

LJUBICA PAVLOVIĆ¹
ZAGORKA
AĆIMOVIĆ-PAVLOVIĆ²
LJUBIŠA ANDRIĆ¹
AUREL PRSTIĆ²

¹Institute for Technology of
Nuclear and Other Mineral Raw
Materials, Belgrade, Yugoslavia

²Faculty of Technology and
Metallurgy, Belgrade

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KINETICS OF GIBBSITE LEACHING IN SODIUM HYDROXIDE AQUEOUS SOLUTION

In order to study the kinetics and mechanism of the reaction, laboratory leaching was carried out with industrially produced gibbsite $\gamma\text{-Al}(\text{OH})_3$ in aqueous solutions containing an excess of sodium hydroxide. The results obtained reaction temperature, duration and base concentration varied. The basic kinetic parameters were determined from: the reaction rate constant $k=8.72 \cdot 10^7 \exp(-74990/RT)$ and the process activation energy in the range $E_a=72.5\text{--}96.81 \text{ kJ/mol}$.

Gibbsite leaching in an aqueous solution of NaOH is a heterogeneous process consisting of chemical reaction and mass transfer to the boundary reaction area. Both processes may further comprise a whole series of individual stages: it is generally known that the stage with the slowest rate determines the total reaction rate [1–3].

In heterogeneous reactions where mass transfer rate plays an important role, the variables are numerous and complex. The reaction rate is influenced to a large extent by the positions of the phase boundary areas, which are in turn determined by the structure of the solid, the dispersion level, porosity and geometrical shape of the reacting particles.

Determination of the reaction rate in a heterogeneous process, besides being of practical importance, provides the possibility of theoretical by explaining the rate constants and process development mechanism, which was the aim of this study in which the leaching process in industrial gibbsite was examined.

EXPERIMENTAL

Gibbsite $\gamma\text{-Al}(\text{OH})_3$, produced industrially according to the Bayer process at the Alumina Plant Podgorica, was rinsed with distilled water until a negative reaction to phenolphthalein was attained, and then dried in an air stream at 80°C. Granulometric analysis was carried out with standard sieves for particles up to 40 μm . The obtained results are presented in Fig. 1.

The composition of the gibbsite sample was determined by chemical analysis $\text{Al}_2\text{O}_3\text{--}63.78$; $\text{H}_2\text{O--}34.26$; $\text{SiO}_2\text{--}0.55$; $\text{Na}_2\text{O--}0.97$ (wt%) and other impurities (TiO_2 , ZnO , P_2O_5 , MnO_2) up to 100%. Na_2O may be due to the excess of rinse base, sodium

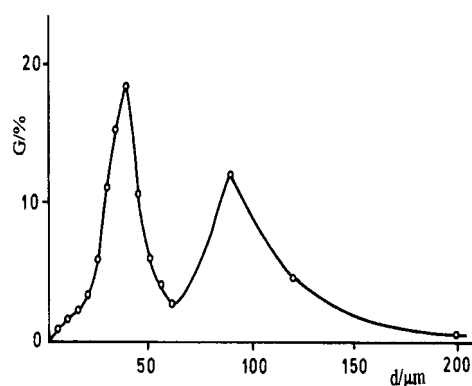


Figure 1. Granulometric analysis of the gibbsite sample

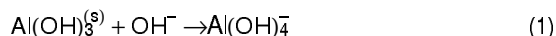
aluminium silicate (hence the presence of O_2) or to the base built into the gibbsite crystal itself.

Identification of gibbsite from DTA curves was carried out on the basis of endothermal patterns at 275°C, 375°C and 560°C. Total mass loss of 34.31 wt% was observed in the temperature interval from 25–1000°C by thermogravimetry.

Pure gibbsite phase was identified on the basis of the d values and the corresponding intensities in the X-ray patterns.

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

In order to study the leaching kinetics in industrial gibbsite according to the reaction.



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

- leaching temperature, $T = 323\text{--}363 \text{ K}$
- sodium hydroxide concentration, $\rho = 145.7\text{--}307.75 \text{ g/cm}^3$
- leaching duration, $\tau = 300\text{--}900 \text{ s}$.

The following parameters were kept constant: granulometrical composition, volume of NaOH solution

Author address: Lj. Pavlović, Institut za tehnologiju nuklearnih i drugih mineralnih sirovina, Franša D Eperea 86, 11000 Beograd
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(0.250 dm³), gibbsite mass per reaction mixture volume (80 g/dm³), stirring rate (1 s⁻¹).

The experiment was carried out in a three-necked flask (0.5 dm³) immersed in an oil bath to reach the operating temperature, the flask being equipped with a thermometer and stirrer.

The experimental method enabled the course of the reaction to be followed under isothermal conditions from the beginning by determining the increase in Al₂O₃ concentration in the liquid phase. The volumetric method according to Hermann was used for analysis.

RESULTS AND DISCUSSION

Figs. 2 and 3 show the changes in Al₂O₃ concentration with time.

These curves show that the reaction rate increases with increasing temperature. At lower temperatures, lower concentrations and prolonged leaching duration, the curves tend to increase slowly. At higher temperatures, the curves increase more abruptly, while at the highest temperature (363 K) the reaction reached 100% yield in a very short time.

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

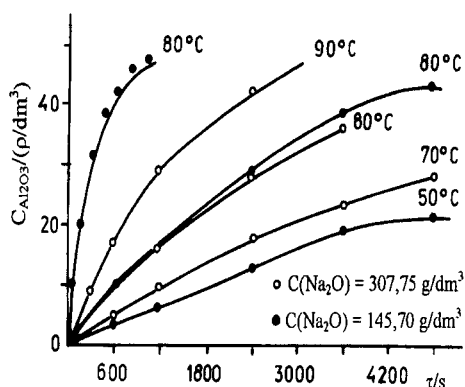


Figure 2. ρ - τ curve of gibbsite leaching in NaOH solution at concentration of 145.7 g/dm³ and 307.75 g/dm³ Na₂O

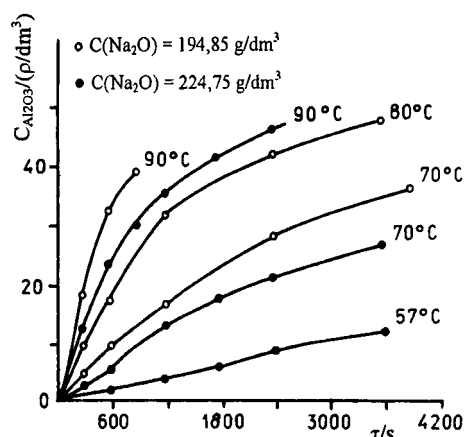


Figure 3. ρ - τ curves of gibbsite leaching in NaOH solution at concentrations of 194.85 g/dm³ and 224.75 g/dm³ Na₂O

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

where: k – is the reaction rate constant, c – the concentration, n – the reaction order.

The 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 – in the Al₂O₃ concentration in undissolved gibbsite at the moment of reaching isothermal conditions (0-time) and C_A – the increase in concentration in the liquid phase from 0-time to the determined reaction duration. The data were also fitted to the Kazeev equation (2):

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

where: α – is the conversion rate, K – the parameter determining the process development rate, n – the 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 Savković [2], 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:

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

where α is the conversion rate:

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

The 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 Al₂O₃ concentration upon time yields straight lines (Figs. 4 and 5).

The highest dispersion of the results was noticed for the highest NaOH concentration ($\rho_{\text{NaOH}} = 307.75$ g/dm³). This result may deviate due to a relatively high reaction rate at high NaOH concentrations. 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 the reaction mechanism could change at higher base concentrations, so that the assumed kinetic equation would no longer correspond to the actual mechanism. Fitting of the Kazeev equation (4) to the data by means of the least squares method (Figs.

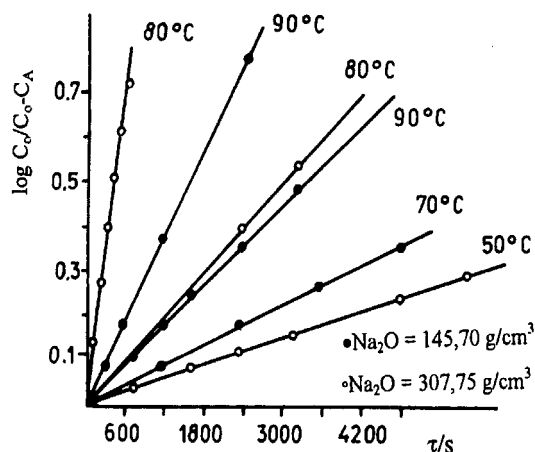


Figure 4. Logarithmic changes of the Al_2O_3 concentration upon time for the gibbsite leaching reaction in NaOH solution at concentrations of 145.7 and 307.75 g/dm^3 Na_2O

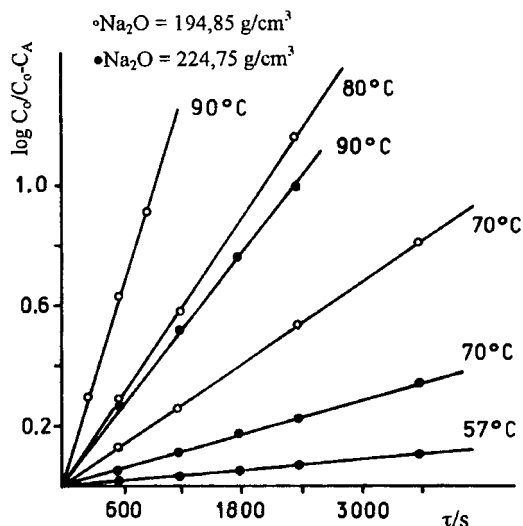


Figure 5. Logarithmic changes of the Al_2O_3 concentration upon time for the gibbsite leaching reaction in NaOH solution at concentrations of 194.85 and 224.75 g/dm^3 Na_2O

6 and 7) yielded the parameter n , the values of which ranged from 0.89 to 1.04 (mean value 0.98 ± 0.08).

Fig. 4 shows logarithmic changes in the Al_2O_3 concentration upon time for the gibbsite leaching reaction in NaOH solution at concentrations of 145.7 and 307.75 g/dm^3 Na_2O . Fig. 5 shows the same changes at concentrations of 194.85 and 224.75 g/dm^3 Na_2O .

According to Kazeev, the parameter n is determined by the mechanism of 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.

Fig. 6 shows the dependence of $\log[-\log(1-\alpha)]$ vs. $\log(\tau/s)$ for the gibbsite leaching reaction in NaOH

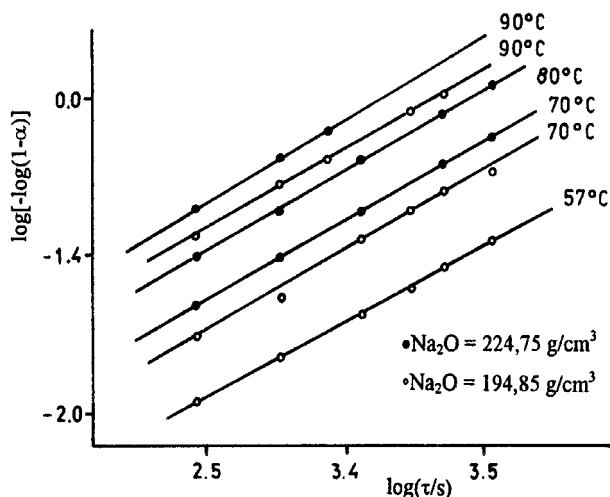


Figure 6. The dependence of $\log[-\log(1-\alpha)]$ vs. $\log(\tau)$ for the gibbsite leaching reaction in NaOH solution at concentrations of 194.84 and 224.75 g/dm^3 Na_2O

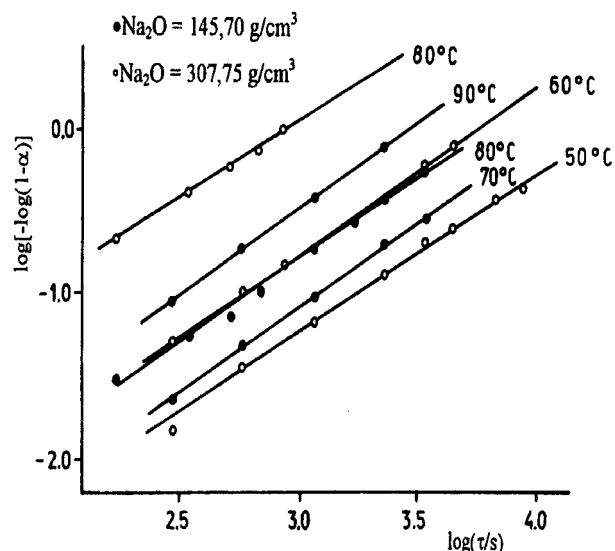


Figure 7. The dependence of $\log[-\log(1-\alpha)]$ vs. $\log(\tau)$ for the gibbsite leaching reaction in NaOH solution at concentrations of 145.70 and 307.75 g/dm^3 Na_2O

solution at concentrations of 194.84 and 224.75 g/dm^3 Na_2O . Fig. 7 shows the same dependence at concentrations of 145.70 and 307.75 g/dm^3 Na_2O .

Table 1 shows the values of the rate constants with their standard errors, where k_1 designates constants calculated by means of the least squares method according to the first order equation, and k_2 designates constants calculated according to the Savković equation (5) from parameters K and n of the Kazeev equation (4).

The data in Table 2 show that the gibbsite leaching reaction rate at Na_2O concentrations of 145.70 g/dm^3 and 224.75 g/dm^3 doubles if the temperature increases 10 K. At 307.75 g/dm^3 of Na_2O the rate increases 3.35 times. This agrees with the known empirical fact indicated by Van't Hoff for reactions the rates of which are determined by the reaction stage. The Arrhenius plot

Table 1. Comparative values of the reaction rate constants gibbsite leaching in aqueous NaOH solution

$\rho(\text{Na}_2\text{O})$ (g/dm ³)	T (°C)	N	$(k_{10,95} \cdot \text{s}) \cdot 10^4$ (s ⁻¹)	$(k_{20,95} \cdot \text{s}) \cdot 10^4$ (s ⁻¹)
145.70	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
194.85	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
224.75	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
307.75	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

Table 2. Dependence of the reaction rate constants in industrial gibbsite leaching upon temperature

$\rho(\text{Na}_2\text{O})$ (g/dm ³)	T (°C)	$k \cdot 10^4$ (s ⁻¹)	$k(T + 10) / k(T)$
145.70	70	1.68	1.98
	80	3.32	2.16
	90	7.16	
224.75	70	3.48	2.18
	80	7.58	2.05
	90	15.51	
307.75	50	1.09	3.35
	60	3.65	

of the temperature dependence of the rate constants is shown in Fig. 8. The results of the least square computations are presented in Table 3.

The activation energy gradually increases with increasing NaOH concentration up to the concentration of 224.75 g/dm³ Na₂O and at a concentration of 307.75 g/dm³ Na₂O the activation energy is much higher. This could also be due to errors in determination of the concentration.

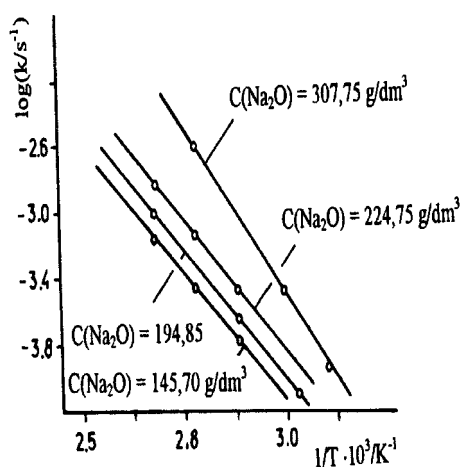
Figure 8. The dependence of $\log k$ vs. $1/T$ for the gibbsite leaching reaction in NaOH solution of varying concentrations

Table 3. Process activation energy for gibbsite leaching

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

The variation in the activation energy due to base concentration changes, which are small in the concentration interval from 145.70 to 224.75 g/dm³ Na₂O, allow calculation of the mean activation energy for this concentration range $E_a = 74.99 \pm 3.17$ kJ/mol.

The Arrhenius equation will take the form: $k = 8.72 \cdot 10^7 \exp(-74990/RT)$. The calculated activation energy values are of the same order of magnitude as those determined by [5] (81.93 kJ/mol) for the synthetic gibbsite leaching process.

The effect of the NaOH concentration upon the leaching 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 [5].

CONCLUSIONS

1. The gibbsite leaching process takes place according to a first order kinetic equation, which was noticed at the highest base concentration (307.75 g/dm³ Na₂O). This fact might be due to experimental errors in determination of the concentration or to changes in the reaction mechanism.

2. The calculated value for parameter n of the Kazeev equation is 0.98 ± 0.08 , which indicates that the gibbsite leaching reaction takes place in the kinetic area, i.e. the chemical reaction rate determines the total process rate.

3. The gibbsite leaching reaction rate doubles if the temperature increases by 10 K in the base concentration range from 145.70 to 224.75 g/dm³ Na₂O, which is in accordance with the well-known empirical fact for reactions the rates of which are determined by the chemical reaction rate.

4. The average activation energy value for the gibbsite digestion process, calculated using the Arrhenius equation, has the following form: $k = 8.72 \cdot 10^7 \exp(-74990/RT)$.

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IZVOD

KINETIKA LUŽENJA GIBSITA U VODENOM RASTVORU NATRIJUMHIDROKSIDA

(Naučni rad)

Ljubica Pavlović¹, Zagorka Aćimović-Pavlović², Ljubiša Andrić¹, Aurel Prstić²

¹Institute for the Technology of Nuclear and Other Mineral Raw Materials.

Franchet d'Esperey St 86. 11000 Belgrade.

²Faculty of Technology and Metallurgy. Karnegieva St 4. 11000 Belgrade

U cilju proučavanja kinetike i mehanizma reakcije ispitivano je luženje industrijski dobijenog gibsita $\gamma\text{-Al}(\text{OH})_3$ u vodenom rastvoru koji je sadržao NaOH dodat u višku. Prilikom eksperimenta varirani su sledeći parametri: temperatura, vreme trajanja reakcije i koncentracija. Na osnovu dobijenih rezultata izračunati su: konstanta brzine reakcije $k=8.7 \cdot 10^7 \exp(-7490/RT)$ i vrednosti aktivacione energije procesa luženja u intervalu $E_a=72.57\text{--}96.81$ kJ/mol.

Key words: Gibbsite $\gamma\text{-Al}(\text{OH})_3$ • Sodium hydroxide • Kinetics • Leaching • Activation energy • Ključne reči: Gibsit • Natrijumhidroksid • Kinetika • Luženje • Energija aktivacije •