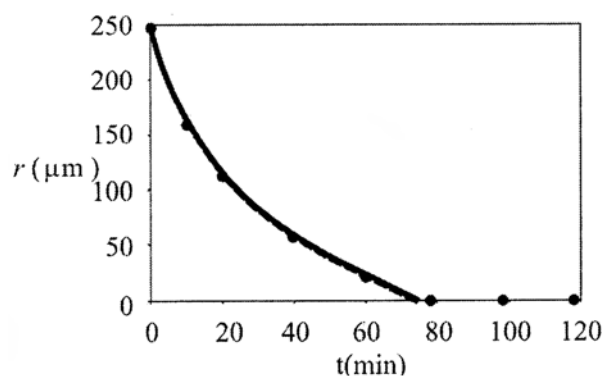


Figure 6. Sand particle size according to modified shrinking core model, where activation energy is constant

$$\frac{d\alpha}{dt} = \frac{a_1}{R_p} \cdot \exp\left[-\frac{E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{T'}\right) + \frac{a_2 \cdot \alpha^{a_3}}{R \cdot T}\right] \cdot (C_{\text{OH}^-}^0 - \alpha \cdot C_{\text{OH}^-}^{st})^b (1 - \alpha)^{2/3} \quad (11)$$

where: a_1 is constant, a_2 , a_3 – parameters related to the change of activation energy, $C_{\text{OH}^-}^{st}$ – the stoichiometric hydroxide molality, $C_{\text{OH}^-}^0$ – initial hydroxide molality, R_p – the mean particle radius and T' – absolute reference temperature.

Variable activation energy shrinking core model takes into account the change of the activation energy as the reaction proceeds.

Using experimental results (diagram shown on Fig. 7) thick full line was plotted, and adjustable parameters were found. Using eqs. (11) and (3) it is possible to plot the change of radius with time (Fig. 8, full line). Dashed line on Fig. 7 and Fig. 8 represents the experimental results. This diagram shows that after about 70 min dissolution process is completed, whereby diameter of sand particles becomes zero, which represents the real nature of this process.

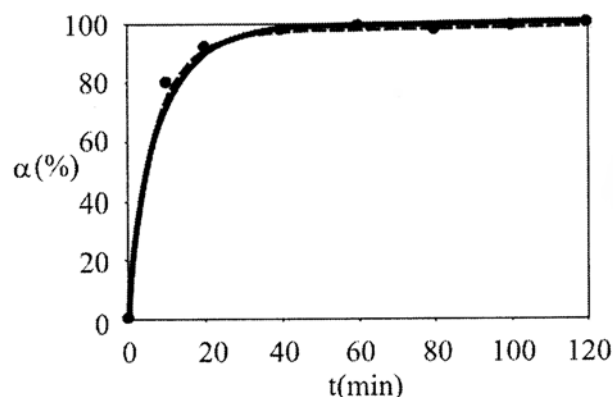


Figure 7. Conversion rate

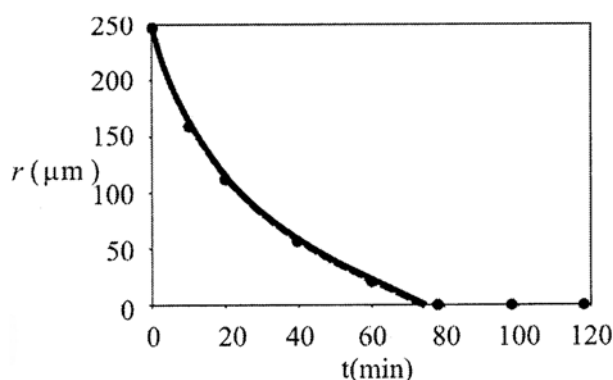


Figure 8. Sand particle size according to modified shrinking core model with variable activation energy

CONCLUSION

The dissolution of silica into sodium hydroxide solution at high T and p was investigated by taking into consideration the parameters of temperature, particle size and hydroxide ion molality. It is obvious that modified shrinking core models (constant and variable activation energy) gain the best results. The kinetic data for modified shrinking core models fit very well to experimental results. These models represent the real nature of dissolving process, especially near the end of dissolving process, when the mean diameter of particles being zero, in contrast to the empirical and shrinking core models, where the mean particles becomes zero in infinity (not in real reaction time).

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IZVOD

ŠARŽNO RASTVARANJE KVARCNOG PESKA U VODENOM RASTVORU NATRIJUM HIDROKSIDA – KINETIČKI MODELI

(Stručni rad)

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Rastvaranje kvarcnog peska u vodenom rastvoru NaOH, u molarnom odnosu $\text{SiO}_2/\text{Na}_2\text{O} = 2$, složen je hemijski proces koji se odigrava pri povišenom pritisku i temperaturi. U industrijskoj primeni poželjno je imati jednostavan model za svrhu predviđanja toka procesa. U ovom radu je razvijeno nekoliko kinetičkih modela, koji su upoređeni sa eksperimentalnim podacima. Za izvođenje matematičkog modela usvojeno je da su čestice kvarcnog peska glatke sfere, čiji se prečnik smanjuje tokom odigravanja procesa. Ispitivan je uticaj veličine čestice, radne temperature i molalитета hidroksilnih jona na brzinu procesa. Na osnovu dobijenih rezultata jasno je da ovi modeli dobro opisuju proces rastvaranja i da se mogu primeniti za predviđanje toka procesa rastvaranja.

Ključne reči: Matematički model
• Rastvaranje • Kinetika • Kvarcni pesak •

Key words: Mathematical model
• Dissolving • Kinetics • Quartz sand •