Aluminium Dissolution Kinetics in Caustic Media

A Literature Review

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Significance

Leaching / Dissolution behaviour and kinetics of Al(III)-containing Minerals such as Gibbsite, Bayerite, Boehmite & bauxite ores in Aqueous Media is of interest & importance to several industries:

High Nuclear Waste Processing

Minerals Processing: Bayer Process Alumina Refining

Minerals Weathering: Environmental issues

Al(III)-containing Hydroxide/oxides Phases & their Relative Solubilities

Amorphous/gel Al(OH)3 phase

Bayerite (α–$Al(OH)_3$)

Gibbsite (γ-$Al(OH)_3$)

Boehmite (γ-AlOOH)

Diaspore (α-AlOOH)

Decreasing

Solubility

in aqueous (alkaline

or acidic) media –:
Al(III) is amphoteric

Alumino-silicate phases (amorphous, Zeolite, Sodalite & Cancrinite) phases may co-exist

The phase(s) that may exist and which dissolve will depend upon prevailing solution chemistry, temperature, pressure & hydrodynamics

Fundamental Knowledge gap & Questions underpinning Significance of dissolution studies

1. What are the mechanisms of Al(III) hydroxide dissolution ?
2. Which solution species are present in Al(III) undersaturated caustic or acidic liquors?
3. What is the nature of the interfacial layer which forms and evolves?
4. What are the rate controlling factors for Al(OH) crystal dissolution?
5. What kinetics or rate laws of dissolution can be established for different Al(III) hydroxide phases
6. What "constitutive" or "colligative" property roles do dissolved ions of metal salts (Na^+ vs K^+) and organics play in the dissolution process and impact upon the rates?

Dissolution Rate Laws issues to consider: Solution Speciation, phase & thermodynamic properties

1. Specifically what solution species are present in Al(III) rich solutions at high pH or caustic levels?

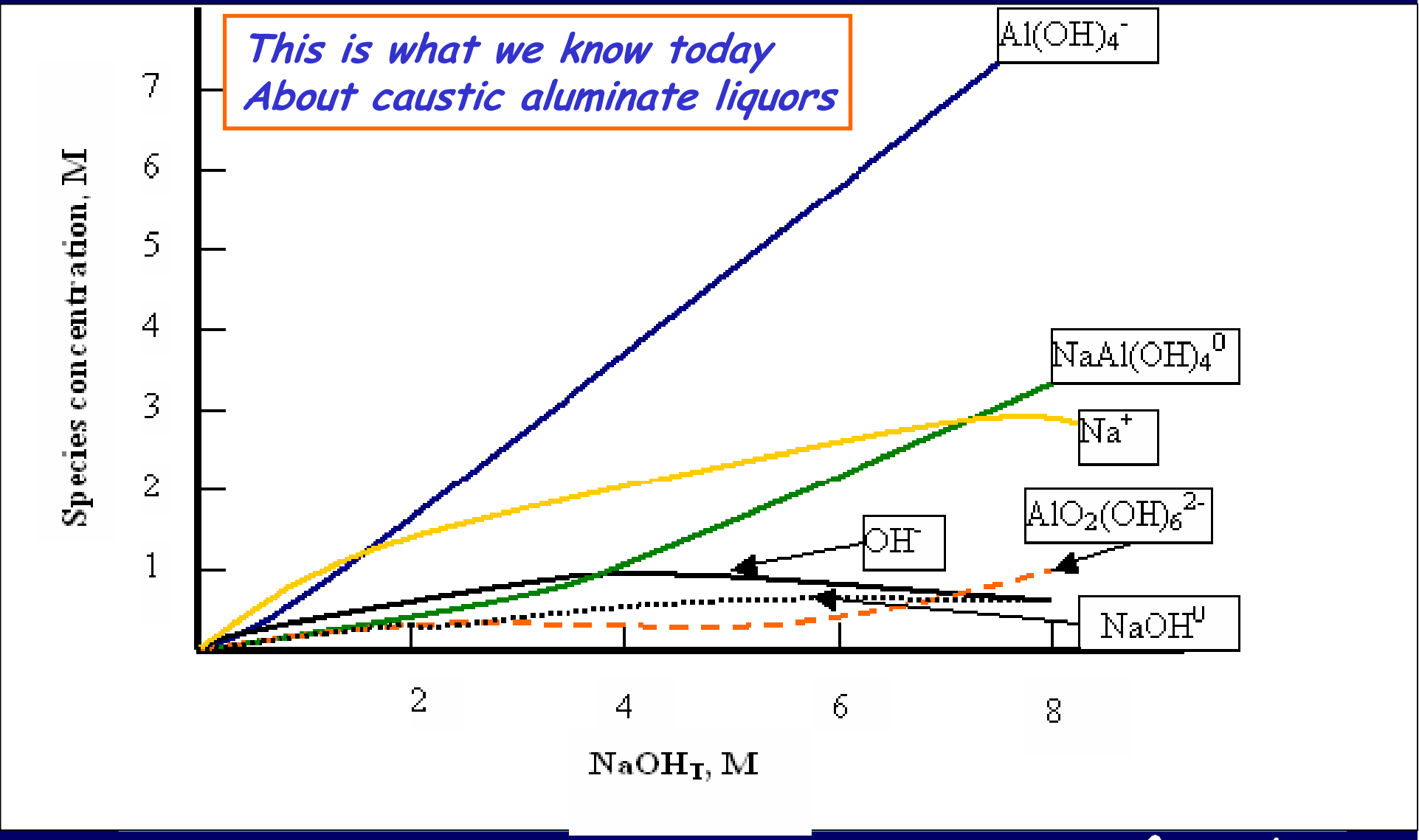
   It always a problem determine the chemical potentials, activity and activity coefficients of Al(III) speciation at high ionic (>> 1 M)

2. What is the role of water activity?

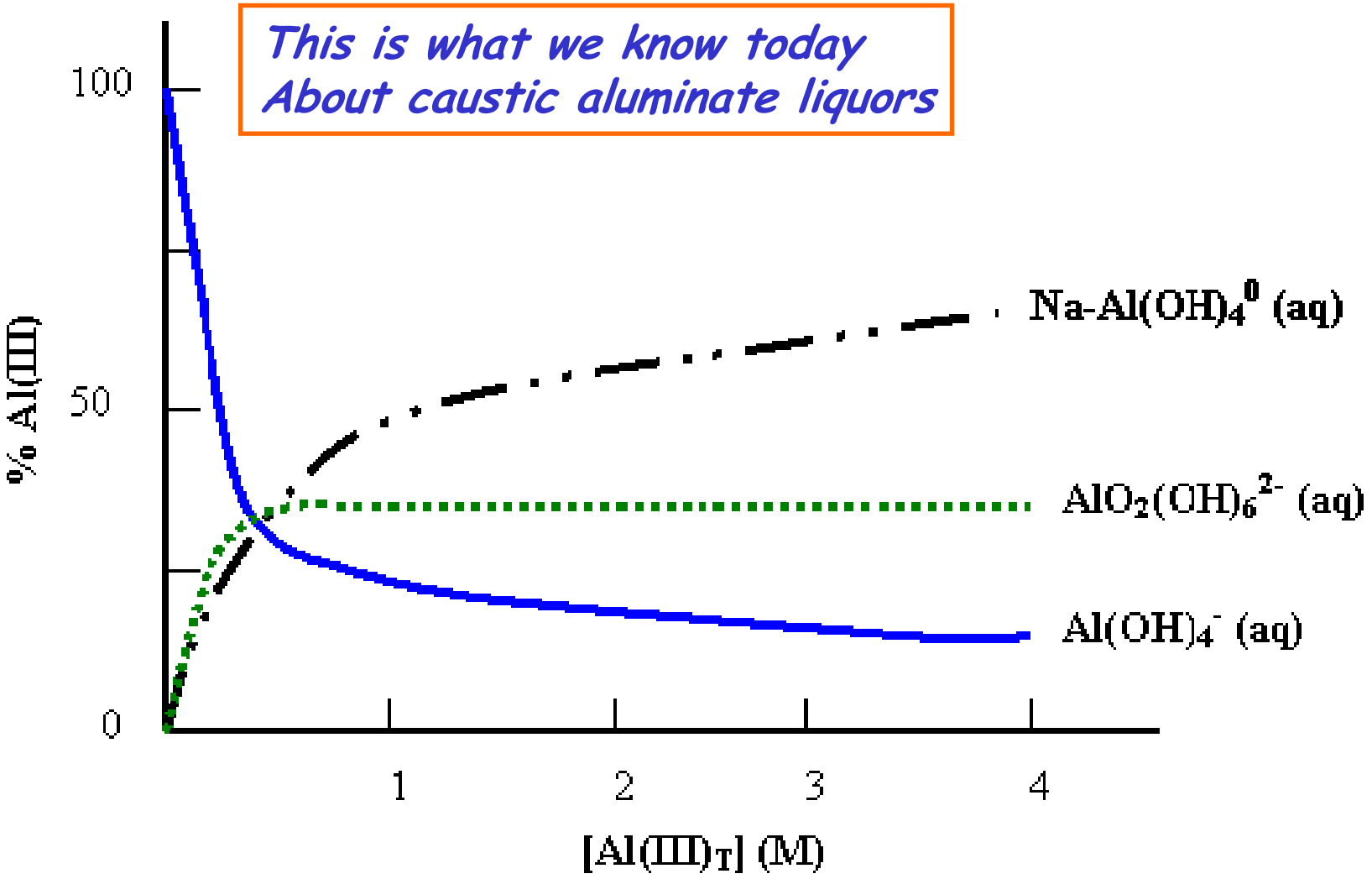
   Consider 2 solutions containing the different molar concentrations or ionic strength of caustic (e.g. NaOH) but similar concentrations of dissolved aluminium.

3. Do reliable equilibrium Al(III) solubility data & activity diagrams exist at operating conditions of interest?

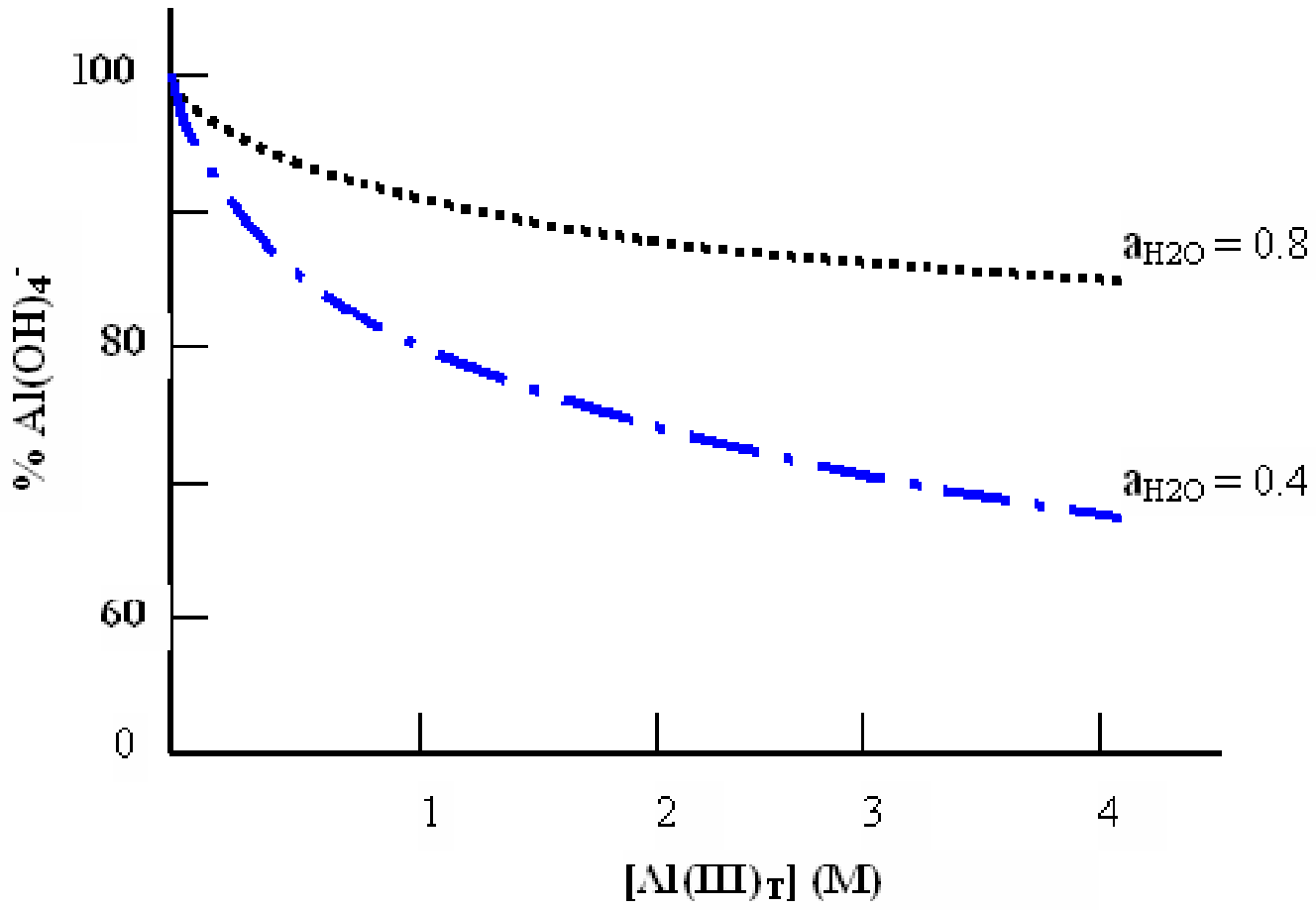
Solution Speciation & thermodynamic properties



Al(III) Speciation & thermodynamic properties



Al(III) Speciation & Water activity may vary with ionic strength



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Kinetics of Dissolution, R, : Rate laws

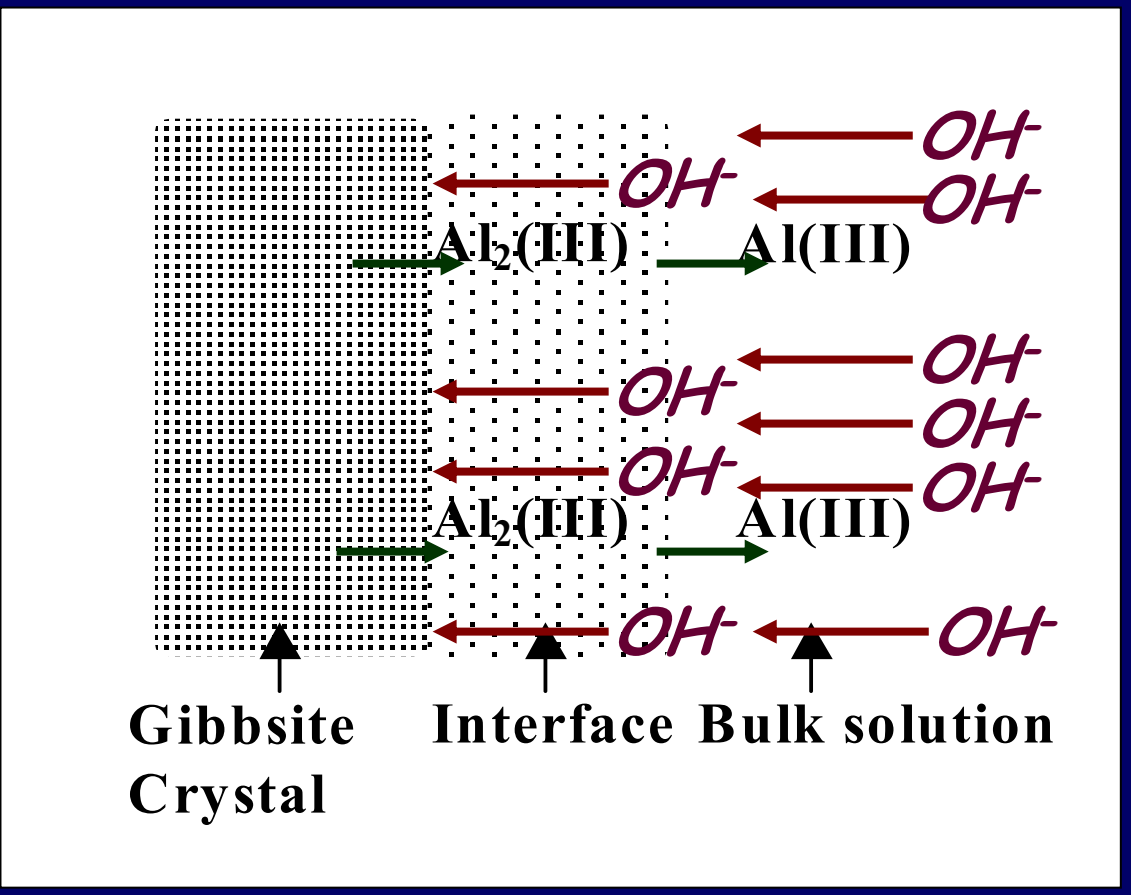
R = f{seed surface area .speciation, impurities, solubility/undersaturation water activity/ionic strength, Temperature, Agitation rate, Pressure … + etc.}

Kinetics = the rate at which the dissolution reaction mechanism proceeds

Gibbsite Crystal Dissolution behaviour in NaOH Solution

What are the mechanisms of Al(III) hydroxide dissolution?

Gibbsite: $Al(OH)_3(s) + xNaOH(aq) \Rightarrow NaAl(OH)_4(aq) + yNaOH(aq)$



Na^+-OH^- species volume diffusion to $Al(OH)_3$ surface sites.

OH^- attack of the $Al(OH)_3$ Octahedral structure

$Al(OH)_3$ ° octahedral to tetrahedral Al(III) monomeric ($Al(OH)_4^-$) & dimeric species

Modelling dissolution of Al(OH): Elementary reaction steps:

(Dhillon, 1971; Linge, 1975; Jones and Linge, 1975, Addai-Mensah et al., 2000)

a) Diffusion of attacking ions (OH^-) from the bulk solution to the Al(OH) particle surface (volume diffusion)

b) Ions movement at the crystal surface between sites (surface diffusion)

c) Adsorption of the attacking OH^- ions at the surface (adsorption)

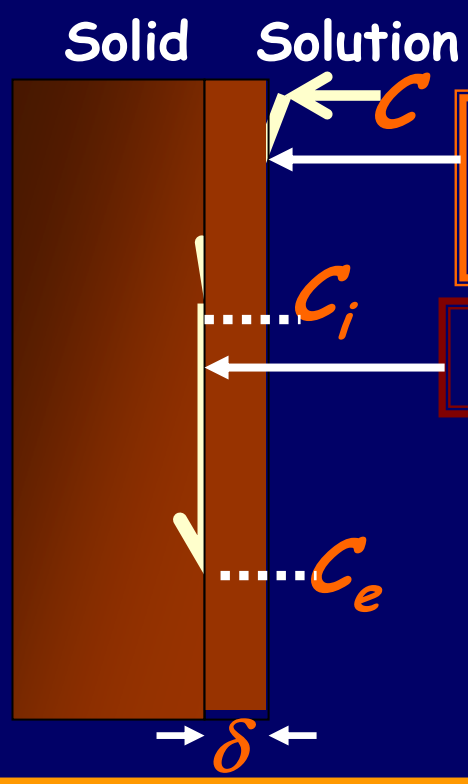
c) Solution/Solid interface reactions* at preferred dislocation/kink sites.

e) Detachment and desorptive transfer of reaction products from the crystal/solid surface (desorption)

f) Diffusion from the particle surface to the bulk (volume diffusion).

**Solvation/desolvation and complexation of OH^- & Al(III) species: hydrated inner & outer sphere complexes.*

Kinetics of Dissolution / Rate laws



2 Resistances-in-Series Rate Laws

Volume diffusion $R_d = k_d.(C_i - C)$ -(1

$k_d = D/V\delta$

Surface reaction $R_r = k_r.SA.(C_e^n - C_i^n)$ -(2

D = diffusion coefficient; V = Volume of solution

R_d = mass transfer rate constant, SA= Surface Area

R_r = chemical reaction rate constant

n = reaction order, $1 \leq n \leq 4$ may apply

d = thickness of conc./ Nerst boundary layer

Total reaction resistance, $1/R = 1/k_d + 1/k_r = (k_r + k_d)/k_r.k_d$

Unless sufficient agitation rate is applied or power input is moderate to high, the 2 resistances of both steps will prevail during dissolution. Mass transfer resistance, $1/k_d$, is only negligible at high agitation rate.

Dissolution Rates: Empirical power Laws

Where surface reaction is very fast (at very high Temperatures), $R_r >> R_d$

Then dissolution rate $R = k_d.(C_e - C)$ -(3

Nerst (1904) Eq. or Mass transfer or volume diffusion-controlled model

Where volume diffusion is very fast, $R_d >> R_r$

Then dissolution rate $R = k_r.SA.(C_e^n - C^n)$ -(4

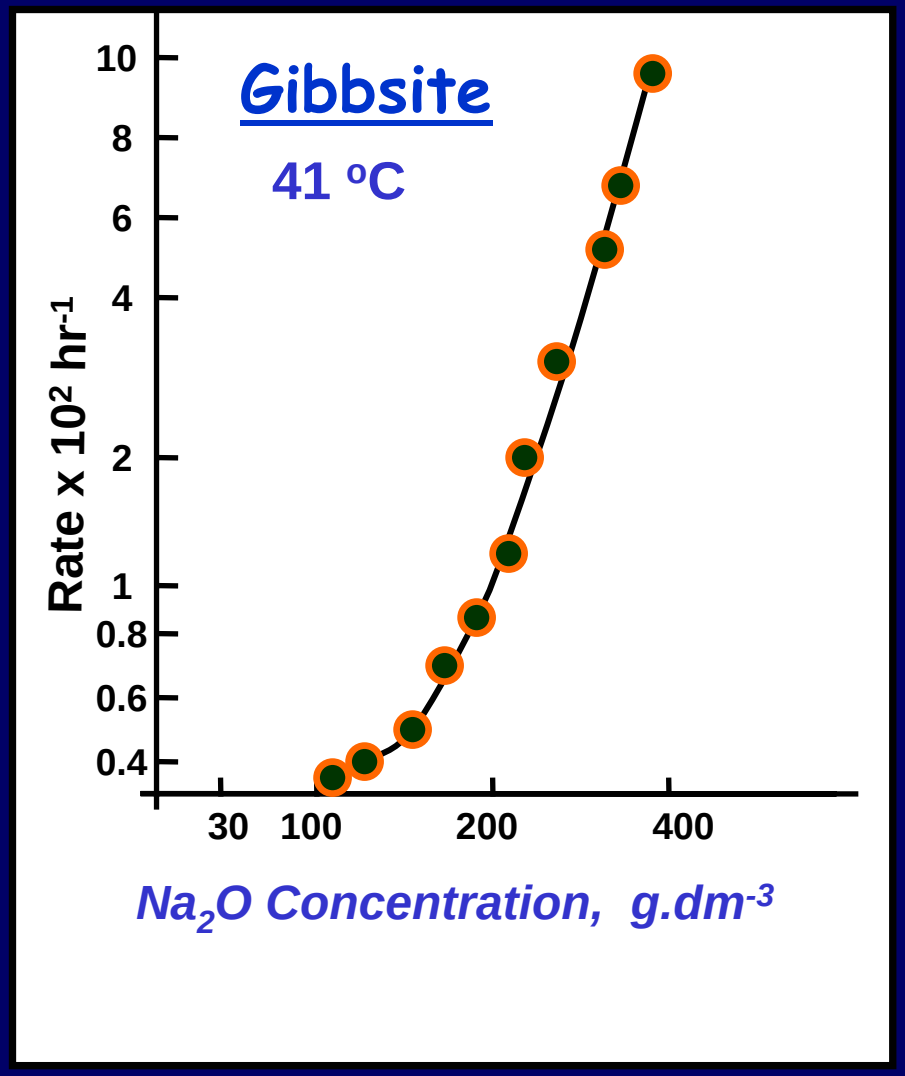
or $R = k_r.SA.(C_e - C)^n$

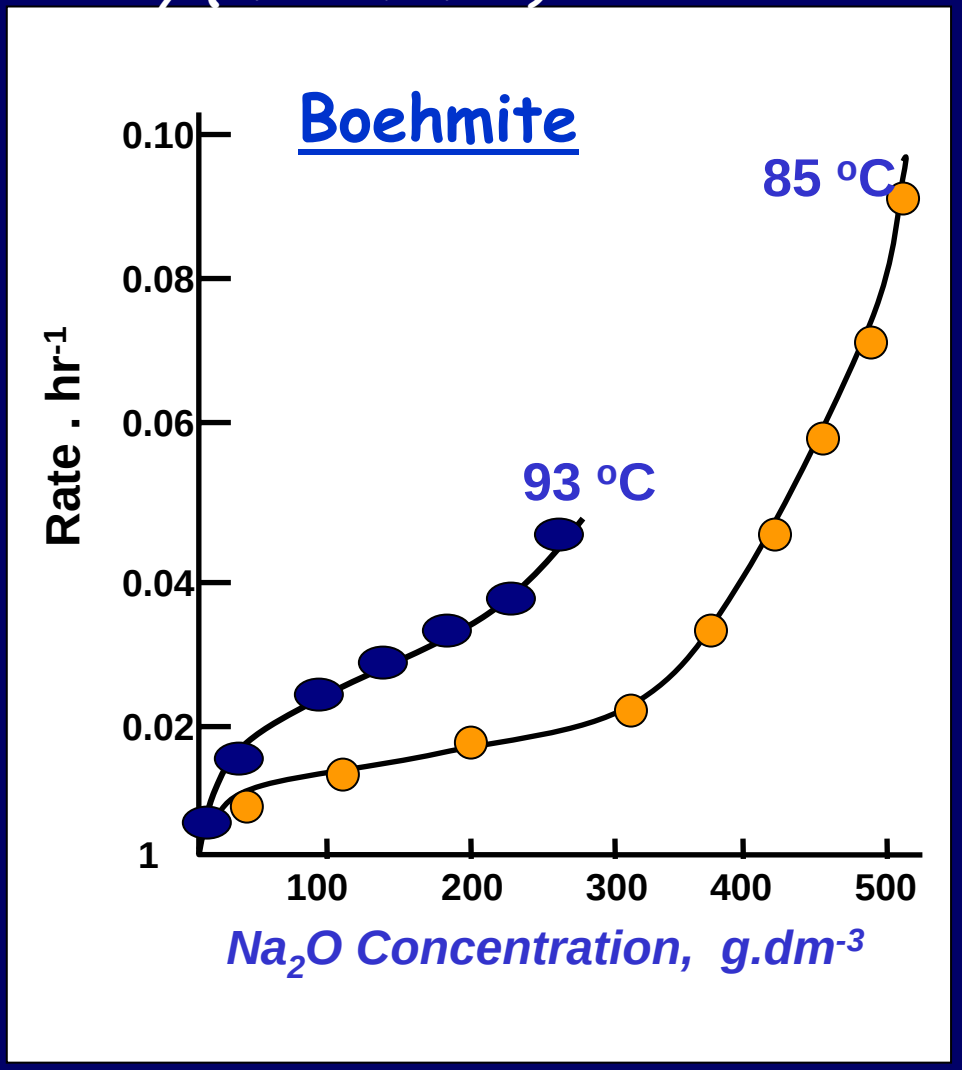
Chemical reaction-controlled model

Very often, for Chemical reaction-controlled dissolution rate, the order n bears no relationship with the true elementary, rate determining steps or speciation stoichiometry. Hence is empirically determined.

Gibbsite Dissolution behaviour & kinetics in NaOH

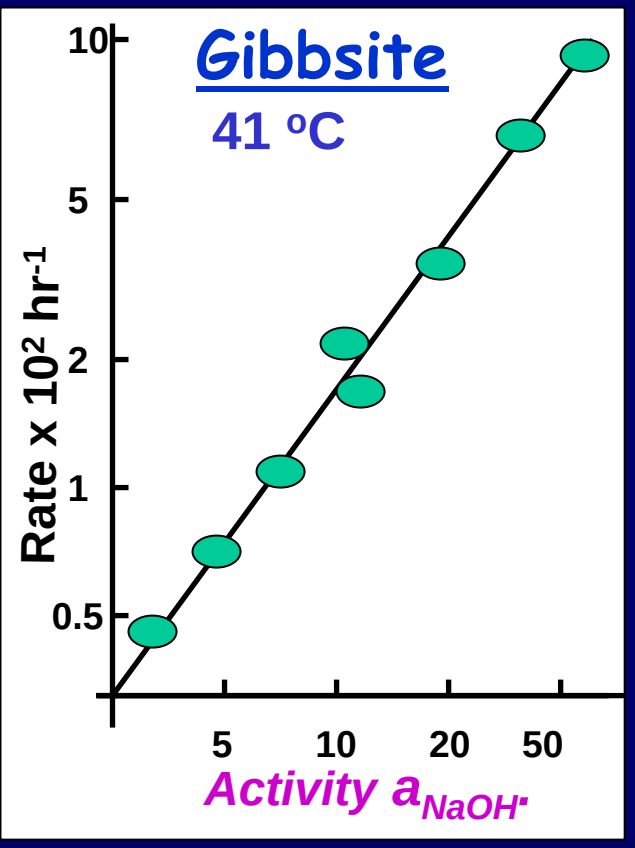
(Scotford & Glastonbury (1971 & 1972)

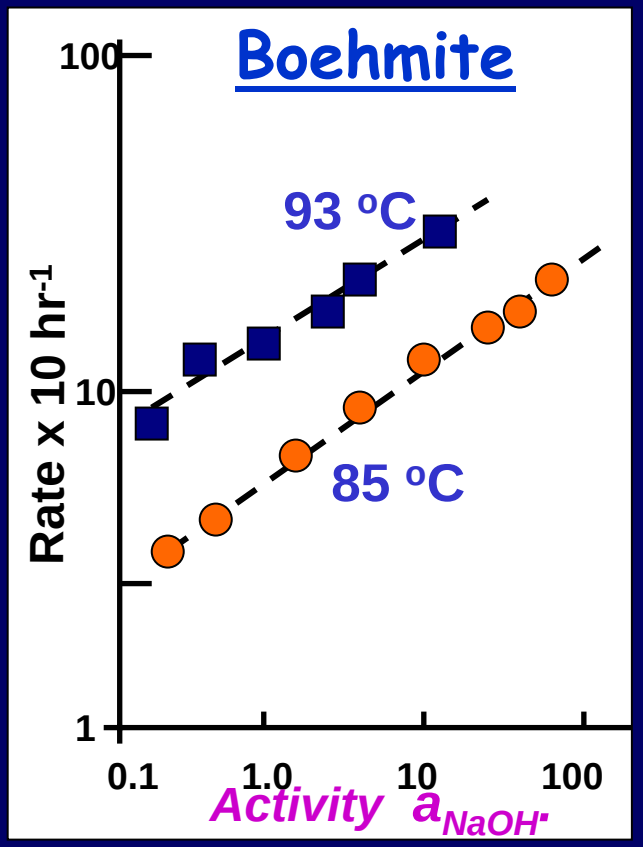


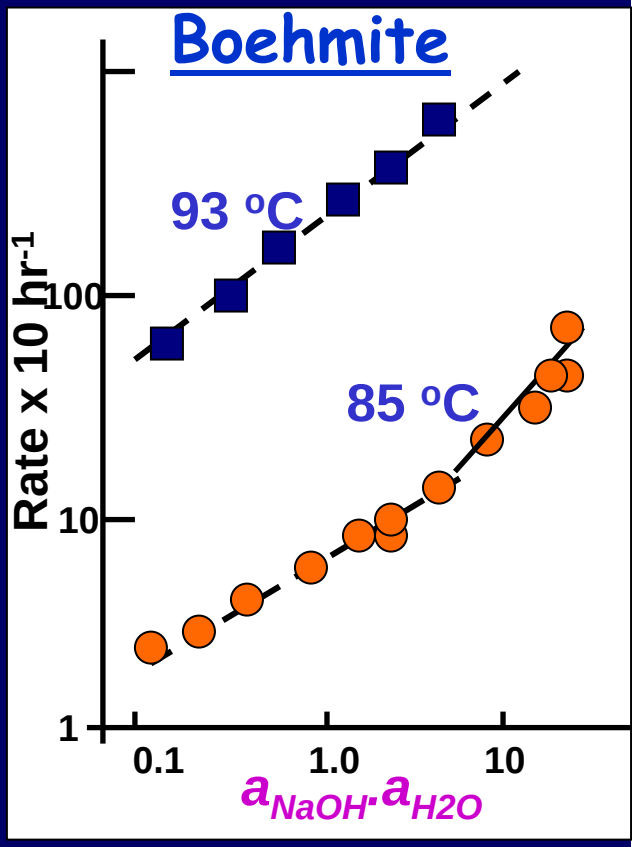


Boehmite Dissolution behaviour & kinetics in NaOH

(Scotford & Glastonbury (1971 & 1972)





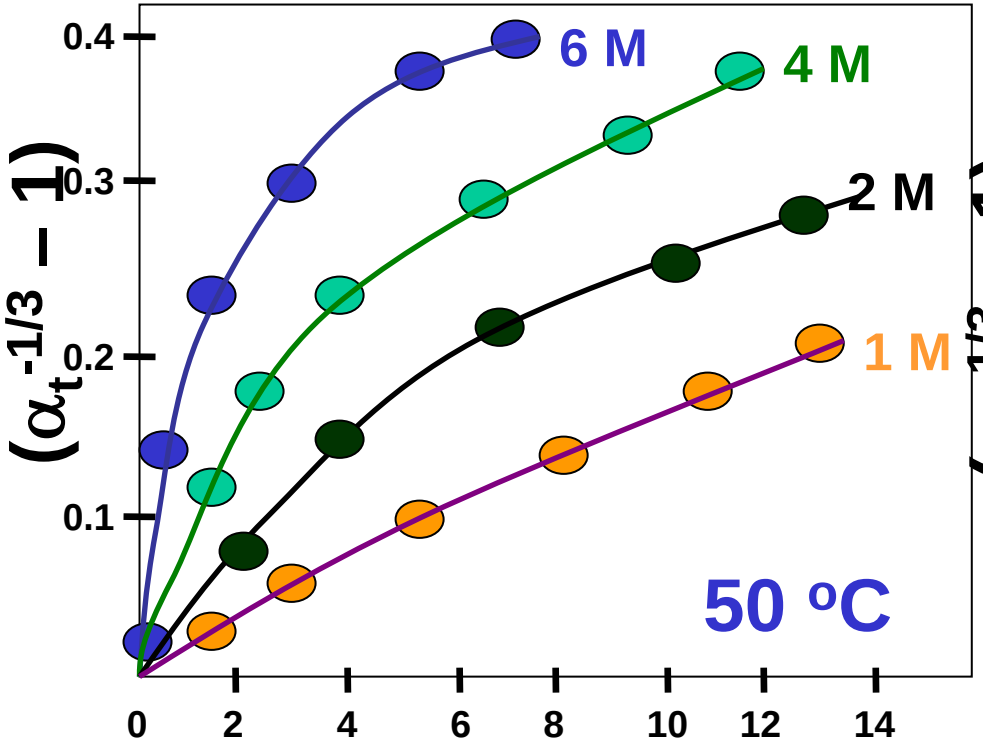


Boehmite Dissolution behaviour in NaOH

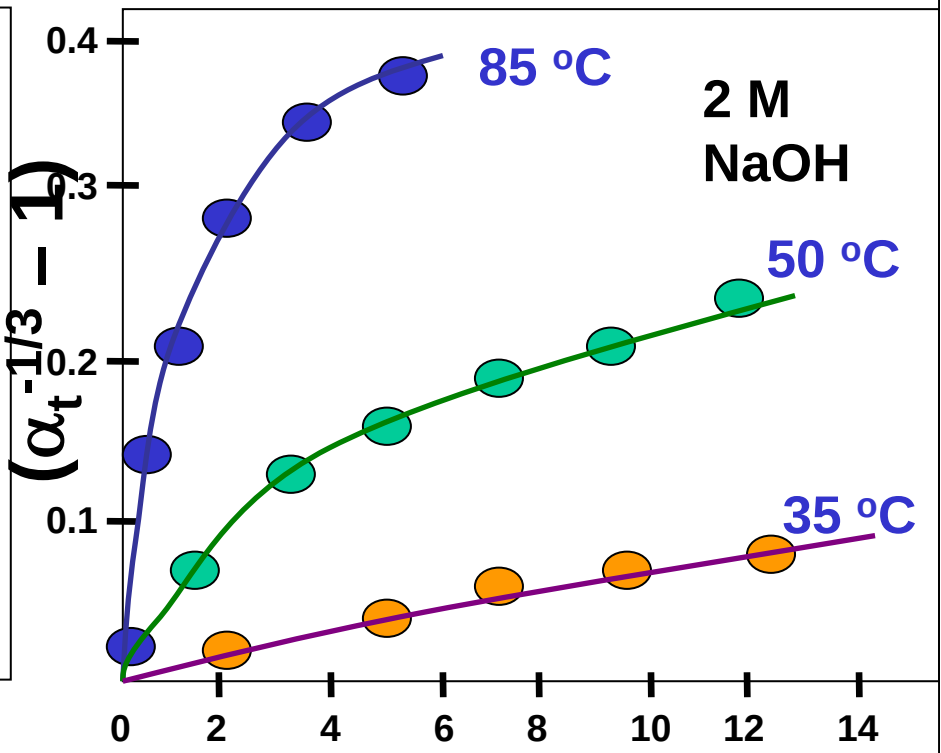
(Pacter (1976)):

Influence of NaOH Conc.

Note: caustic conc dependency.



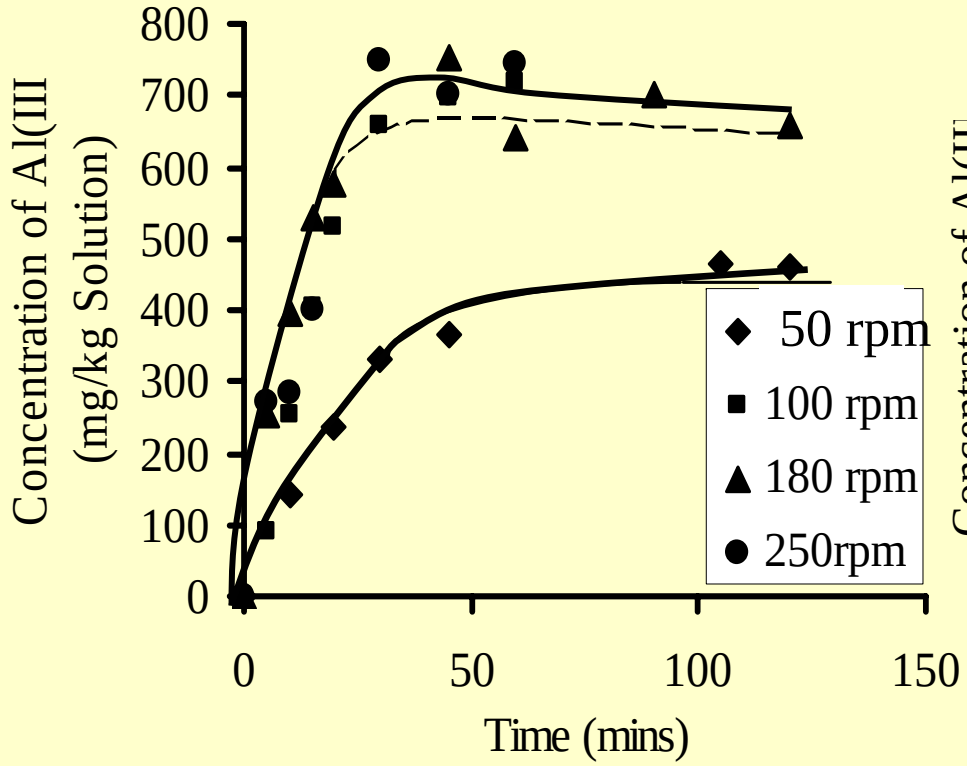
Influence of Temperature



Gibbsite Crystal Dissolution behaviour in Caustic Medium

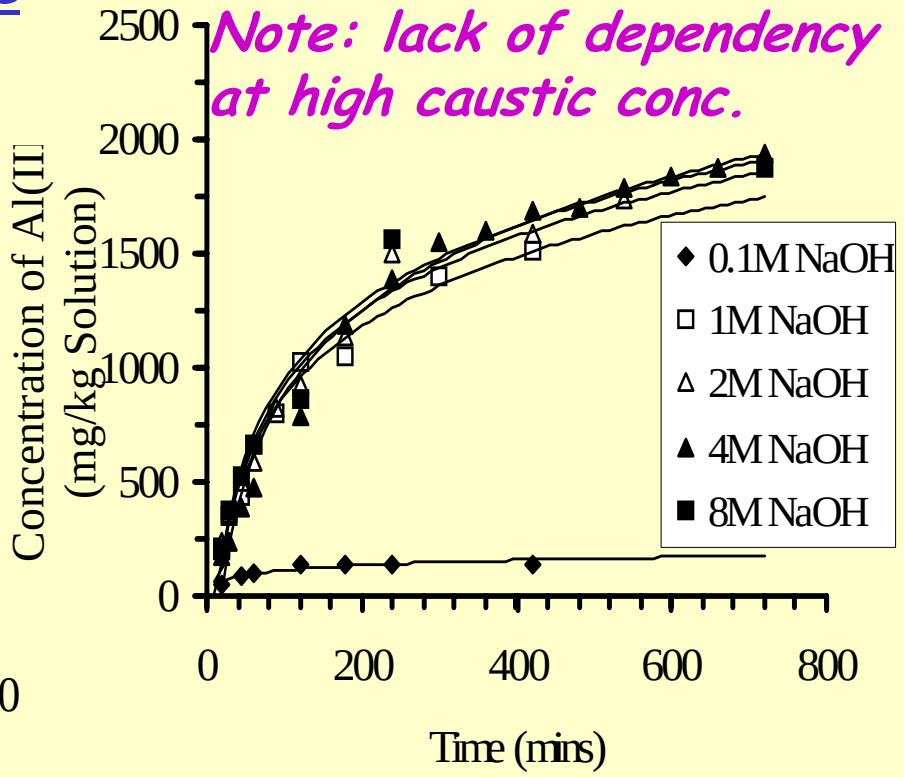
(Addai-Mensah et al. (2000)):

Influence of Agitation rate



Influence of NaOH Conc.

Note: lack of dependency at high caustic conc.

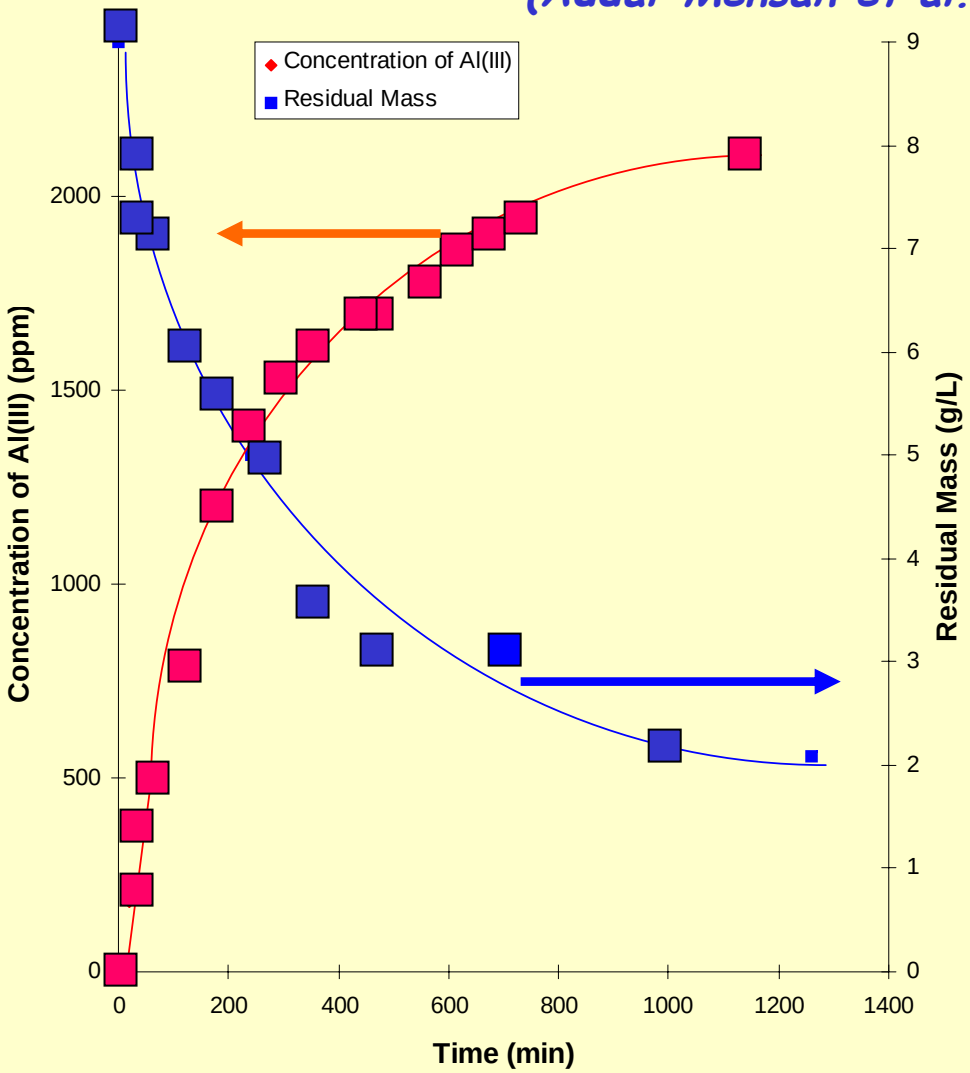


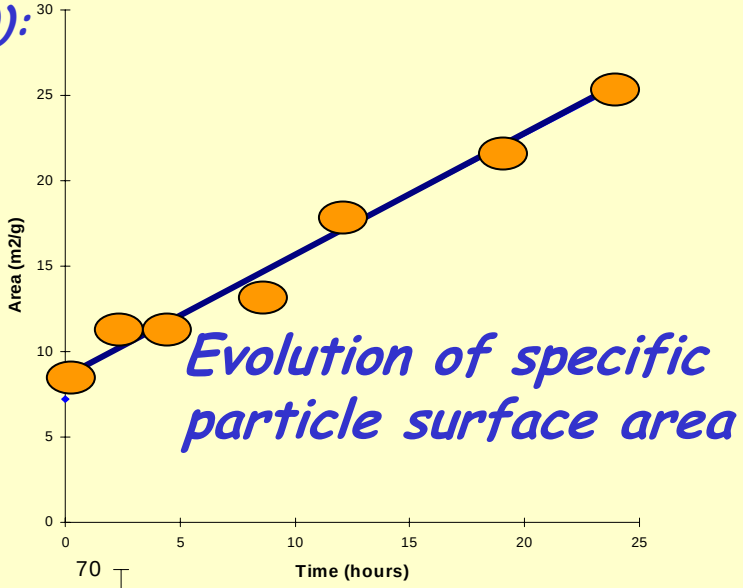
Temperature low= 25 –65 °C, Low Solid content = 1 wt% gibbsite

At higher solid content, strong dependency on dissolution rate on caustic concentration may be displayed – e.g. Glastonbury (1967)

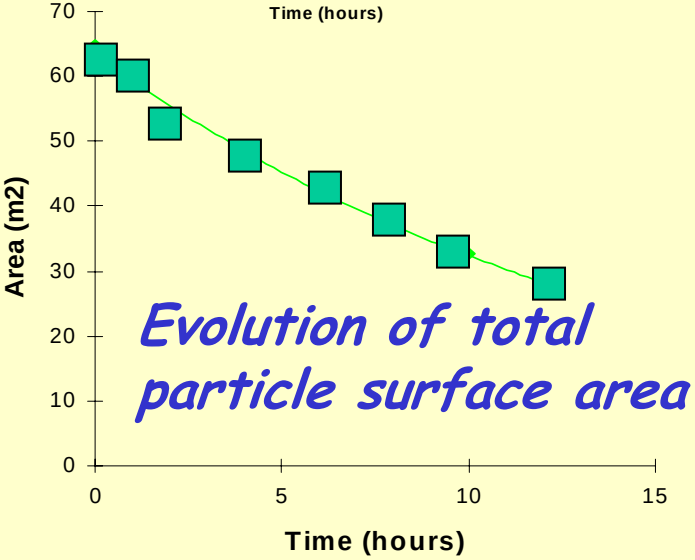
Gibbsite Crystal Dissolution behaviour in Caustic Medium

(Addai-Mensah et al. (2006)):



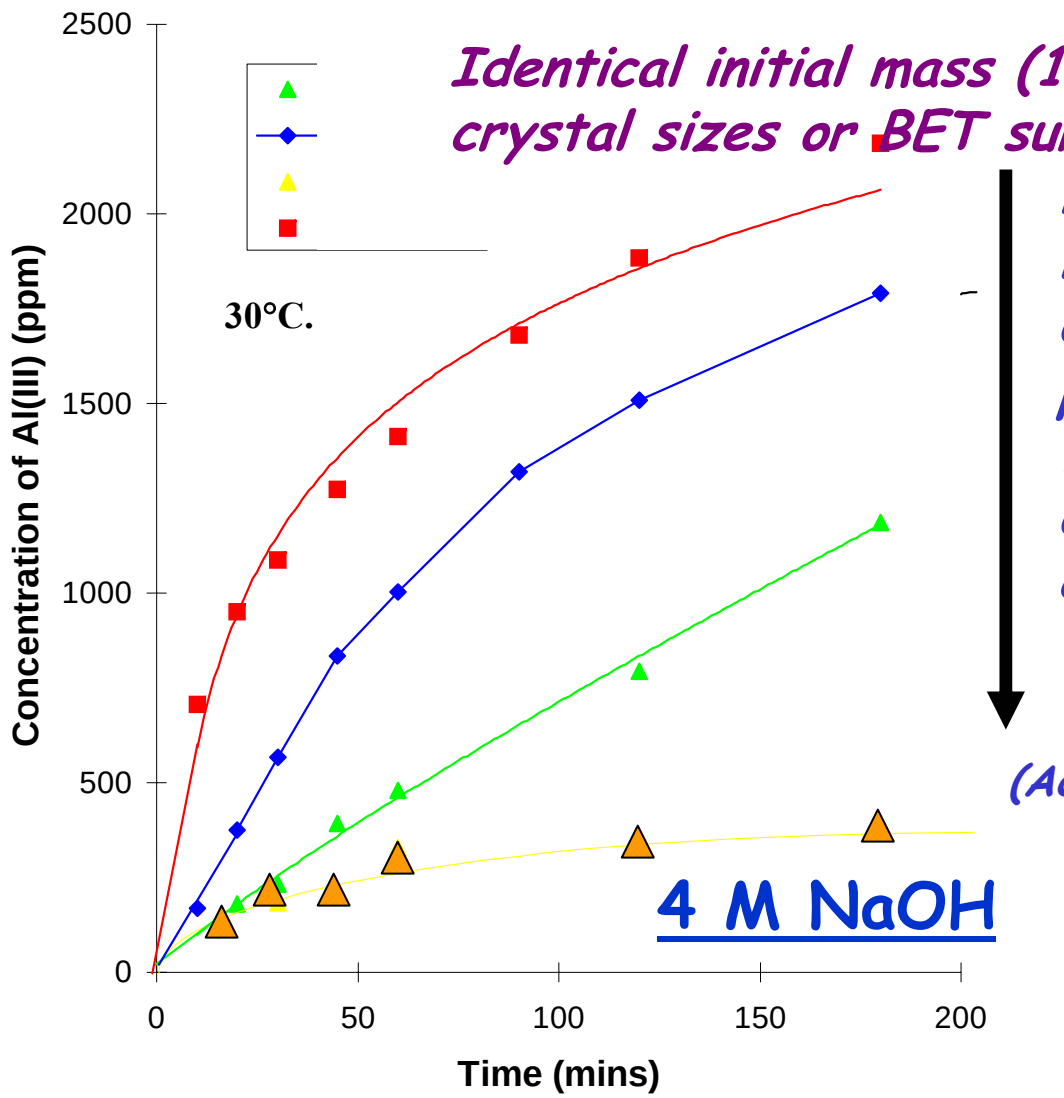


Evolution of specific particle surface area



Evolution of total particle surface area

Role of Gibssite Surface Area upon Dissolution in NaOH



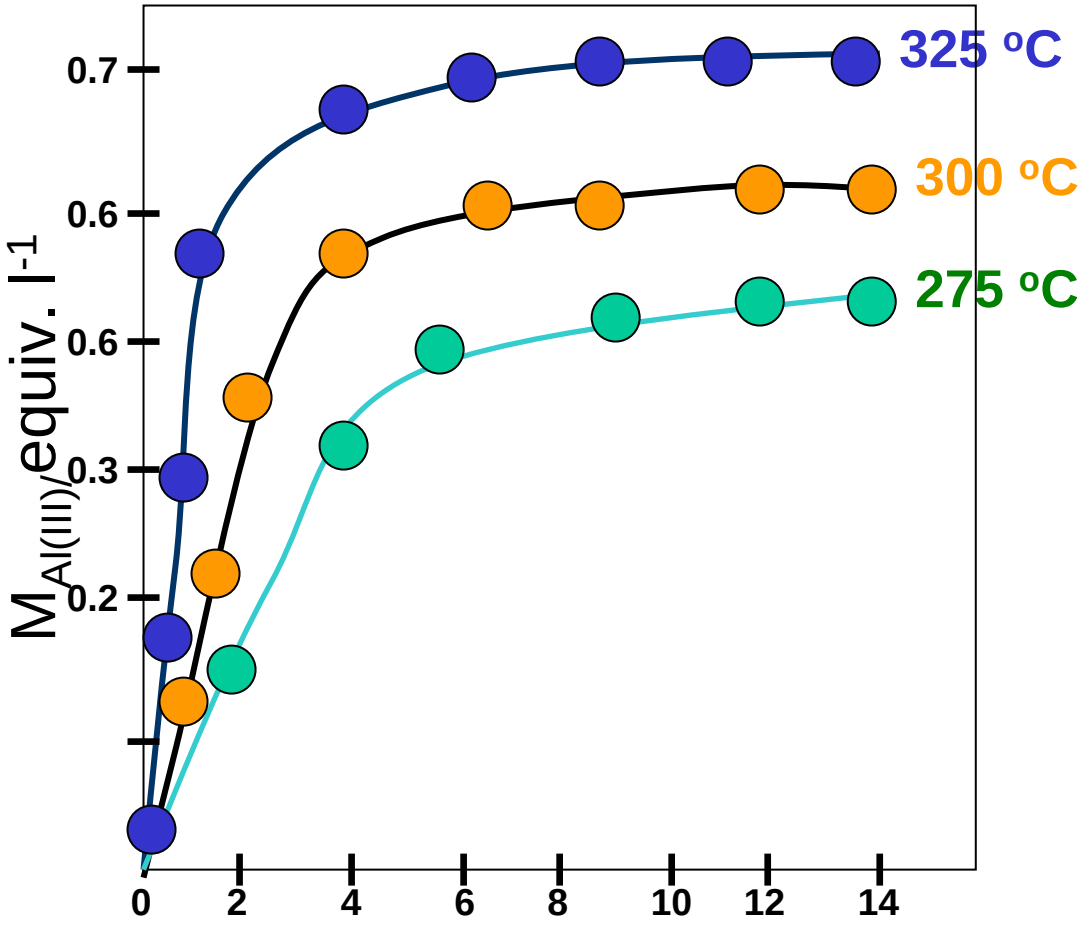
Identical initial mass (10 g/l) but different crystal sizes or BET surface areas

Decreasing initial BET surface area or increasing particle size at fixed initial mass of gibbsite seed crystals

(Addai-Mensah et al. (2006)):

Diaspore Crystals Dissolution behaviour in ~1 M NaOH

Influential role of dissolution reaction temperature

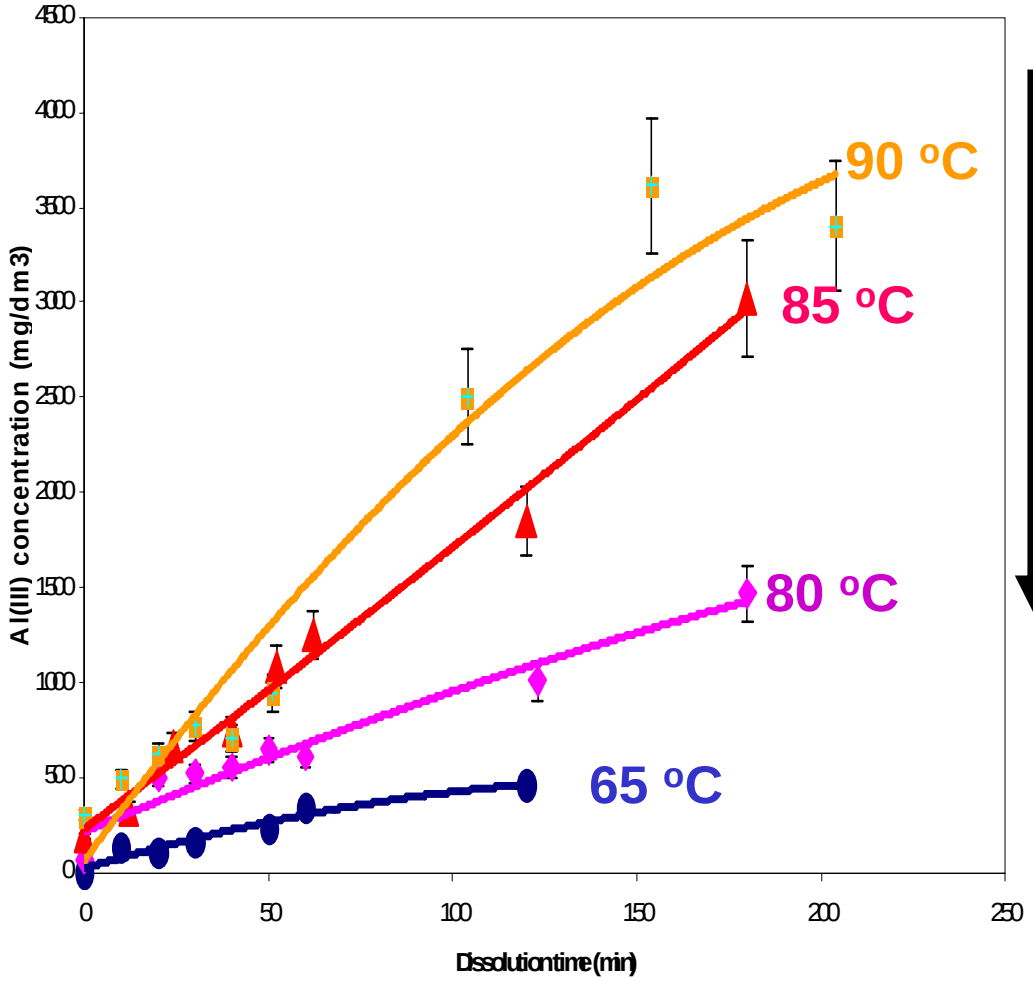


Decreasing dissolution Temperature results in dramatic decrease dissolution kinetics

(Chang et al., 1979.)

Boehmite Crystal Dissolution behaviour in Caustic Medium

Influential role of dissolution reaction temperature



Decreasing dissolution Temperature results in dramatic decrease dissolution kinetics

4 M NaOH, 110 g AlOOH/ dm^3 solution. (Addai-Mensah, 2006.)

Gibbsite & Boehmite Dissolution Kinetics Models

Solutions: 4 – 6 M NaOH NaOH Temp. = 50 – 100 °C

High seed charge = SA = 4880 m²/l Agitation rate = 300 rpm

Strong NaOH dependence. (Glastonbury; 1967).

$$R = SA \cdot k_o \exp(-E_a/RT)(C_{NaoH})^{1.73}$$

$$\text{Rate} = R, \quad [\text{g Al(III)}.\ \text{cm}^{-2}\ .\ \text{sec}^{-1}]$$

Gibbsite: $k_o = 4.6\times10^5$ and $E_a = 100 \pm 5$ kJ/mol

Boehmite: $k_o = 6.7\times10^2$ and Ea = 100 ± 5 kJ/mol

(Chemical Reaction-controlled)

Gibbsite & Boehmite Dissolution Kinetics Models

Solutions: 3 – 6 M NaOH NaOH Temp. = 41 – 100 °C

High seed charge = SA = 4880 m²/l Agitation rate = 300 rpm

NaOH and Water activity dependence.

Model by Scotford and Glastonbury; 1972.

$$\text{Boehmite } R = SA \cdot k_o \exp(-65{,}000/T)(C_{NaoH})(a_{H2O})^{0.5}$$

$$\text{Gibbsite } R = SA \cdot k_o \exp(-68{,}000/T)(C_{NaoH})a_{H2O}$$

Gibbsite: $SA.k_o = 3.0\times10^{18}$ and $E_a = 128.5 \pm 5$ kJ/mol

Boehmite: $SA.k_o = 4.5\times10^{15}$ and Ea = 120 ± 5 kJ/mol

(Chemical Reaction-controlled)

Gibbsite Crystal Dissolution kinetics in Caustic Medium

Solutions: 2 – 8 M NaOH NaOH, SA = 30 -60 m^2/l, Temp. = 30 – 90 °C, Addai-Mensah et al.2000.

$$R = d\Delta C/dt = k_r.SA.(C_{eAl}^2 - C_{Al}^2)$$

$$Log[(C_{eAl}+C_{Al})/(C_{eAl}-C_{Al})] = 2.SA.C_{eAl}.k_r.t$$

Temperature (T, °C)	Rate Constant (k) [(mg/kg solution)$^{-1}$.m^{-2}.min^{-1})
30.0	4.43
50.0	40.12
70.0	348.84
90.0	2995.00

$k_o \exp(-E_a/RT)$ E_a = 95 -100 ± 5 kJ/mol

(Chemical Reaction-controlled)

Gibbsite & Boehmite Dissolution rates

Gibbsite Vs Boehmite: Example

Dissolution rate R (at 50 ^{o}C) = 8.18 $\times 10^{-10}$ g Al . cm^{-2} . sec^{-1}
Dissolution rate R (at 90 ^{o}C) = 1.1 $\times 10^{-7}$ g Al . cm^{-2} . sec^{-1}

The dissolution rates of Boehmite crystals will be ~ 600 – 700 times slower than those of gibbsite given above.

Gibbsite, Boehmite & Diaspore Dissolution rates

$$R = SA \cdot k_o \exp(-E_a/RT)(C_{NaoH})^n . a^p_{H20}$$

C_{NaoH} =Caustic activity/concentration,
p= exponent of caustic activity/concentration

a_{H20} =water acivity, p= exponent of water activity

e.g. $R = SA \cdot k_o \exp(-E_a/RT)(C_{NaoH})^{1.73}$ (where p = 0)

E_a = 95 - 140 kJ/mol, similar for most AlOH phases

but beware, k_o values differ dramatically,

$k_{oBayerite} > k_{oGibbsite} > k_{oBoehmite} > k_{oDiaspore}$

Note: Dissolved impurity ions if present will exert their influence