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## Kinetic Aspects of the Gibbsite Digestion Process in Aqueous Solution of Sodium Hydroxide

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In order to study the kinetics and mechanism of the reaction, laboratory digestions were carried out of industrially produced gibbsite mineral  $\gamma$ -Al(OH)<sub>3</sub> in aqueous solutions containing an excess of sodium hydroxide. Reaction temperature, duration and base concentration were varied. From the results obtained basic kinetic parameters were computed: reaction rate constants ( $k$ ) and process activation energy ( $E_a$ ).

### INTRODUCTION

Gibbsite digestion in aqueous solution of NaOH is a heterogeneous process consisting of the chemical reaction and the transfer of the mass to the boundary reaction area. Both of these processes may further comprise a whole series of individual stages; it is generally known that the stage with the least rate determines the total reaction rate.<sup>1,2,3</sup>

In heterogeneous reactions where the mass transfer rate plays an important role, the variables are much greater in number and become more complex. The reaction rate is greatly influenced by places of phase boundary areas, which are in turn determined by the structure of the solid, dispersion grade, porosity and geometrical shape of reacting particles.

Determination of reaction rate in heterogeneous processes, besides being of practical importance, provides a possibility of theoretical explanation of the rate constants and process development mechanism, which was the aim of this work where the digestion process in industrial gibbsite was examined.

### EXPERIMENTAL

#### Sample Preparation and Identification

Gibbsite  $\gamma$ -Al(OH)<sub>3</sub> sample produced industrially according to the Bayer process in the alumina Plant Mostar, was rinsed with distilled water until the negative reaction to phenolphthalein, and then dried at 80 °C. Granulometrical analysis was carried out with standard sieves for particles up to 40  $\mu$ m, and with automatic sedimentation scales for those smaller than 40  $\mu$ m. Figure 1 presents the obtained results graphically.

The composition of industrial gibbsite used as sample was determined by chemical analysis: 63.78, 34.26, 0.55 and 0.97% for Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>O, SiO<sub>2</sub> and Na<sub>2</sub>O, respectively. Other impurities (TiO<sub>2</sub>, ZnO, P<sub>2</sub>O<sub>5</sub>, MnO<sub>2</sub>) may add us indefinitely to 100%. Na<sub>2</sub>O may be due to the rinse base excess, sodium-aluminium silicate

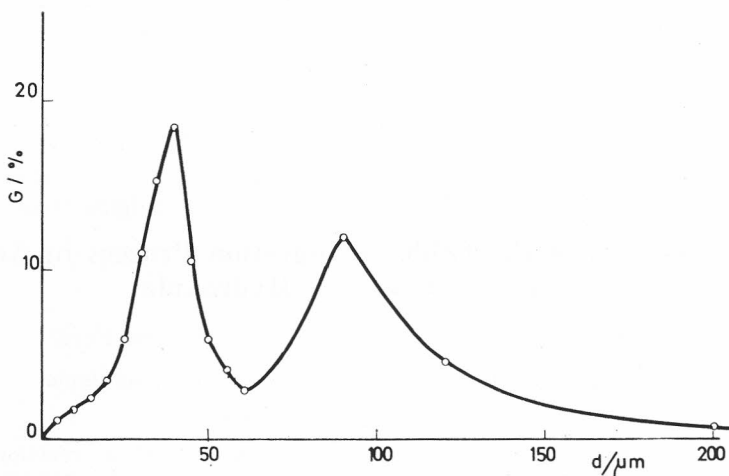


Figure 1. Graphic representation of granulometric analysis of the gibbsite sample.

(hence the presence of  $\text{SiO}_2$ ), or to the base built into the structure of gibbsite crystal itself.

Identification of gibbsite from the DTA curve was carried out on the basis of endothermal patterns at  $275^\circ\text{C}$ ,  $375^\circ\text{C}$  and  $560^\circ\text{C}$ . From TG curve a total mass loss of 34.31% was determined in the temperature interval from 25 to  $1000^\circ\text{C}$ .

On the basis of  $d$  values and corresponding intensities in X-ray patterns, a pure gibbsite phase was identified.

The infrared spectrum of the sample indicated gibbsite identification on the basis of two absorption bands:  $\nu(\text{OH})$  at  $3500$  and  $3600\text{ cm}^{-1}$  and  $\delta(\text{OH})$  at  $975$  and  $1025\text{ cm}^{-1}$ .

### Laboratory Digestion

In order to trace the digestion kinetics in industrial gibbsite according to the reaction



the influence of temperature, reaction duration and base concentration upon the reaction rate was examined. The variable parameters were:

- digestion temperature,  $T/^\circ\text{C} = 50 \dots 90$ ;
- sodium hydroxide concentration,  $\rho/(\text{g}/\text{dm}^3) = 145.70 \dots 307.75$
- digestion duration,  $\tau/\text{s} = 300 \dots 900$

Constant parameters were: granulometrical composition, volume of NaOH solution ( $0.250\text{ dm}^3$ ), gibbsite mass per reaction mixture volume ( $80\text{ g}/\text{dm}^3$ ), stirring rate ( $1\text{ s}^{-1}$ ).

The experiment was carried out in a three-necked flask ( $0.5\text{ dm}^3$ ) immersed in the oil bath to reach the operating temperature, the flask being equipped with a thermometer and a stirrer. The experimental method of work enabled the course of the reaction to be traced under isothermal conditions from the beginning by determining the increase in  $\text{Al}_2\text{O}_3$  concentration in the liquid phase. Volumetric method according to Hermann<sup>4</sup> was used for analysis.

## RESULTS AND DISCUSSION

Figures 2 and 3 show graphically the changes in  $\text{Al}_2\text{O}_3$  concentration with time.

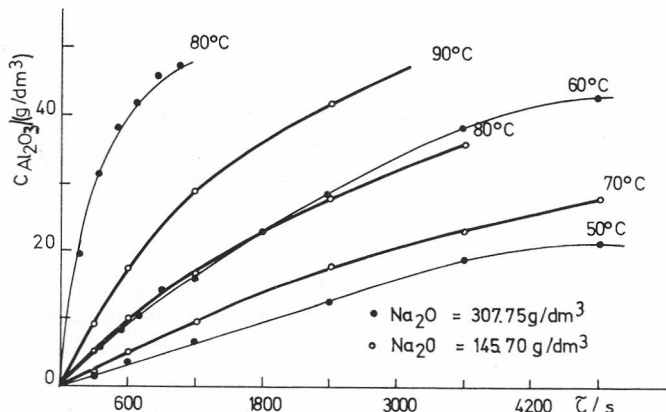


Figure 2.  $\rho-\tau$  curves of gibbsite digestion in NaOH solution at concentration 145.7 g/dm<sup>3</sup> and 307.75 g/dm<sup>3</sup>  $\text{Na}_2\text{O}$ .

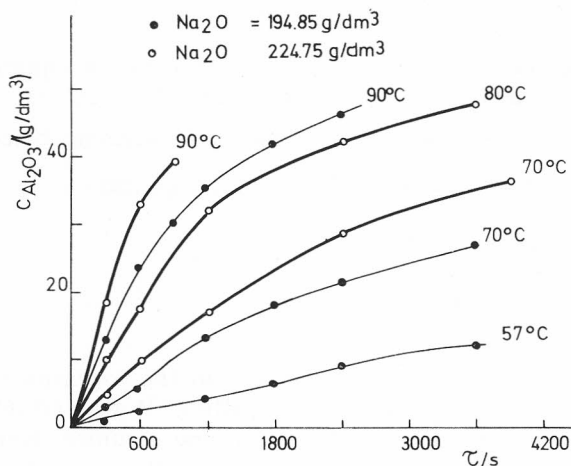


Figure 3.  $\rho-\tau$  curves of gibbsite digestion in NaOH solution at concentration 194.85 g/dm<sup>3</sup> and 224.75 g/dm<sup>3</sup>  $\text{Na}_2\text{O}$ .

These curves show that with increasing in temperature the reaction rate also increases. At lower temperatures, lower concentrations and prolonged digestion duration, the curves tend to increase slowly; at higher temperatures the curves increase more abruptly, while at the highest temperature (90 °C) the reaction reached a ca. 100% yield in a very short period of time.

The experimental results were treated by means of the common rate equation:

$$-\frac{dc}{d\tau} = k \cdot c^n \quad (2)$$

where  $k$  = reaction rate constant,  $c$  = concentration,  $n$  = reaction order. Logarithmic form of equation (2) is a straight line with a slope of 0.4343  $k$ :

$$\log \frac{C_G}{C_G - C_A} = 0.4343 \cdot k \cdot \tau \quad (3)$$

where  $C_G$  =  $\text{Al}_2\text{O}_3$  concentration in the non-dissolved gibbsite in the moment of reaching isothermal conditions (0-time) and  $C_A$  = increase in  $\text{Al}_2\text{O}_3$  concentration in the liquid phase from 0-time to the determined reaction duration. The data were also fitted to the Kazeev equation<sup>2</sup>

$$\alpha = 1 - \exp(-K \cdot \tau^n) \quad (4)$$

where  $\alpha$  = conversion rate,  $K$  = parameter determining the process development rate,  $n$  = parameter determining the process development mechanism. For  $n \geq 1$  the process takes place in the kinetic area, and for  $n \leq 1$  it takes place in the diffusion area.

According to Saković,<sup>2</sup> parameter  $K$  is related to the reaction rate constant  $k$  as shown in the relation:

$$k = n \cdot K^{1/n} \quad (5)$$

In the processing of experimental data by means of equation (2) it was assumed that the reaction was of the first order ( $n = 1$ ).

Equation (4) can be linearized by taking logarithms twice:

$$\log [-\log(1 - \alpha)] = n \log \tau + \log 0.4343 \cdot k \quad (6)$$

where  $\alpha$  is the conversion rate:

$$\alpha = \frac{C_G}{C_A} \quad (7)$$

Applicability of the above kinetic equations to the experimental results was examined by graphical and least squares fitting. It was established that the experimental mechanism corresponds to the one assumed. Namely, graphical representation of the dependence of the logarithmic change in the  $\text{Al}_2\text{O}_3$  concentration upon time yields the lines (Figures 4 and 5).

The highest dispersion of the results was noticed for the highest NaOH concentration ( $\rho_{\text{Na}_2\text{O}} = 307.75 \text{ g/dm}^3$ ). This result may deviate due to a relatively high reaction rate at high concentrations of NaOH. It takes a certain time to initiate and to stop a chemical reaction, so the sampling error is greater if the reaction is faster. It may also be assumed that at higher base concentrations the reaction mechanism could change, so that the assumed kinetic equation would no more correspond to the actual mechanism. Fitting of the Kazeev's equation (4) to the data by means of the least squares method (Figures 6 and 7) yielded the parameter  $n$ , whose values ranged from 0.89 to 1.04 (mean value  $0.98 \pm 0.08$ ).

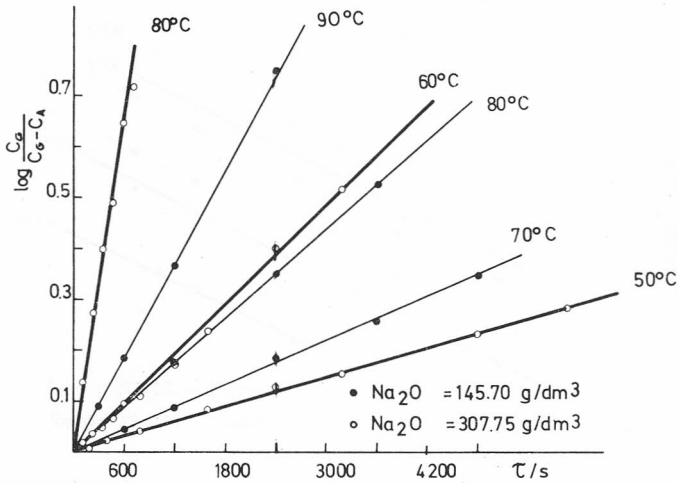


Figure 4. Logarithmic changes in  $\text{Al}_2\text{O}_3$  concentration in dependence upon time for gibbsite digestion reaction in NaOH solution at concentration  $145.7 \text{ g/dm}^3$  and  $307.75 \text{ g/dm}^3 \text{ Na}_2\text{O}$ .

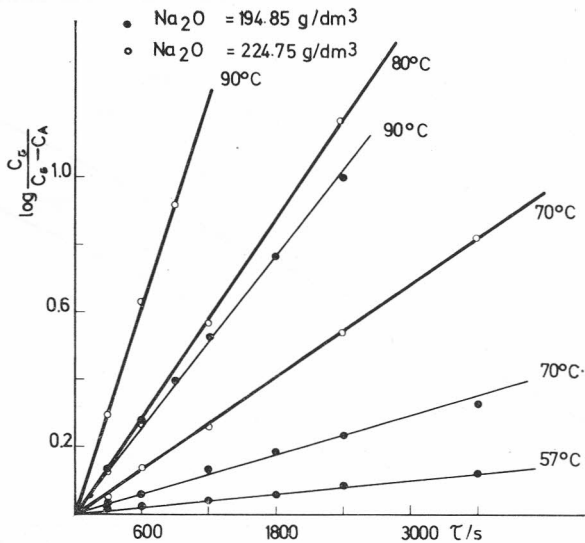


Figure 5. Logarithmic changes in  $\text{Al}_2\text{O}_3$  concentration in dependence upon time for gibbsite digestion reaction in NaOH solution at concentration  $194.85 \text{ g/dm}^3$  and  $224.75 \text{ g/dm}^3 \text{ Na}_2\text{O}$ .

According to Kazeev, the parameter  $n$  is determined by the mechanism of the process development: for values greater than or equal to 1 the process takes place in the kinetic area, and for  $n$  smaller than 1 ( $n = 0.5$ ) in the diffusion area. As the mean value  $n = 0.98$  is very close to 1, it may be assumed that the gibbsite digestion process takes place in the kinetic area, *i. e.* the chemical reaction rate determines the total process rate.

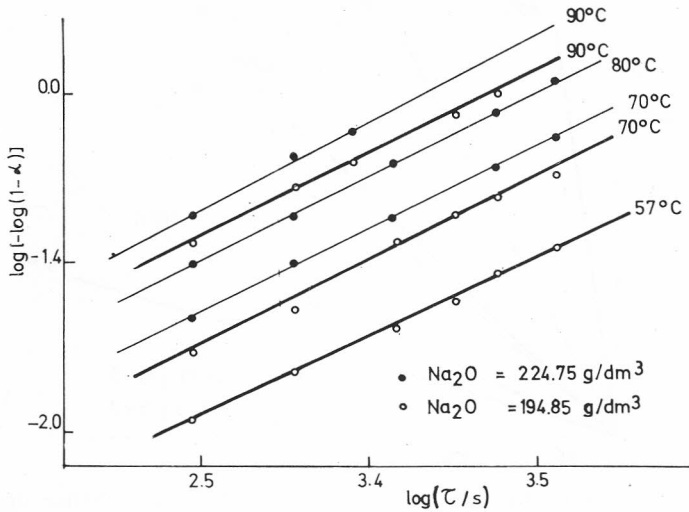


Figure 6. Dependence of  $\log [-\log (1-\alpha)]$  upon  $\log (\tau / s)$  for gibbsite digestion reaction in NaOH solution at concentration  $194.84 \text{ g/dm}^3$  and  $224.75 \text{ g/dm}^3$   $\text{Na}_2\text{O}$ .

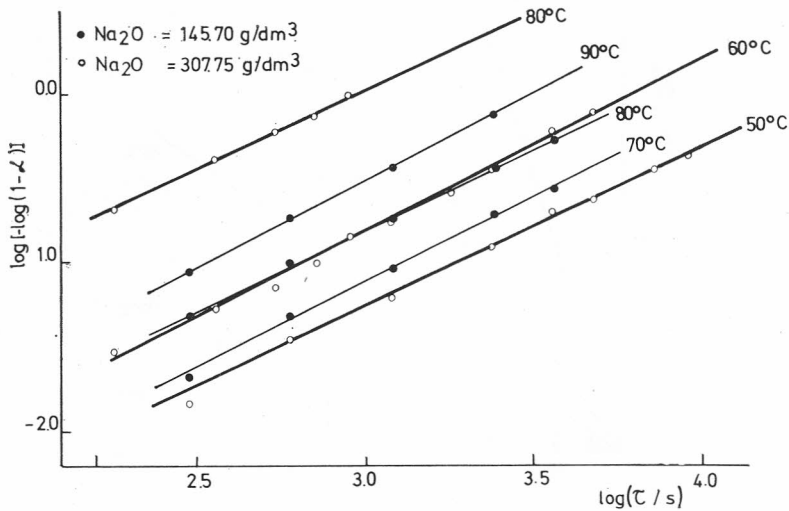


Figure 7. Dependence of  $\log [-\log (1-\alpha)]$  upon  $\log (\tau / s)$  for gibbsite digestion reaction in NaOH solution at concentration  $145.70 \text{ g/dm}^3$  and  $307.75 \text{ g/dm}^3$   $\text{Na}_2\text{O}$ .

Table I shows the values of the rate constants with their standard errors, where  $k_1$  stands for constants calculated by means of the least squares method according to the first order equation, and  $k_2$  stands for constants calculated according to Saković's equation (5) from parameters  $K$  and  $n$  of the Kazeev's equation (4).

TABLE I

Comparative Values for Reaction Rate Constants in Industrial Gibbsite Digestion in Aqueous Solution of NaOH

$\rho(\text{Na}_2\text{O}) = 145.70 \text{ g/dm}^3$

$T$ °C	$N$	$(k_1 \pm t_{0.95} \cdot s) \times 10^4$ s <sup>-1</sup>	$(k_2 \pm t_{0.95} \cdot s) \times 10^{-4}$ s <sup>-1</sup>
70	6	1.68 ± 0,08	1.98 ± 0,17
80	5	3.32 ± 0,08	3.27 ± 0,11
90	4	7.16 ± 0,11	6.98 ± 0,13

$\rho(\text{Na}_2\text{O}) = 194.85 \text{ g/dm}^3$

57	6	0.77 ± 0,04	0.63 ± 0,03
70	6	2.13 ± 0,28	2.59 ± 0,23
90	6	9.41 ± 0,30	9.99 ± 0,52

$\rho(\text{Na}_2\text{O}) = 224.75 \text{ g/dm}^3$

70	5	3.48 ± 0,09	3.44 ± 0,12
80	5	7.58 ± 0,03	7.53 ± 0,12
90	4	15.51 ± 0,01	16.13 ± 0,67

$\rho(\text{Na}_2\text{O}) = 307.75 \text{ g/dm}^3$

50	8	1.09 ± 0,37	1.21 ± 0,29
60	10	3.65 ± 0,23	3.51 ± 0,18
80	6	22.42 ± 2,01	24.48 ± 1,66

$s$  = standard errors

$t_{0.95}$  = Student's variate for  $\alpha = 0.95$  and  $N-2$  degrees of freedom

The above results show good agreement of calculated constant values, except for the  $\text{Na}_2\text{O}$  concentration of  $307.75 \text{ g/dm}^3$  at  $80^\circ\text{C}$ . At this base concentration the spread of the results was highest, and it was to be expected that the constant calculated from the model of a first order reaction should differ from the value obtained from the Kazeev's equation, suggesting that the parameter  $n$  has the lowest value in this case ( $n = 0.89$ ). The results in Table II also indicate the dependence of reaction rate constant upon the base concentration, meaning that the constants calculated are apparent, *i. e.* that the reaction is of the pseudo-first order.

Data in Table II show that gibbsite digestion reaction rate at the  $\text{Na}_2\text{O}$  concentrations of  $145.70 \text{ g/dm}^3$   $\text{Na}_2\text{O}$  and  $224.75 \text{ g/dm}^3$   $\text{Na}_2\text{O}$  doubles if the temperature increases for  $10^\circ\text{C}$ ; at  $307.75 \text{ g/dm}^3$   $\text{Na}_2\text{O}$  the rate increases 3.35 times. This agrees with the well known empirical fact indicated by van't Hoff in 1884. for reactions whose rates are determined by reaction stage.

Arrhenius plot of the temperature dependence of rate constants is shown in Figure 8. The results of the least squares computations are presented in Table III.

TABLE II  
Results Indicating Dependence of the Reaction Rate Constants in Industrial Gibbsite Digestion Upon Temperature

$\rho(\text{Na}_2\text{O}) = 145.70 \text{ g/dm}^3$		
$T$ °C	$k \times 10^4$ s <sup>-1</sup>	$\frac{k(T+10)}{k(T)}$
70	1.68	1.98
80	3.32	2.16
90	7.16	

$\rho(\text{Na}_2\text{O}) = 224.75 \text{ g/dm}^3$		
$T$	$k \times 10^4$	$\frac{k(T+10)}{k(T)}$
70	3.48	
80	7.58	2.18
90	15.51	2.05

$\rho(\text{Na}_2\text{O}) = 307.75 \text{ g/dm}^3$		
$T$	$k \times 10^4$	$\frac{k(T+10)}{k(T)}$
50	1.09	
60	3.65	3.35

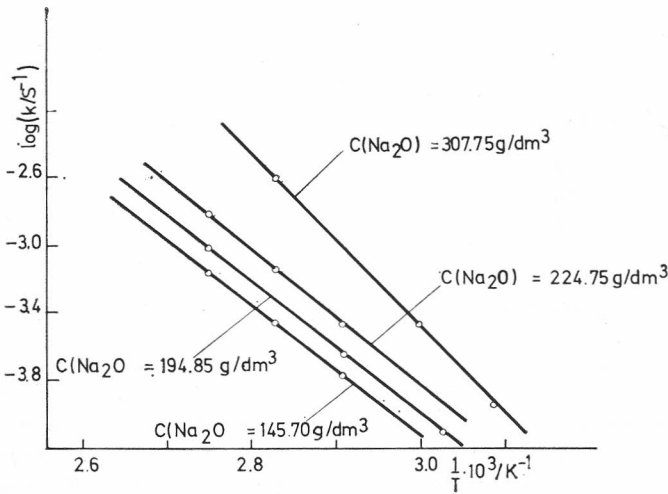


Figure 8. Dependence of  $\log k$  upon  $1/T$  for gibbsite digestion reaction in NaOH solution of varying concentrations.

TABLE III  
Process Activation Energy for Gibbsite Digestion

$\rho(\text{Na}_2\text{O})$ g/dm <sup>3</sup>	$E_a$ kJ/mol
145.70	72.57
194.85	75.97
224.75	76.45
307.75	96.81



The activation energy gradually increases with increasing NaOH concentration, up to the concentration of 224.75 g/dm<sup>3</sup> Na<sub>2</sub>O and at the concentration of 307.75 g/dm<sup>3</sup> Na<sub>2</sub>O the activation energy is much higher. This could also be due to the errors in determination of concentration.

The variation in activation energy due to base concentration changes, being small in the concentration interval from 145.70 to 224.75 g/dm<sup>3</sup> Na<sub>2</sub>O, permits the mean activation energy for this concentration range to be calculated as  $E_a = 74.99 \pm 3.17$  kJ/mol.

The Arrhenius equation will take the form:

$$k = 8.72 \times 10^7 \exp(-74990 \text{ J mol}^{-1}/RT).$$

Calculated activation energy values are of the same order of magnitude as those determined by Japanese authors (81.93 kJ/mol) for synthetic gibbsite digestion process.<sup>5</sup> The effect of the NaOH concentration upon the digestion reaction rate was not quantitatively studied, because the activity of NaOH was not determined, which would be necessary for exact measurements, as proved by Scotford and Glastonbury.<sup>6</sup>

#### CONCLUSIONS

1. The gibbsite digestion process takes place according to the first order kinetic equation. Greater changes in the rate constant dependent upon the duration of reaction are noticed at the highest base concentrations (307.75 g/dm<sup>3</sup> Na<sub>2</sub>O) which may be due to experimental errors in determination of concentration or to the change in the reaction mechanism.

2. The calculated value for parameter  $n$  of the Kazeev's equation is  $0.98 \pm 0.08$ , which indicates that the gibbsite digestion reaction takes place in the kinetic area, *i. e.* the chemical reaction rate determines the total process rate.

3. The gibbsite digestion reaction rate doubles if the temperature increases for 10 °C in the base concentration range from 145.70 to 224.75 g/dm<sup>3</sup> Na<sub>2</sub>O, which is in accordance with the well-known empirical fact for the reactions whose rates are determined by the chemical reaction rate.

4. Average activation energy value for the gibbsite digestion process is calculated from the Arrhenius equation and amounts to  $74.99 \pm 3.17$  kJ/mol at the base concentrations 145.70 to 224.75 g/dm<sup>3</sup> Na<sub>2</sub>O, and temperature 50–90 °C so that the Arrhenius equation is of the following form:

$$k = 8.72 \times 10^7 \exp(-74990 \text{ J mol}^{-1}/RT).$$

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**SAŽETAK**

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**Kinetički aspekti procesa rasčinjavanja gibsita u vodenim otopinama natrij-hidroksida**

Izvršena su laboratorijska raščinjavanja industrijski proizvedenog minerala gibsita  $\gamma\text{-Al(OH)}_3$  u vodenoj otopini natrij-hidroksida radi određivanja kinetike i mehanizma te reakcije. Proces je vođen u laboratorijskoj reakcijskoj posudi, u suvišku otopine natrij-hidroksida, varirajući temperaturu, vrijeme reakcije i koncentraciju lužine. Iz eksperimentalnih podataka izračunani su osnovni kinetički parametri: konstante brzine reakcije ( $k$ ) i energije aktiviranja procesa ( $E_a$ ).