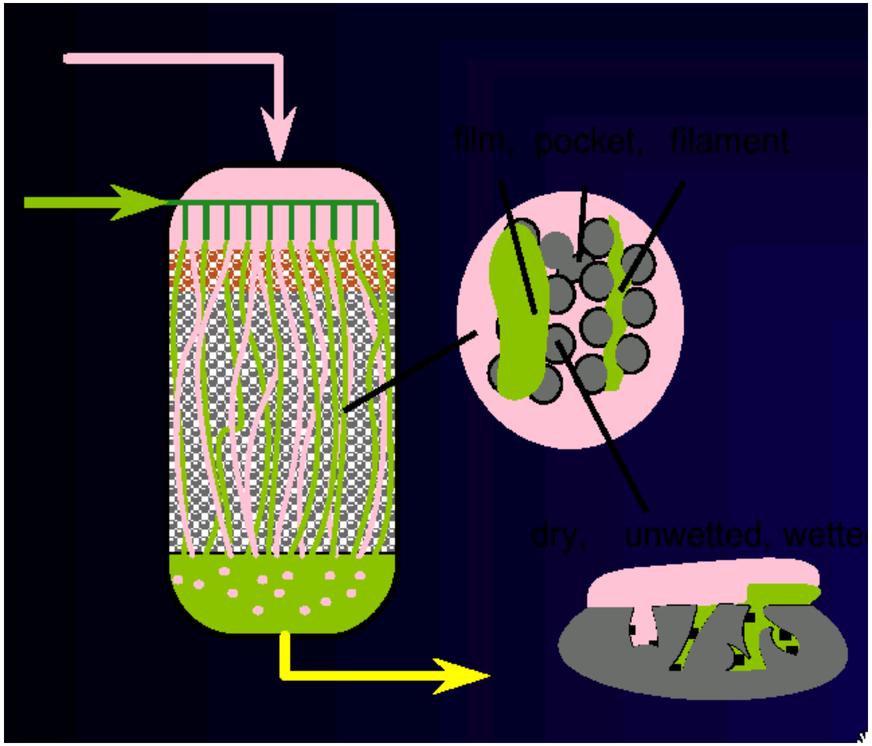
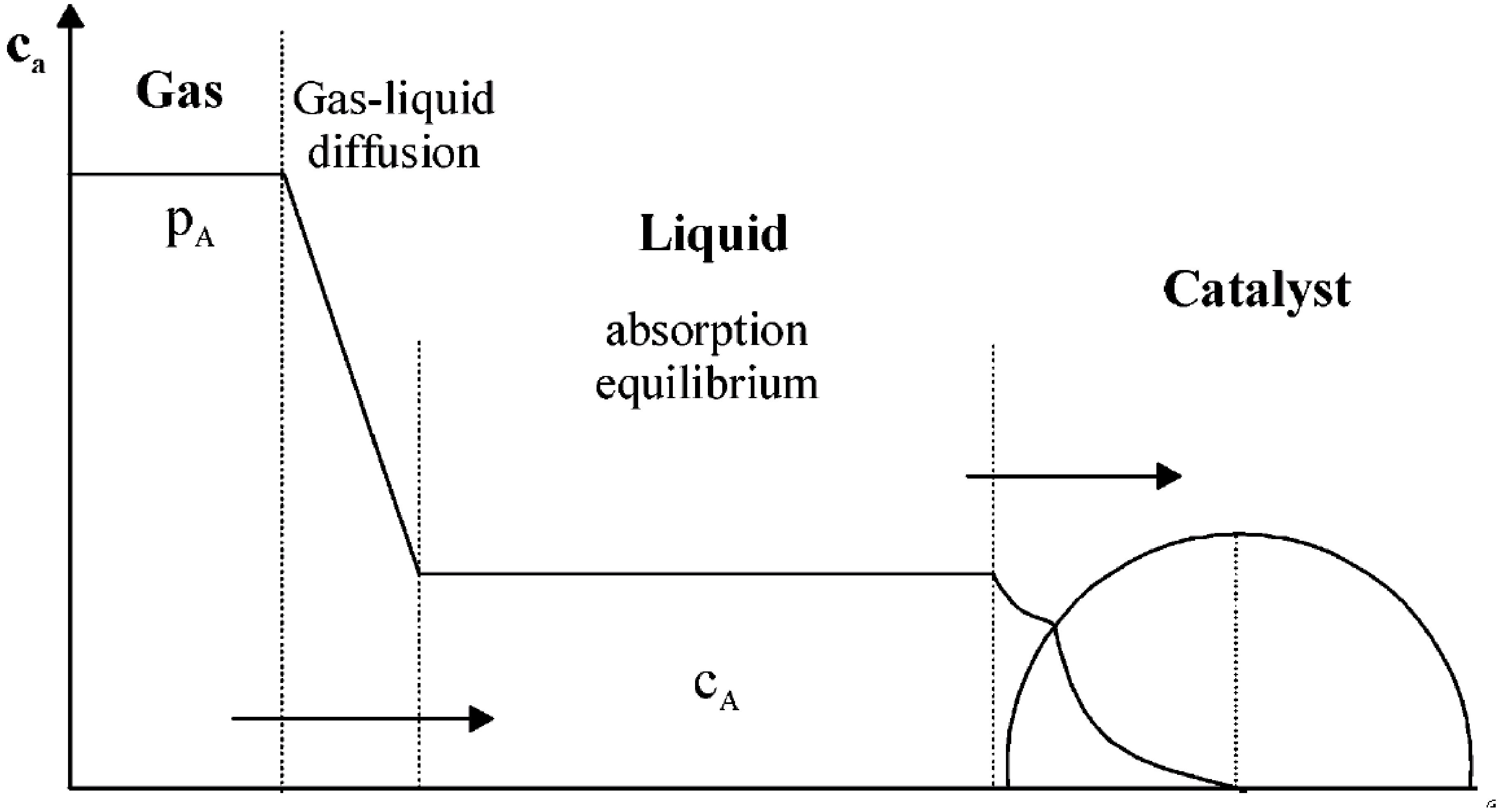
Catalytic three-phase reactors



- Gas, liquid and solid catalyst

Function principle

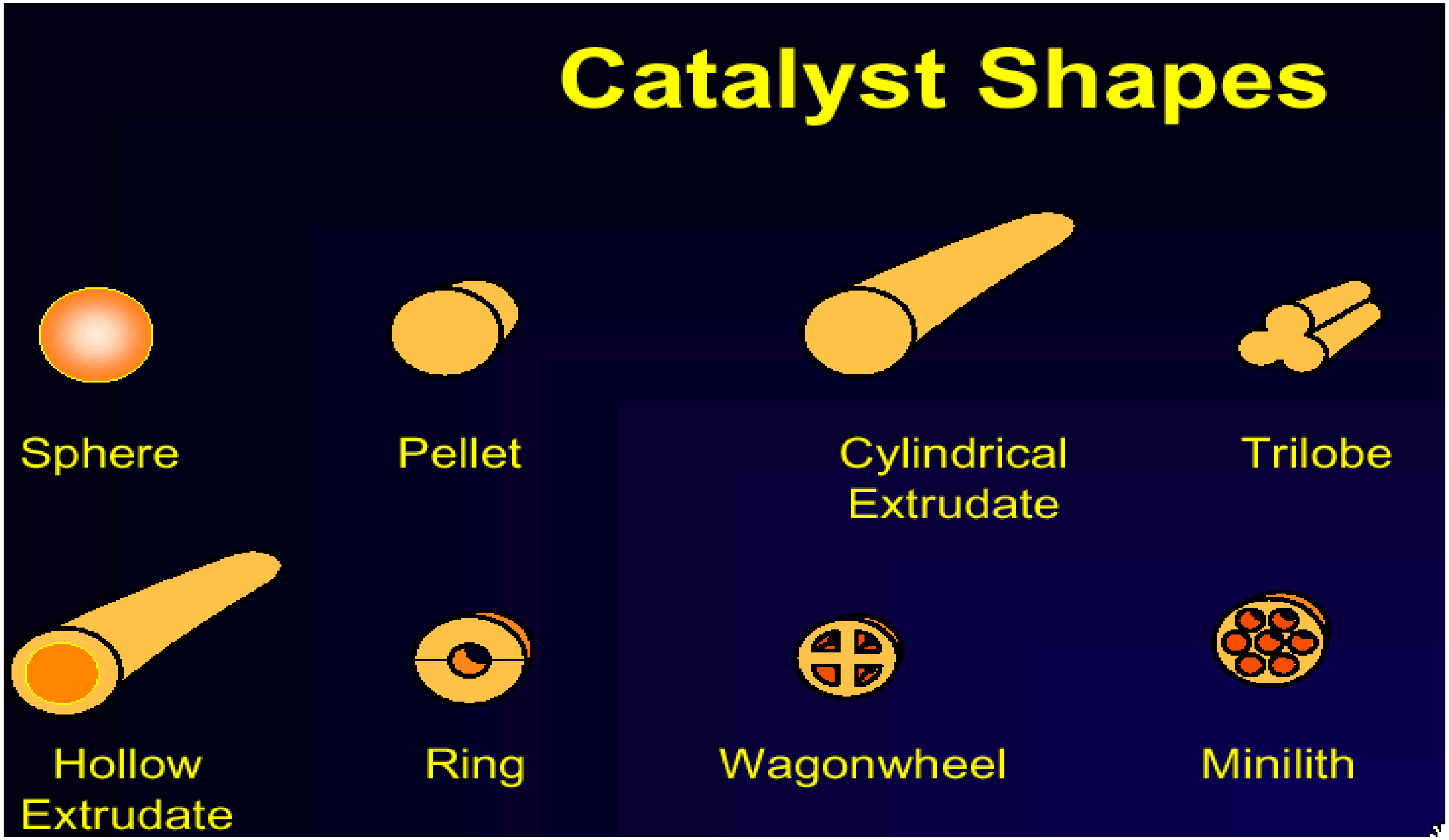
- Some reactants and products in gas phase
- Diffusion to gas-liquid surface
- Gas dissolves in liquid
- Gas diffuses through the liquid film to the liquid bulk
- Gas diffuses through the liquid film around the catalyst particle to the catalyst, where the reaction takes place
- Simultaneous reaction and diffusion in porous particle


c_a
Gas
Gas-liquid diffusion
p_A
Liquid
absorption equilibrium
Catalyst
c_A

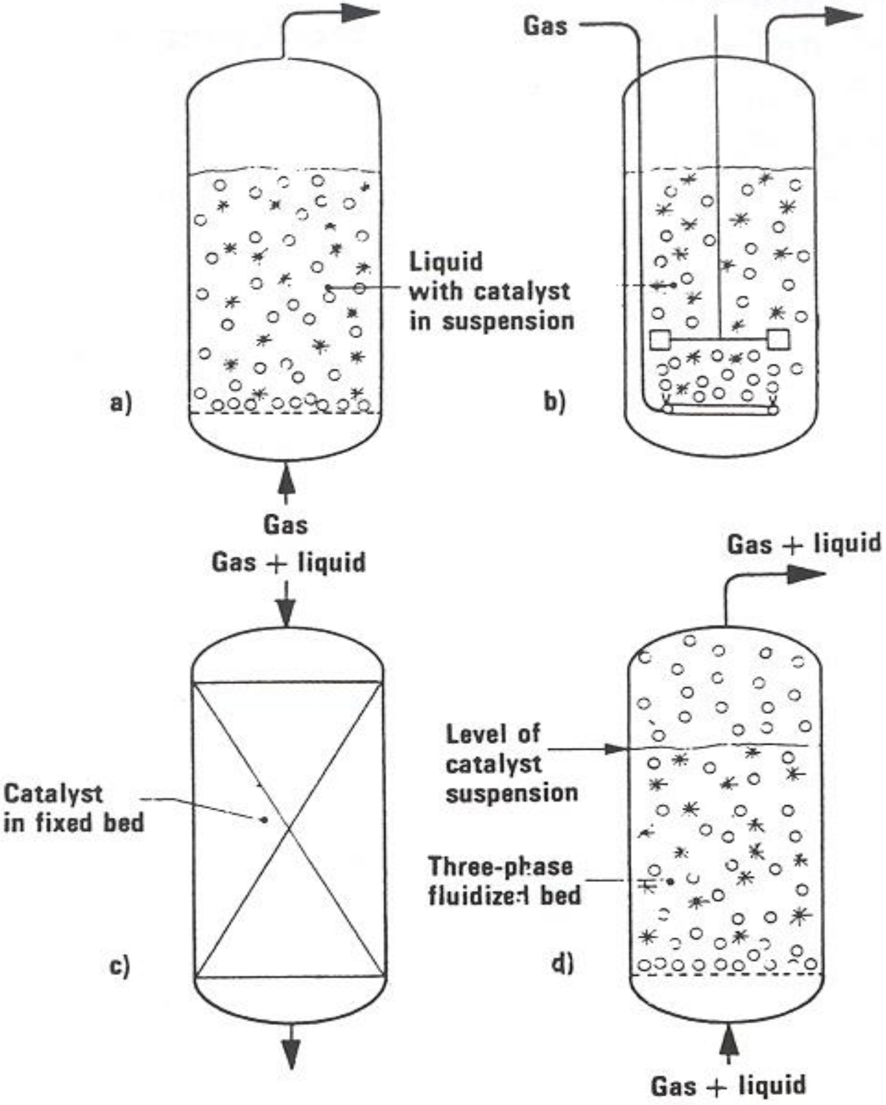
Three-phase reactors – catalyst

- Small particles (micrometer scale < 100 micrometer)
- Large particles (< 1cm)

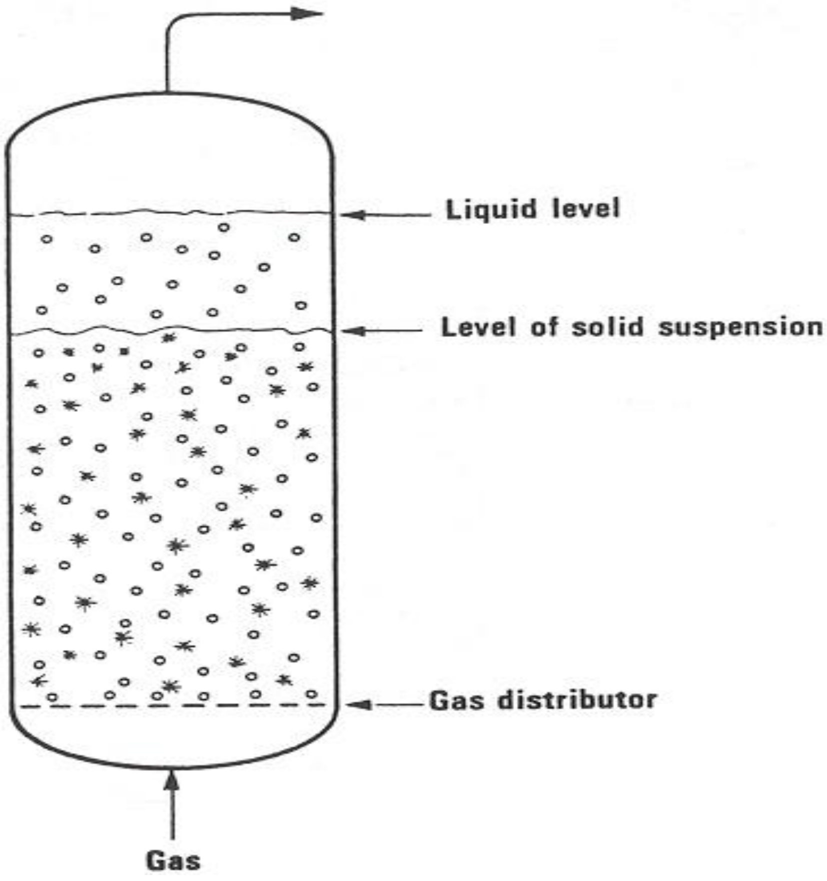
Catalyst design



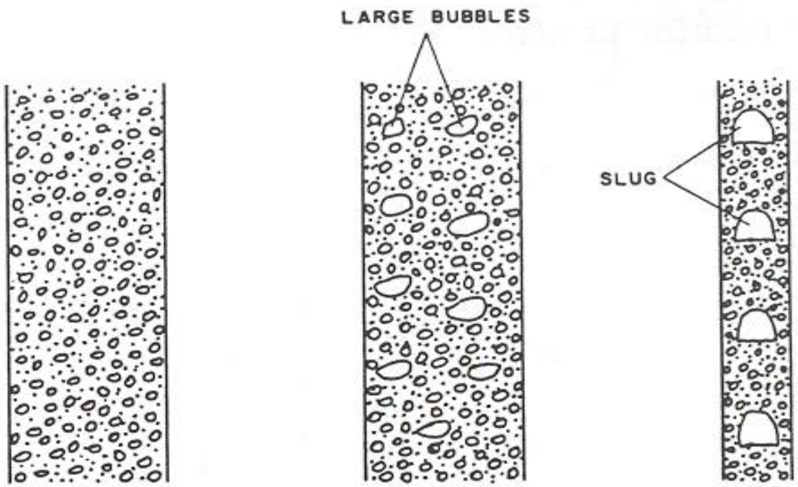
Reactors


Gas
Liquid
with catalyst
in suspension
a)
b)
Gas
Gas + liquid
Gas + liquid
Catalyst
in fixed bed
Level of
catalyst
suspension
Three-phase
fluidized bed
c)
d)
Gas + liquid

Bubble column



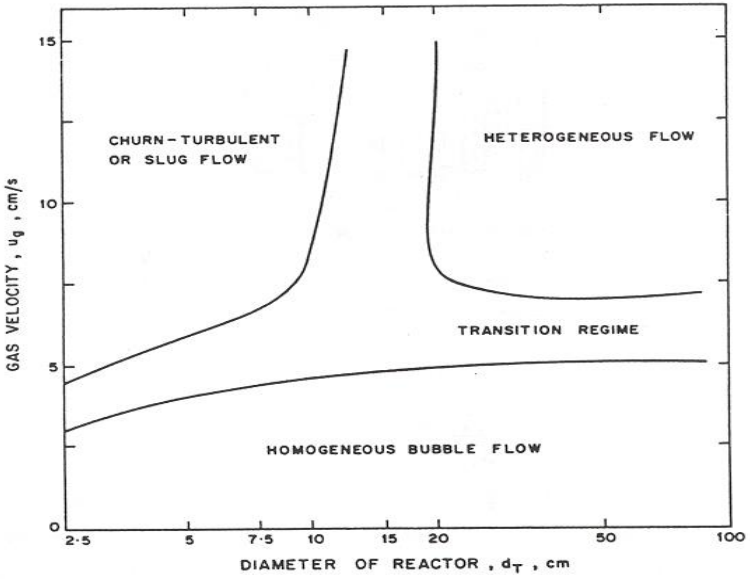
Flow pattern in bubble column



a) HOMOGENEOUS BUBBLE FLOW

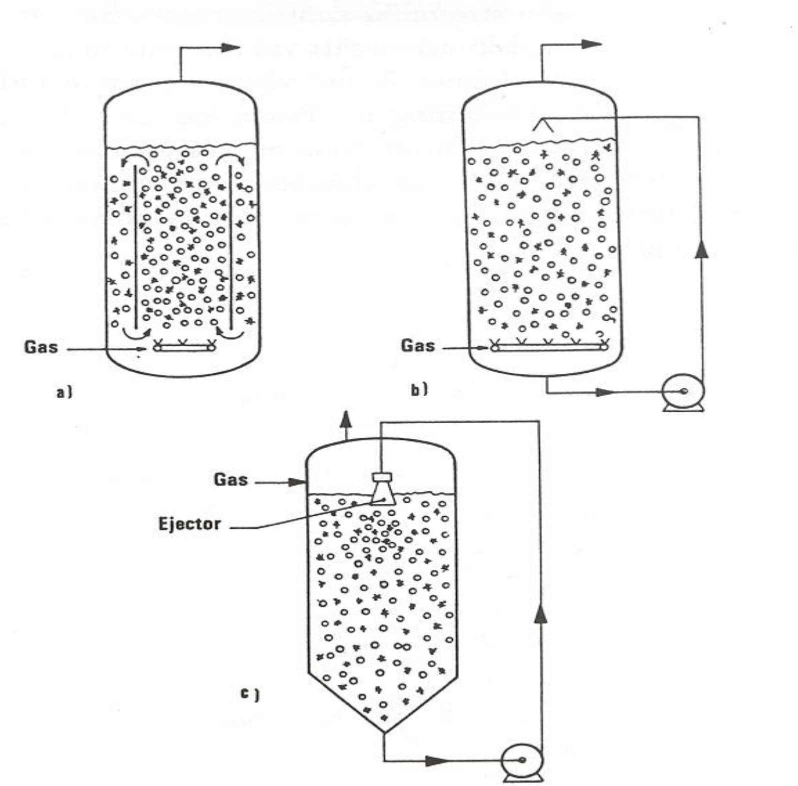
b) HETEROGENEOUS FLOW

c) CHURNTURBULEN OR SLUG FLOW



Tank reactor

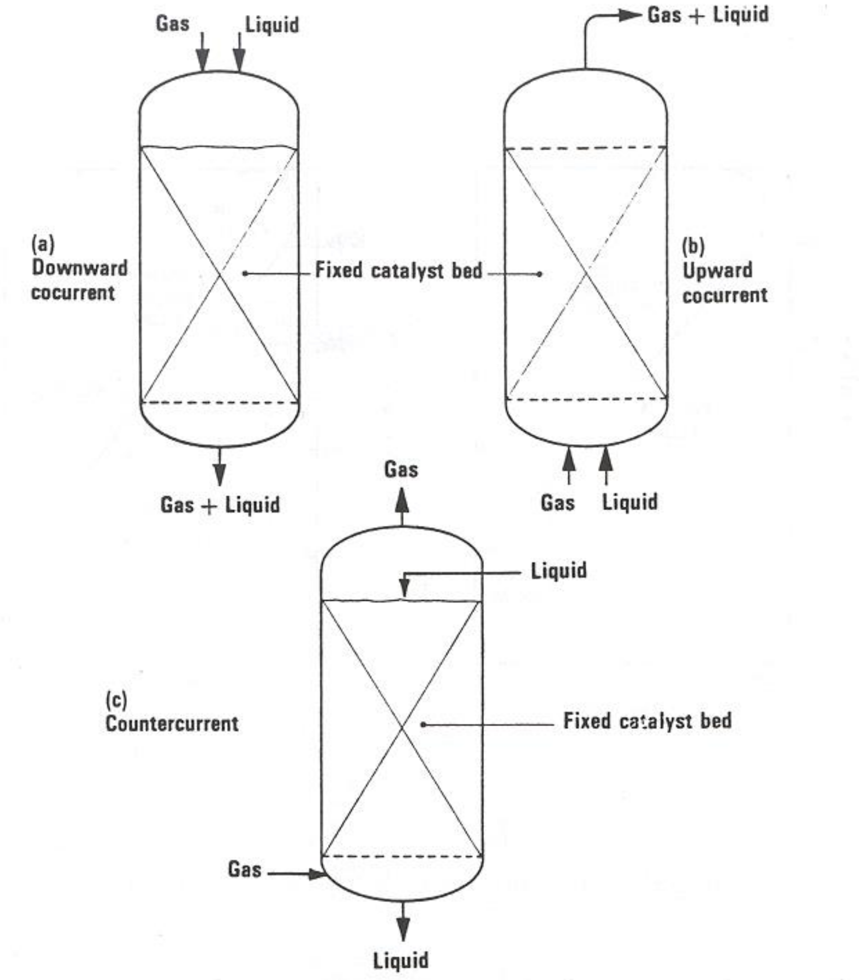
- Often called slurry reactor



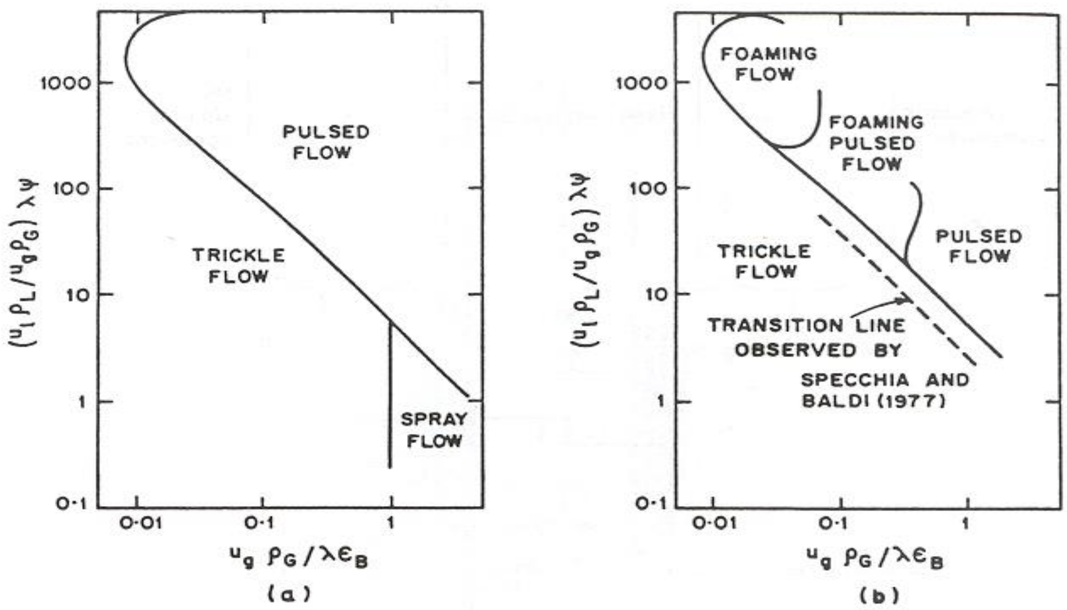
Packed bed – trickle bed

- Trickle bed
  - Liquid downflow – trickling flow
- Packed bed, if liquid upflow

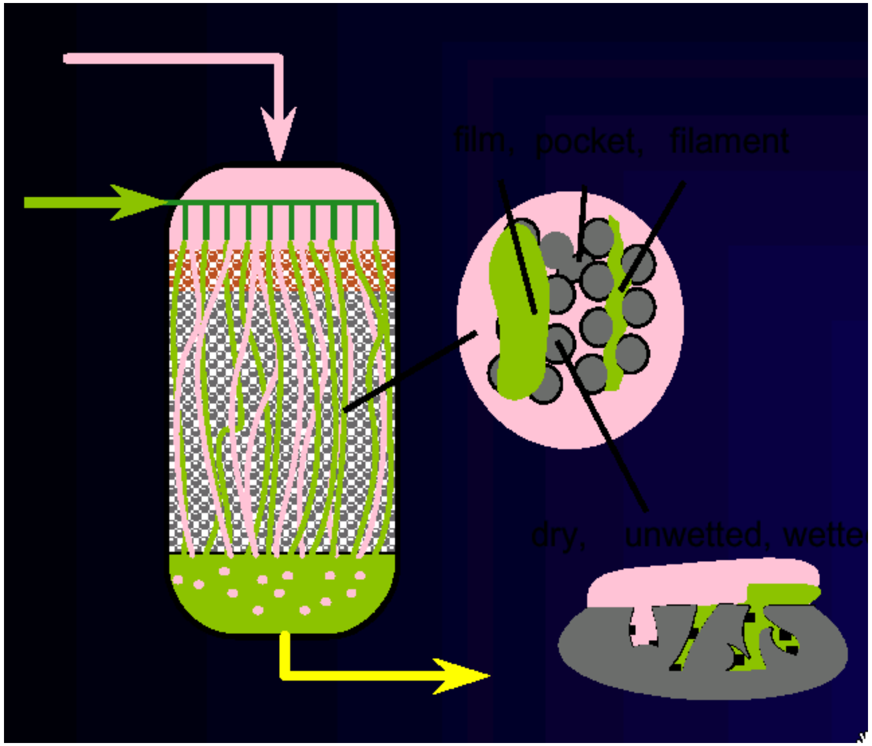
Packed bed- fixed bed – trickle bed



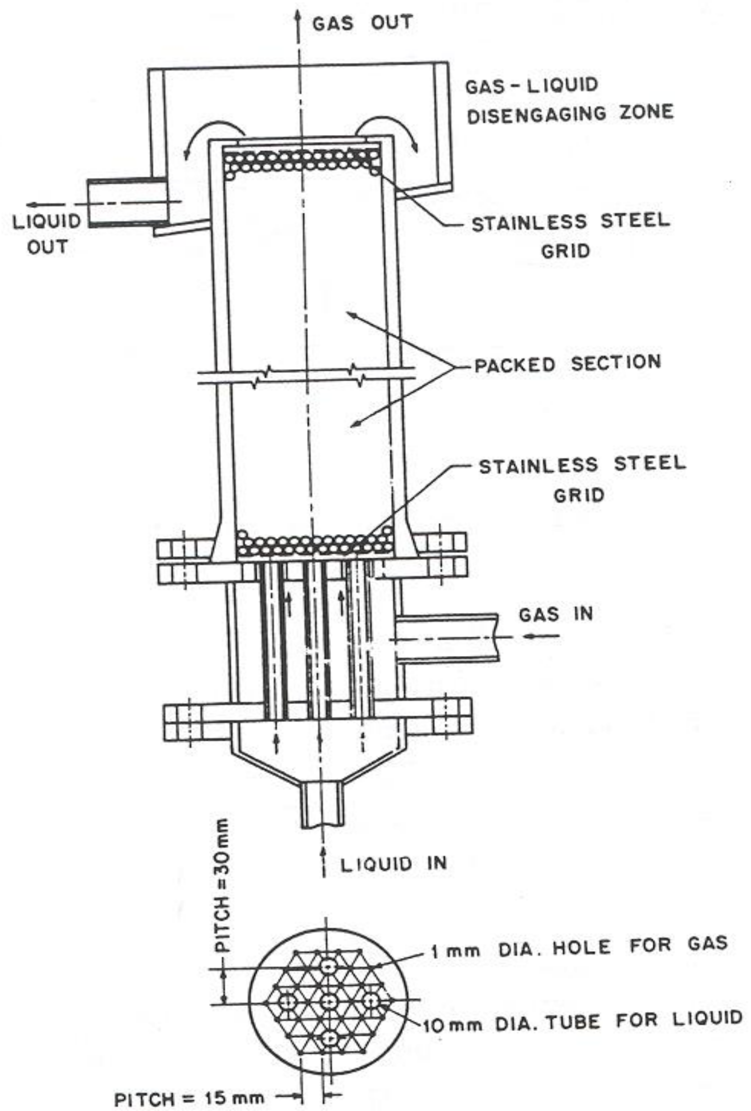
Flow chart: trickle bed



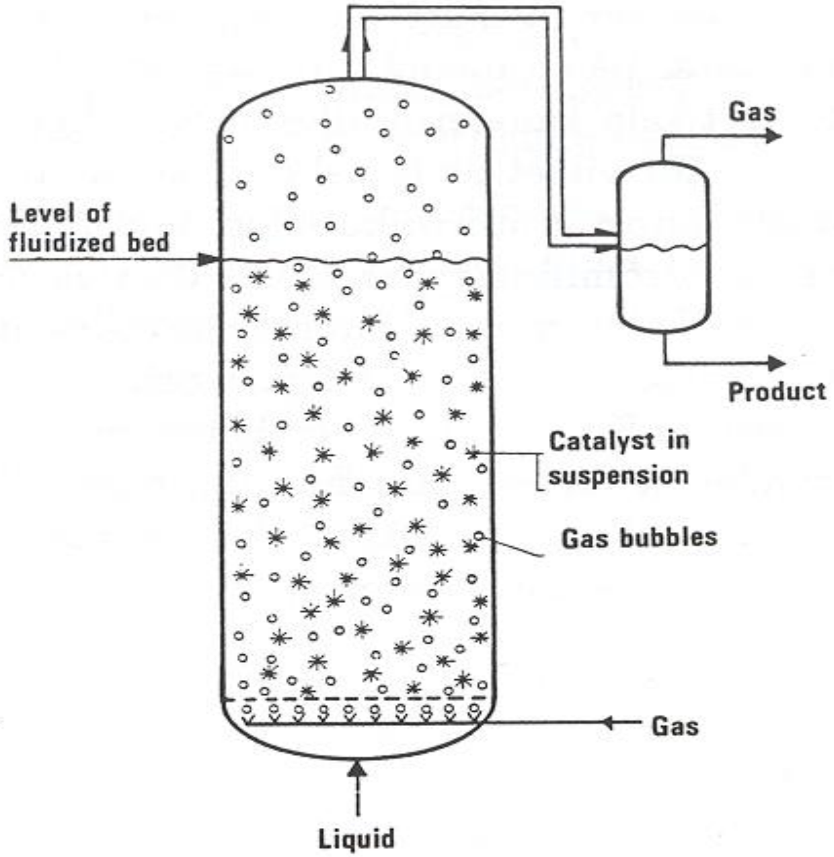
Trickle flow



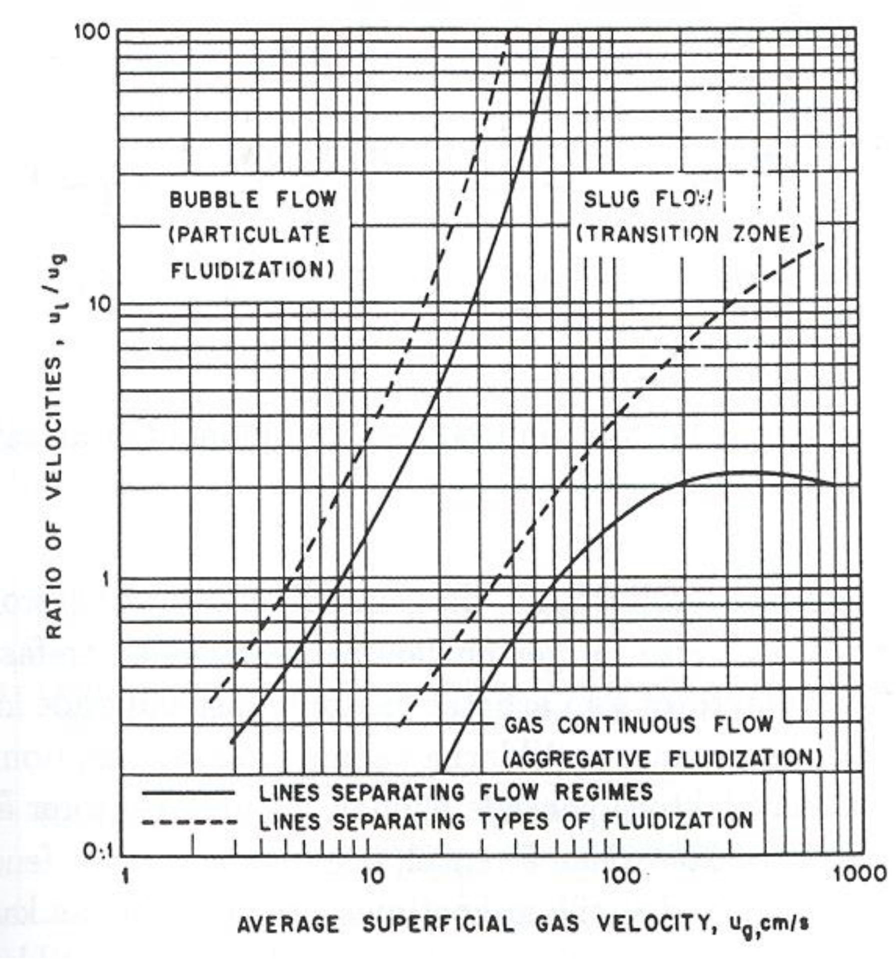
Packed bed


GAS OUT
GAS - LIQUID DISENGAGING ZONE
LIQUID OUT
STAINLESS STEEL GRID
PACKED SECTION
STAINLESS STEEL GRID
GAS IN
LIQUID IN
PITCH = 30 mm
1 mm DIA. HOLE FOR GAS
10 mm DIA. TUBE FOR LIQUID
PITCH = 15 mm

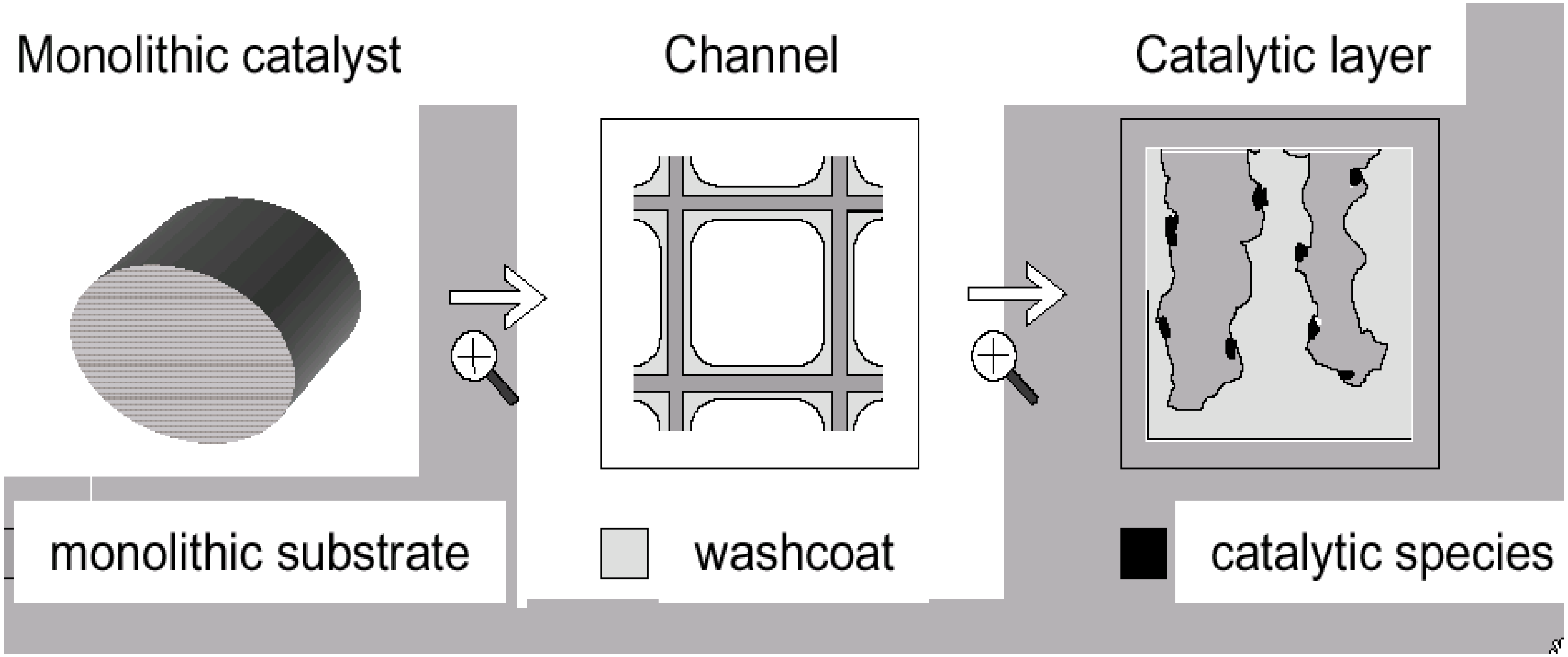
Three-phase fluidized bed



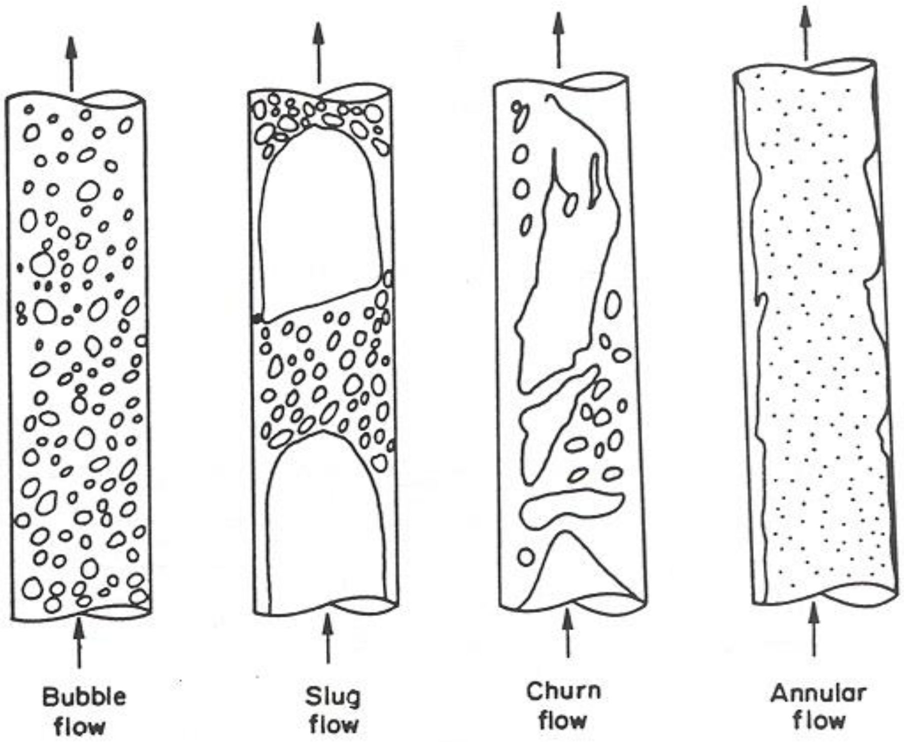
Fluidized bed – flow chart



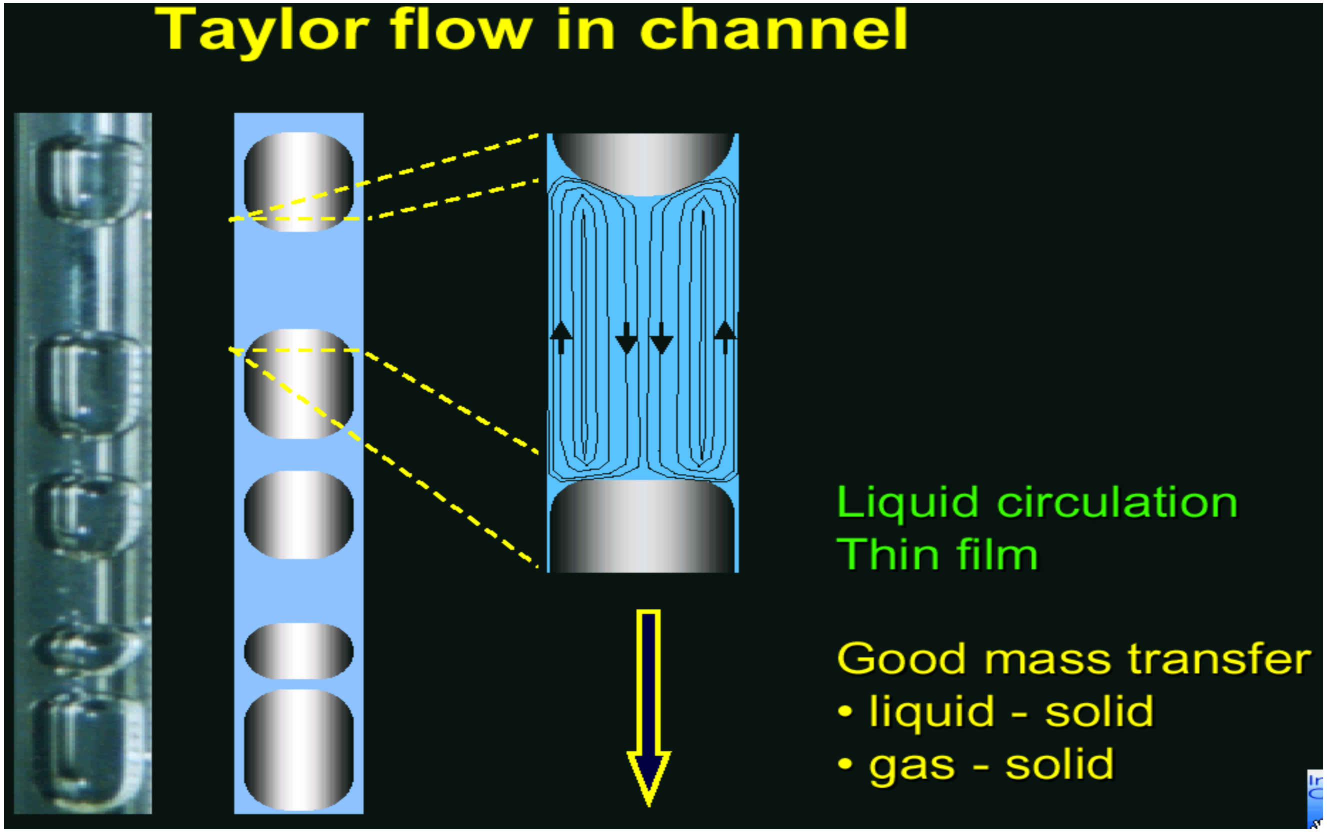
Monolith catalysts



Flow in monoliths



Monolith channel

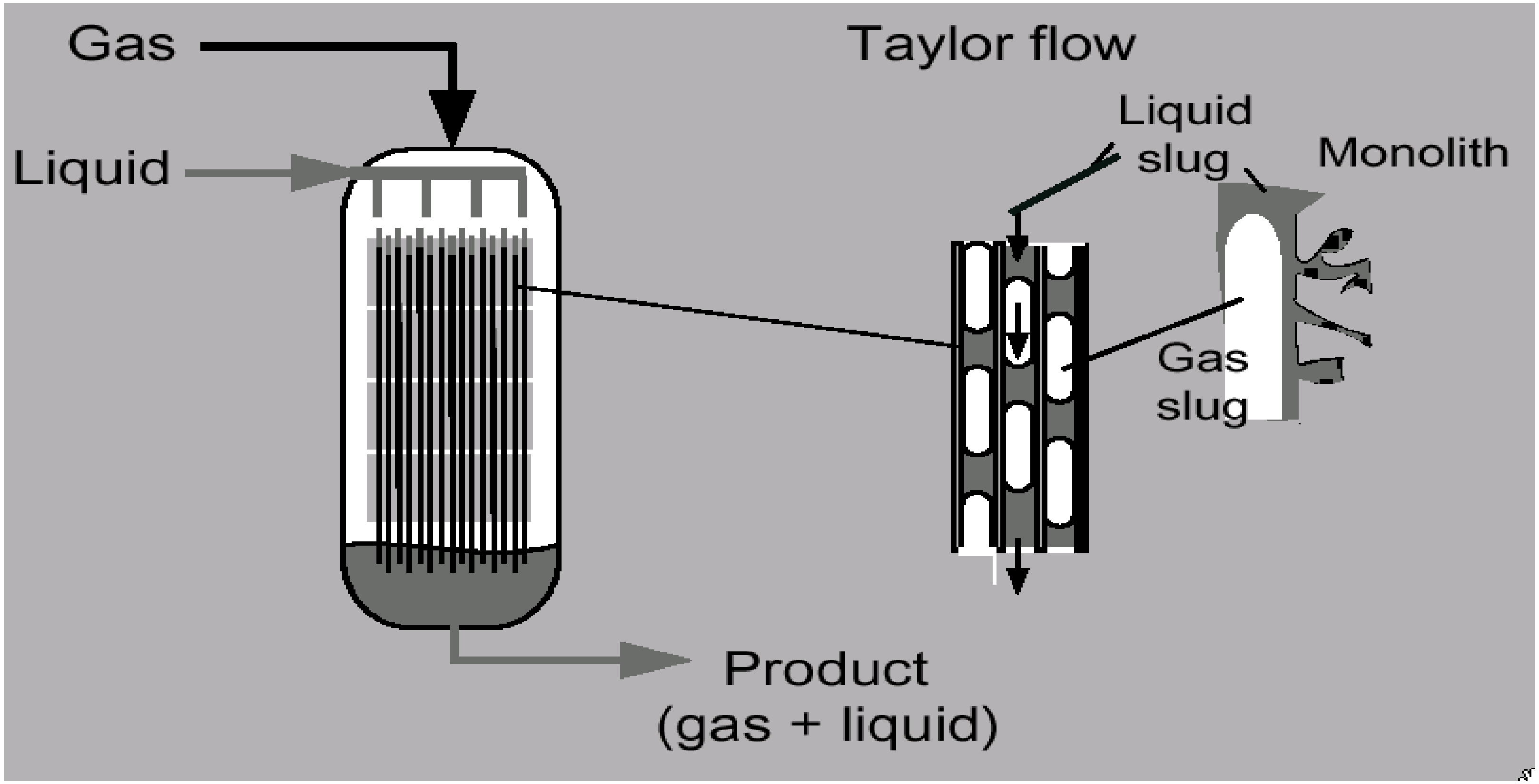


Taylor flow in channel

Liquid circulation
Thin film

Good mass transfer
- liquid - solid
- gas - solid

Three-phase monolith reactor



Three-phase reactors
Mass balances

- Plug flow and axial dispersion
  - Columnr eactor
  - Tube reactor
  - Trickle bed
  - Monolith reactor

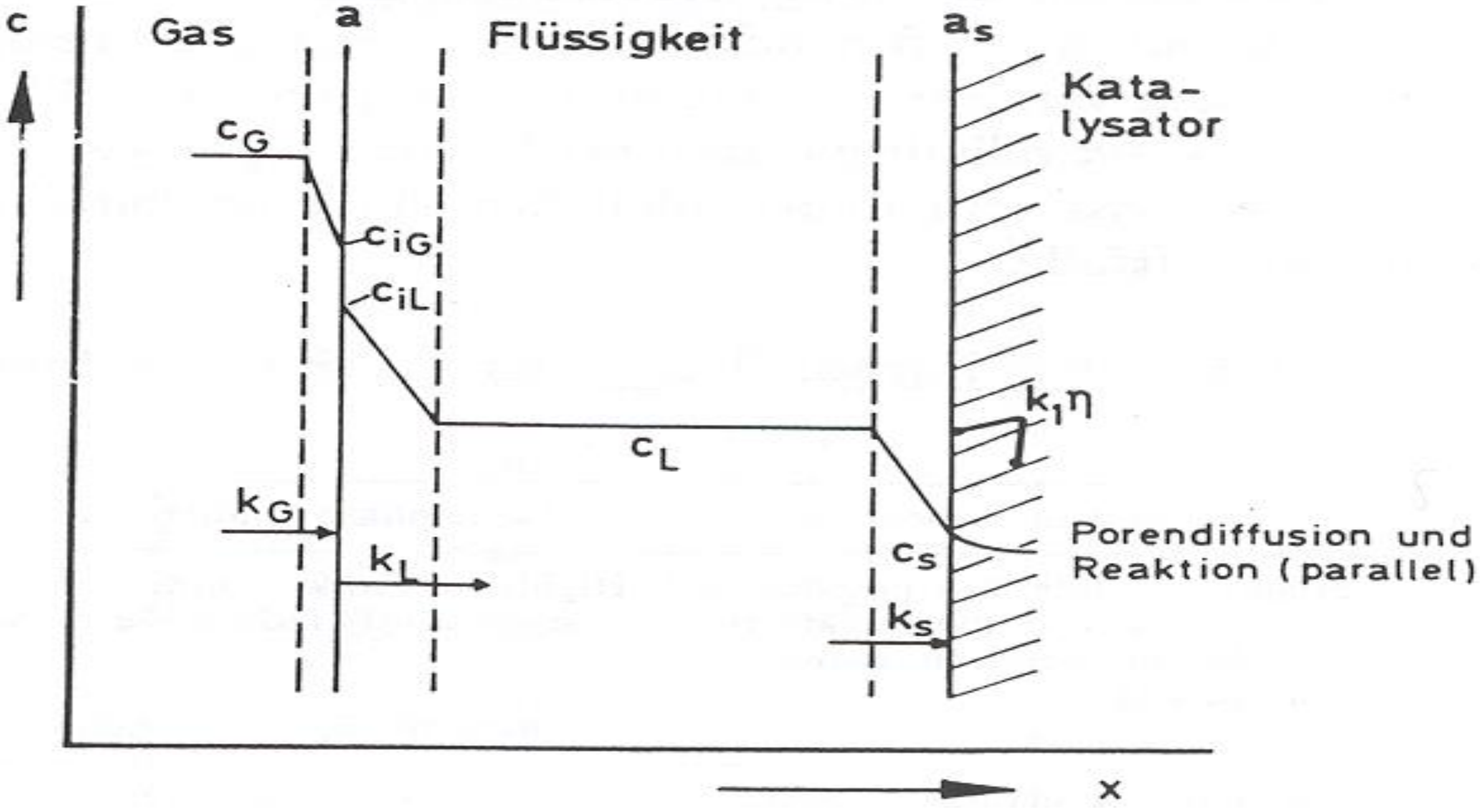
- Backmixing
  - Bubble column
  - Tank reactor

Three-phase reactor
Mass balances

- Mass transfer from gas to liquid, from liquid to catalyst surface
- Reaction on the catalyst surface
- In gas- and liquid films only diffusion transport
- Diffusion flow from gas to liquid

$$N_{Li}^{b} = \frac{c_{Gi}^{b} - K_i c_{Li}^{b}}{\frac{K_i}{k_{Li}} + \frac{1}{k_{Gi}}}$$

Three-phase reactor
Mass transfer



Three-phase reactor
Mass balances

- For physical absorption the fluxes through the gas- and liquid films are equal

$$N_{Li}^{b} = N_{Li}^{s} = N_{Gi}^{s} = N_{Gi}^{b}$$

- Flux from liquid to catalyst particle = component generation rate at steady state

$$N_{Li}^{s} A_p + r_i m_p = 0$$

Three-phase reactor
Mass balances

- Flux through the liquid film defined with concentration difference and liquid-film coefficient

$$N_{Li}^{s} = k_{Li}^{s}\left(c_{Li}^{b} - c_{Li}^{s}\right)$$

- Catalyst bulk density defined by

$$\rho_B = \frac{m_{cat}}{V_L} = \frac{m_{cat}}{\varepsilon_L V_R}$$

Three-phase reactor
Mass balances

$$N_{Li}^{s} = k_{Li}^{s}\left(c_{Li}^{b} - c_{Li}^{s}\right)a_{p} = -\varepsilon_{L}\rho_{B}r_{i}$$

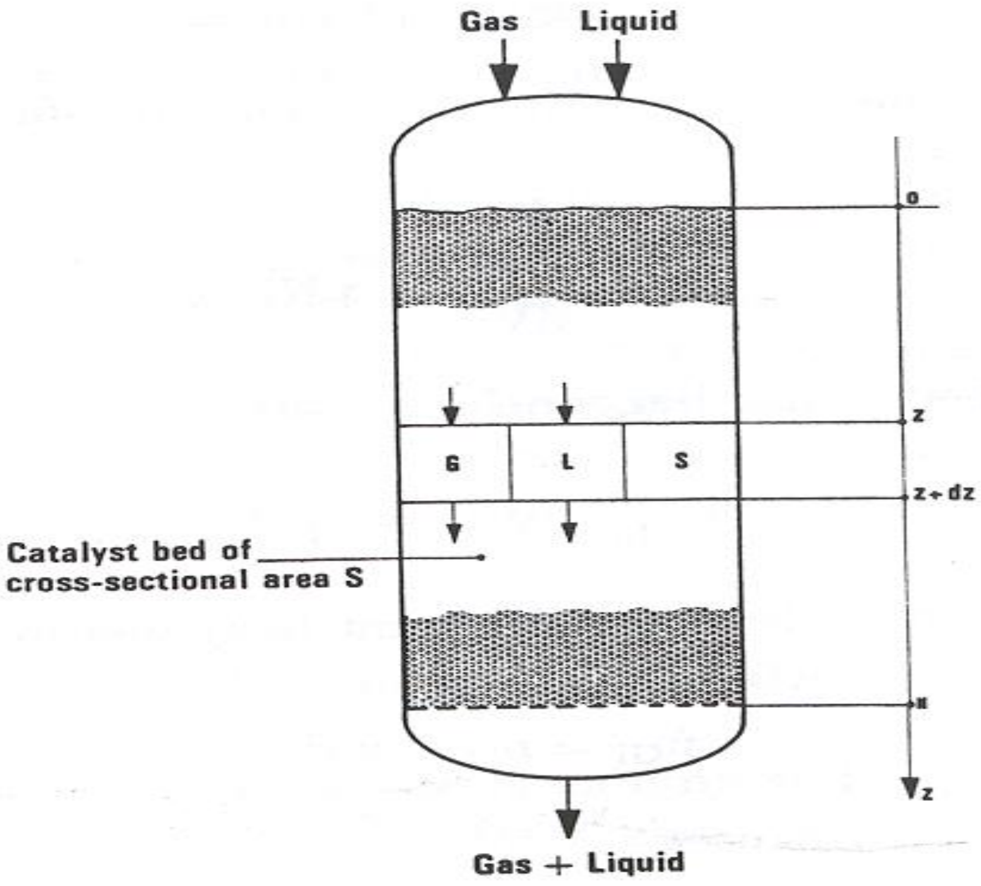
- a_p = total particle surface/reactor volume

Three-phase reactor
Mass balances

- If diffusion inside the particle affects the rate, the concept of effectiviness factor is used as for two-phase reactor (only liquid in the pores of the particles)
- The same equations as for two-phase systems can be used for porous particles

$$R_j = \eta_{ej} R_j^{'}(c_B)$$

Three-phase reactor – plug flow



Three-phase reactor
- plug flow, liquid phase

- For volume element in liquid phase

$$\dot{n}_{Li,in} + N_{Li}^{b}\Delta A = \dot{n}_{Li,ut} + N_{Li}^{s}\Delta A_{p}$$

- Liquid phase

$$\frac{d\dot{n}_{Li}}{dV_R} = N_{Li}^{b}a_{v} + N_{Li}^{s}a_{p}$$

-

Three-phase reactor
Plug flow - gas phase

- For volume element in gas phase

$$\dot{n}_{Gi,in} = \dot{n}_{Gi,ut} + N_{Gi}^{b}\Delta A$$

- Gas phase

$$\frac{d\dot{n}_{Gi}}{dV_R} = \pm N_{Li}^{b} a_v$$

- - concurrent
- + countercurrent

Three-phase reactor
Plug flow

- Initial conditions
  - Liquid phase

$$\dot{n}_{Li} = \dot{n}_{0,Li} \qquad V_R = 0$$

  - Gas phase, concurrent

$$\dot{n}_{Gi} = \dot{n}_{0,Gi} \qquad V_R = 0$$

  - Gas phase, countercurrent $\dot{n}_{Gi} = \dot{n}_{0,Gi} \qquad V = V_R$

Three-phase reactor
- plug flow model

- Good for trickle bed
- Rather good for a packed bed , in which liguid flows upwards
- For bubble column plug flow is good for gas phase but not for liquid phase which has a higher degree of backmixing

Three-phase reactor
- complete backmixing

- Liquid phase

$$\frac{\dot{n}_{Li} - \dot{n}_{0Li}}{V_R} = N_L^b a_v - N_L^s a_p$$

- Gas phase

$$\frac{\dot{n}_{Gi} - \dot{n}_{0Gi}}{V_R} = N_L^b a_v$$

Three-phase reactor
- semibatch operation

- Liquid phase in batch
- Gas phase continuous

$$\frac{dn_{Li}}{dt} = \left(N_L^b a_v - N_L^s a_p\right) V_R$$

$$\frac{dn_{Gi}}{dt} = -\dot{n}_{Gi} - N_{Li}^b a_v V_R + \dot{n}_{0Gi}$$

- Initial condition

$$n_{Li} = n_{0Li} \qquad t = 0$$

$$n_{Gi} = n_{0Gi} \qquad t = 0$$

Parameters in three-phase reactors

- Gas-liquid equilibrium ratio (K_i) from
  - Thermodynamic theories
  - Gas solubility in liquids (Henry's constant)

- Mass transfer coefficients k_{Li}, k_{Gi}
  - Correlation equations

$$k_{Li} = \frac{D_{Li}}{\delta_L} \qquad k_{Gi} = \frac{D_{Gi}}{\delta_G}$$

Numerical aspects

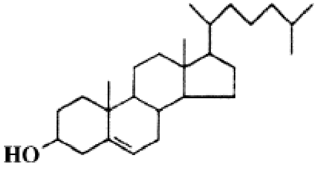
- CSTR – non-linear equations
  - Newton-Raphson method
- Reactors with plug flow (concurrent)
  - Runge-Kutta-, Backward difference -methods
- Reactors with plug flow (countercurrent) and reactors with axial dispersion (BVP)
  - orthogonal collocation

Examples

- Production of Sitostanol
  - A cholesterol suppressing agent
  - Carried out through hydrogenation of Sitosterol on Pd catalysts (Pd/C, Pd/Zeolite)

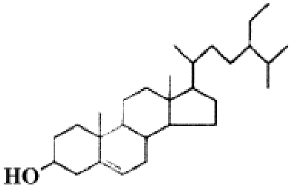
- Production of Xylitol
  - An anti-caries and anti-inflamatory component
  - Carried out through hydrogenation of Xylose on Ni- and Ru-catalysts (Raney Ni, Ru/C)

Exemple: from cholesterol tol sitostanol

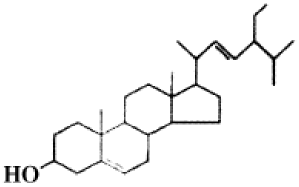


Cholesterol

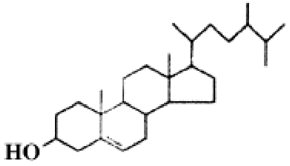
Phytosterols



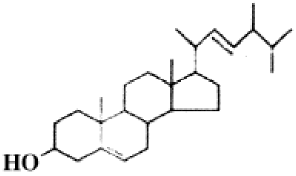
β-Sitosterol



Stigmasterol

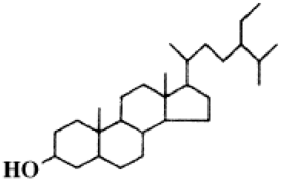


Campesterol

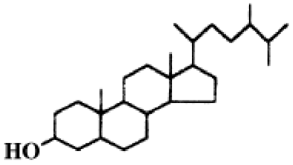


Brassicasterol

Phytostanols



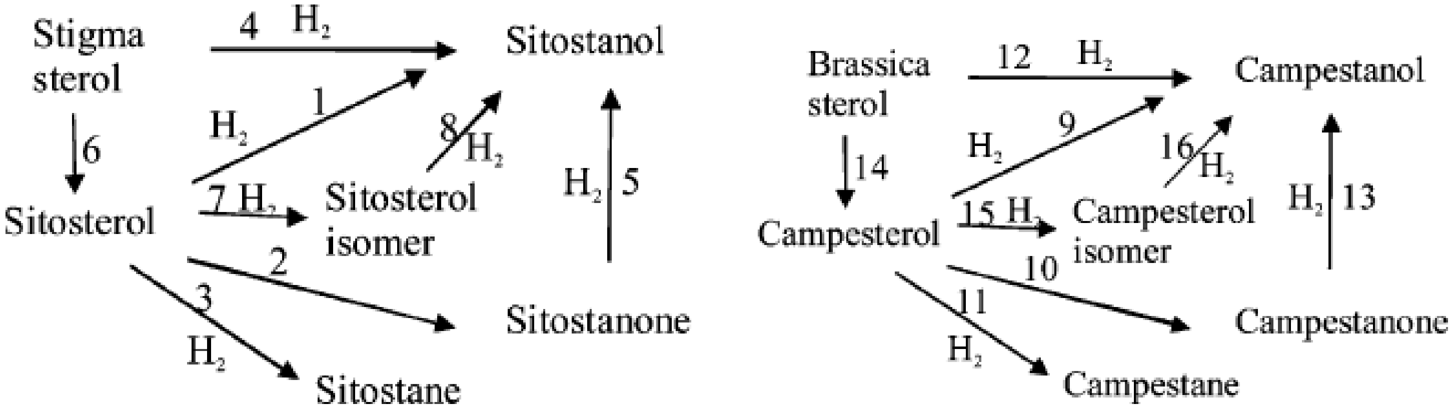
β-Sitostanol



Campestanol

Reaction scheme

A superficially complicated scheme



From laboratory scale to industrial scale

Slurry, three-phase reactor

Lab reactor, 1 liter, liquid amount 0.5 kg

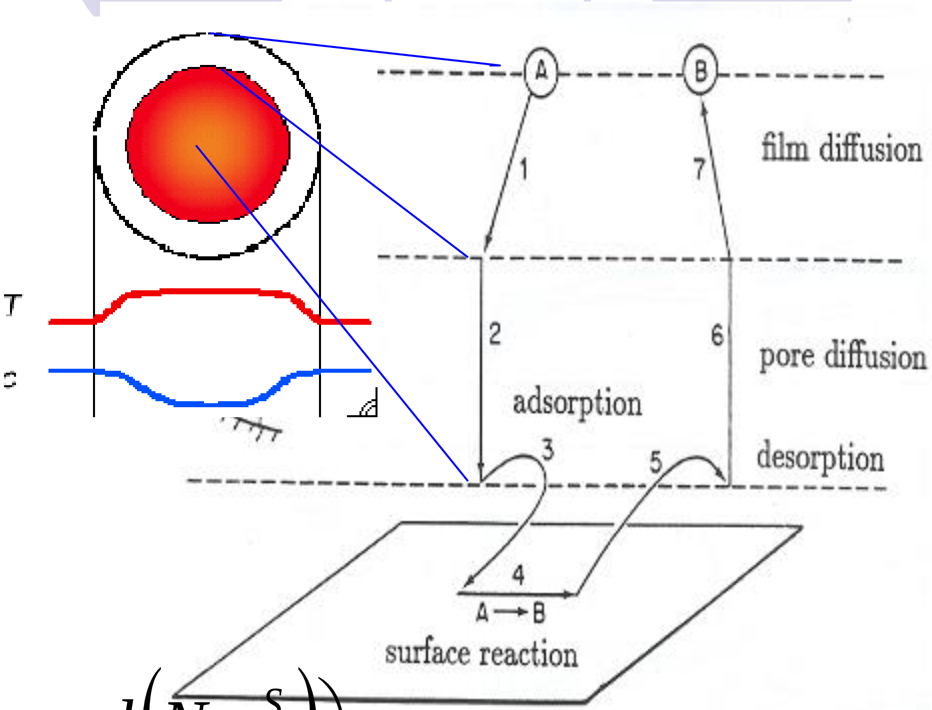
Large scale reactor, liquid amount 8080 kg

Simulation of large-scalle reactor based on laboratory reactor

Catalytic reactor

- Semi-batch stirred tank reactor
  - Well agitated, no concentration differences appear in the bulk of the liquid
  - Gas-liquid and liquid-solid mass transfer resistances can prevail
  - The liquid phase is in batch, while gas is continuously fed into the reactor.
  - The gas pressure is maintained constant.
  - The liquid and gas volumes inside the reactor vessel can be regarded as constant

Mathematical modelling



Reaction, diffusion and catalyst deactivation in porous particles

Particle model $$\frac{dc_i}{dt} = \varepsilon_p^{-1}\left(r_i \rho_p - r^S \frac{d\left(N_i r^S\right)}{dr} \right)$$

Rates $$r_i = \sum_j \nu_{ij} R_j a_j$$

Model implementation

$$N_i = -D_{ei}\left(\frac{dc_i}{dr}\right)$$, where $D_{ei}=(\varepsilon_p/\tau_p)D_{mi}$

$$\frac{dc_i}{dt}\varepsilon_p^{-1} = \left(\rho_p \sum \nu_{ij} R_j a_j + D_{ei}\left(\frac{d^2 c_i}{dr^2} + \frac{s}{r}\frac{dc_i}{dr}\right)\right)$$

Boundary conditions

$$\frac{dc_i}{dr} = 0 \qquad r = 0$$

$$D_{ei}\left(\frac{dc_i}{dt}\right)_{r=R} = k_{Li}\left(c_i - c_i(R)\right) \qquad r = R$$

Catalytic reactor, mass balances

Liquid phase mass balance

$$\frac{dc_i}{dt} = N_i a_p - N_{GLi} a_{GL}$$

Liquid-solid flux

$$N_i = k_{Li}\left(c_i - c_i\left(R\right)\right)$$

Gas-liquid flux

$$N_{GLi} = \frac{c_{Gi}^{b} - K_i c_{Li}^{b}}{\frac{K_i}{k_{Li}} - \frac{1}{k_{Gi}}}$$

Numerical approach

- PDEs discretizied with finite difference formulae
- The ODEs created solved with a stiff algorithm (BD, Hindmarsh)

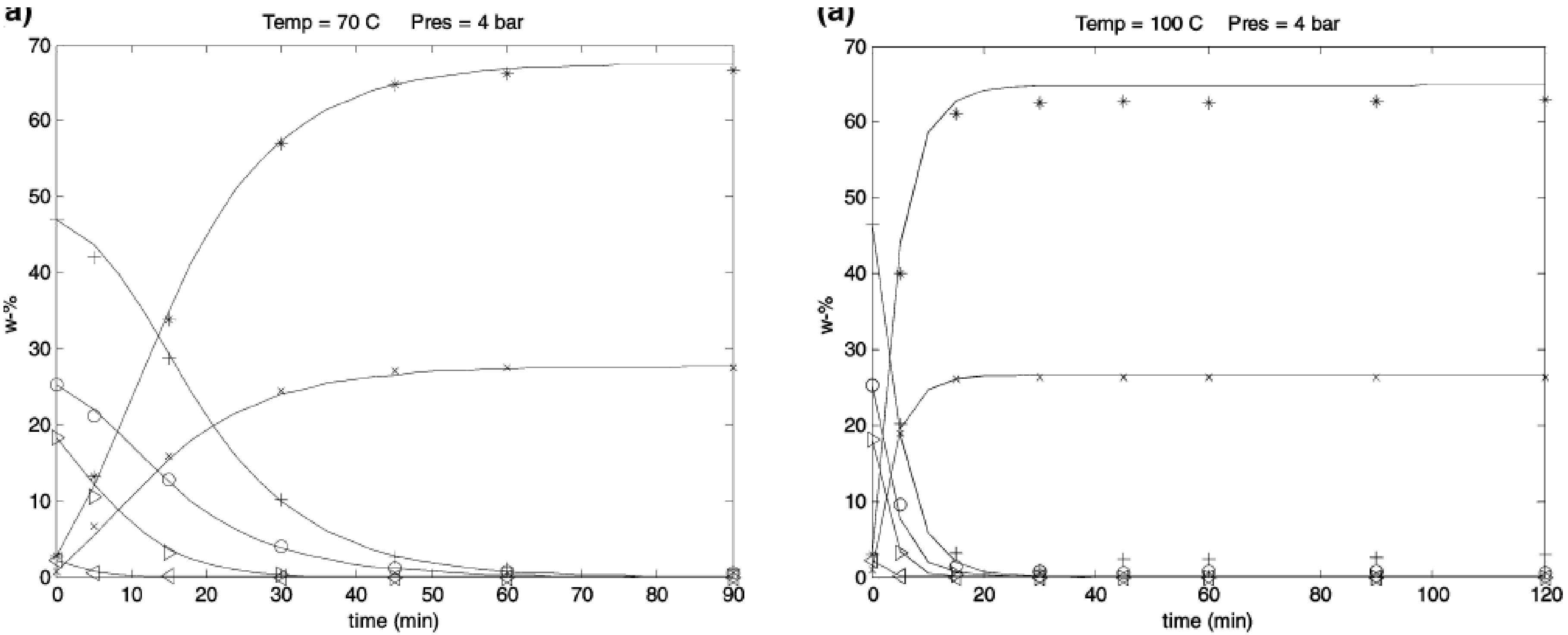
Rate equations

Surface reaction, rate determining

Essentially non-competetive adsorption of hydrogen and organics

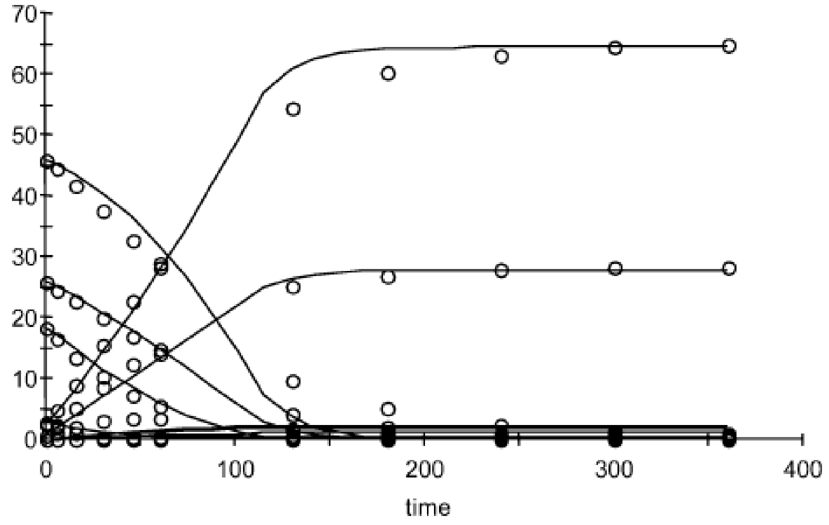
$$r_j = \frac{k'_j K_A K_{H_2} c_j c_{H_2}}{(1 + \sum K_i c_i)(1 + K_{H_2} c_{H_2})}$$

Kinetics in laboratory scale

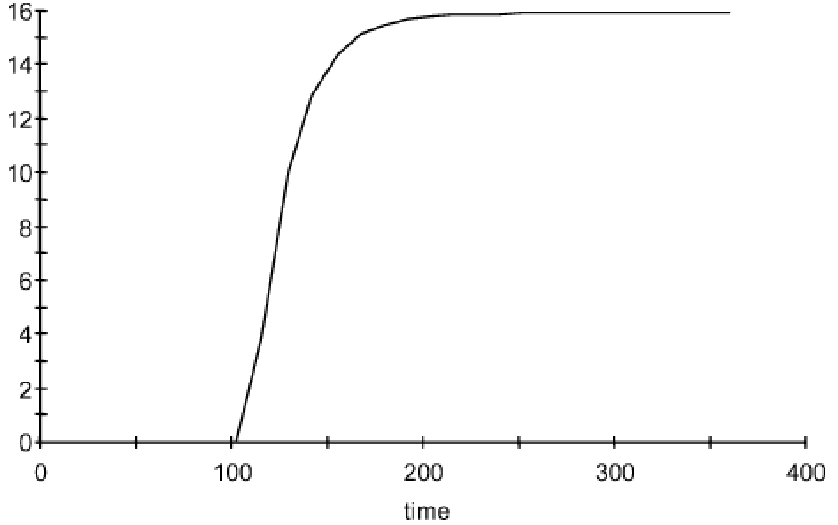


Concentrations as a function of reaction time

Kinetics in plant scale

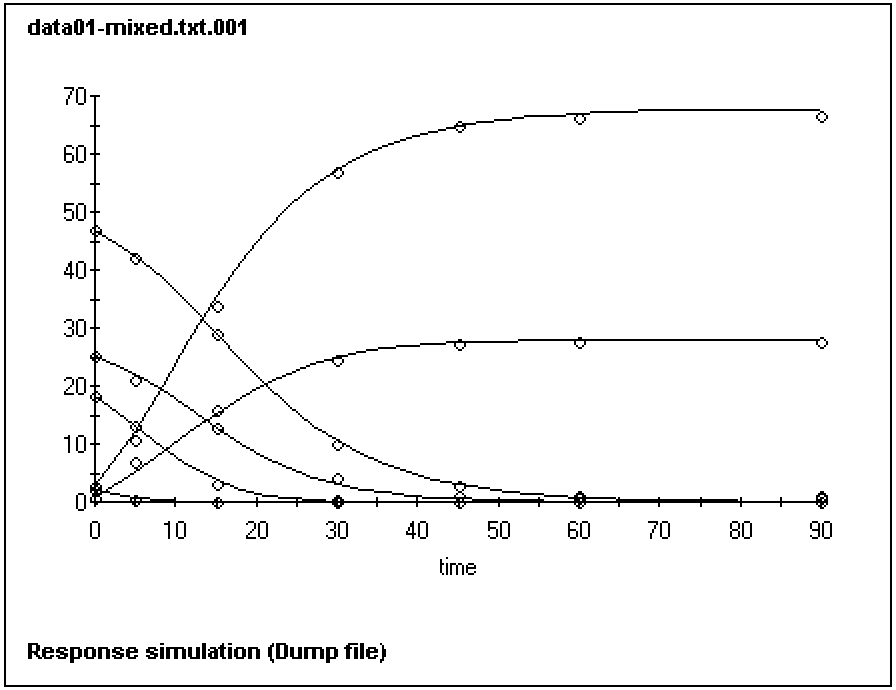


Concentration of organics

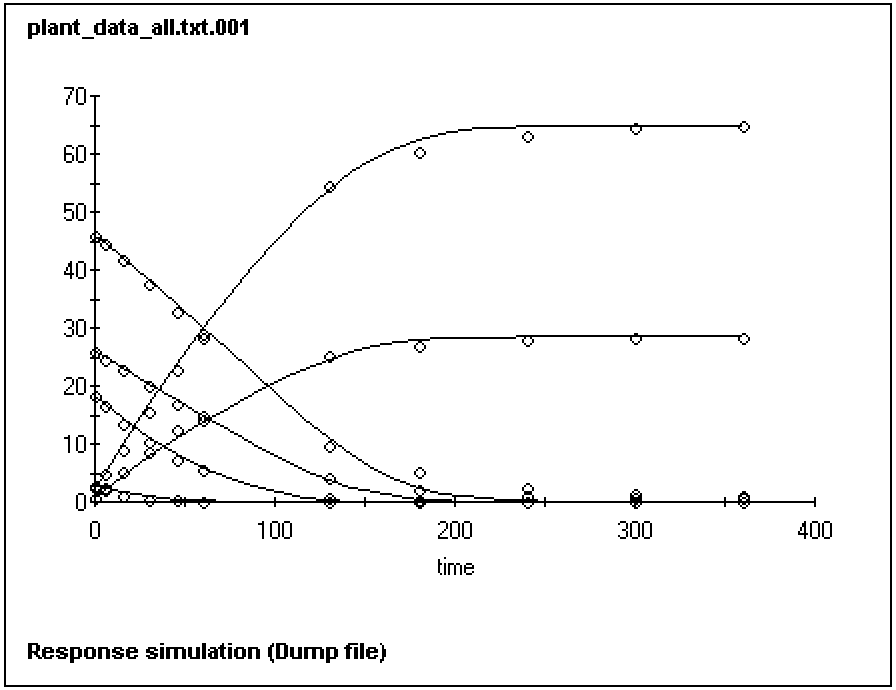


Hydrogen concentration in liquid phase

Comparison of lab and plant scale

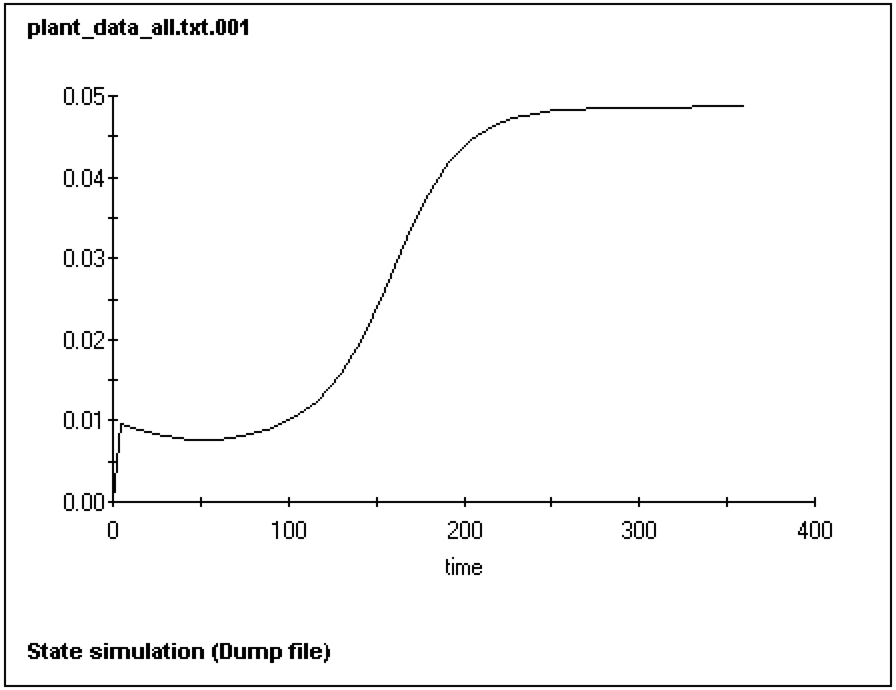


Laboratory

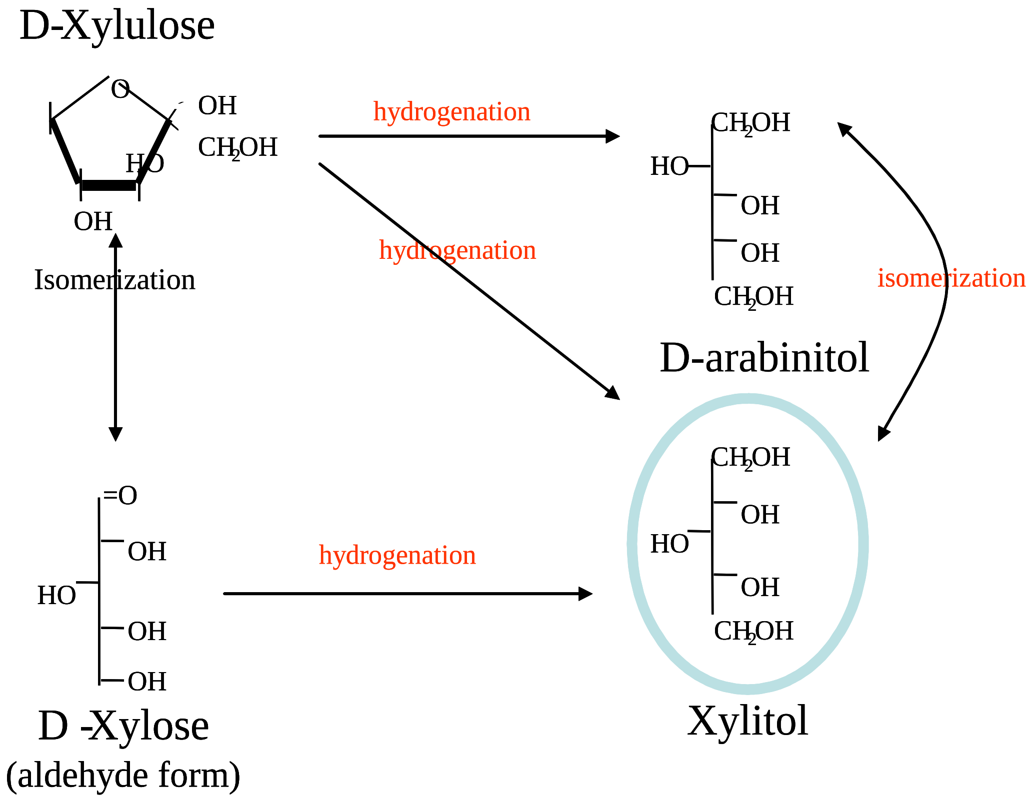


Factory

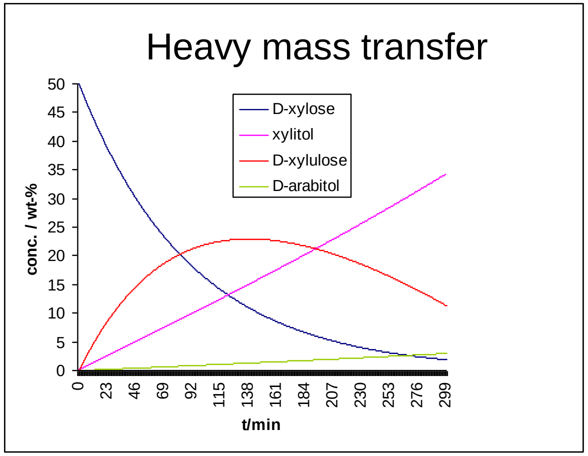
Hydrogen concentration in liquid phase in plant scale



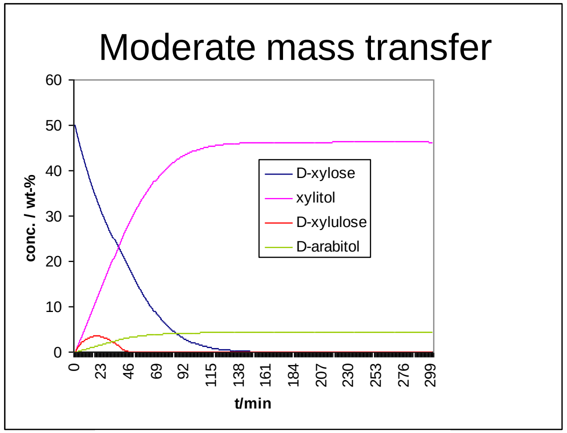
Hydrogenation of Xylose

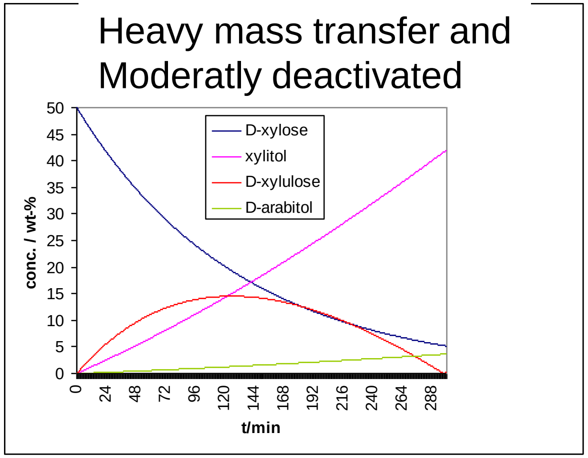


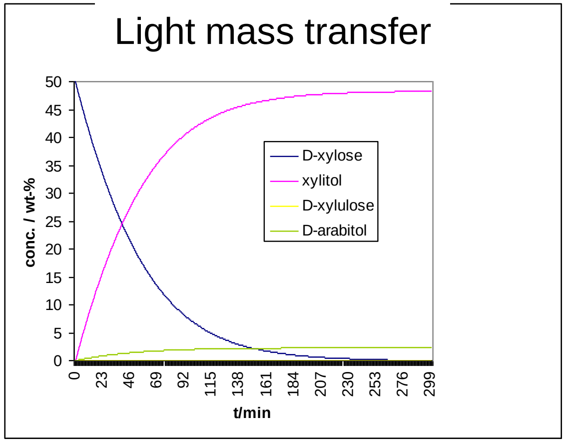
Modelling results
Xylose hydrogenation


Heavy mass transfer

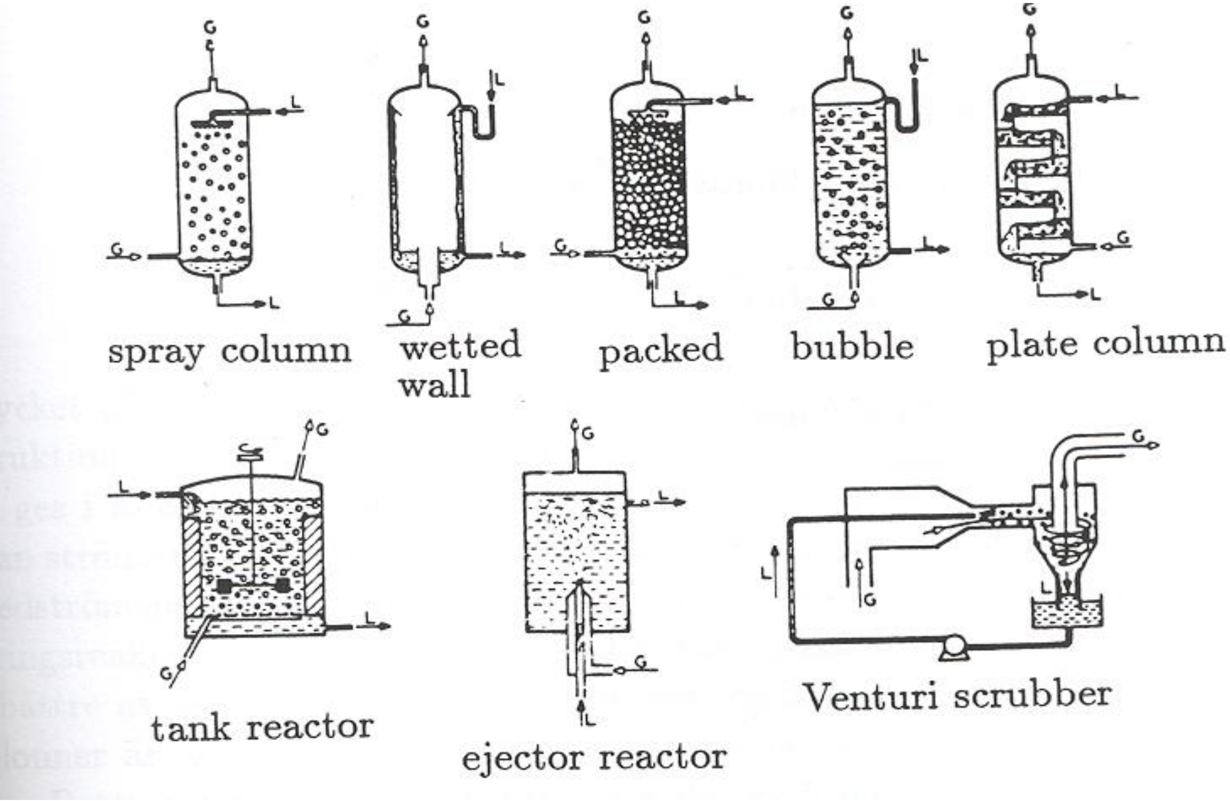
Effect of external mass transfer


Moderate mass transfer


Heavy mass transfer and Moderatly deactivated


Light mass transfer

Gas-liquid reactors



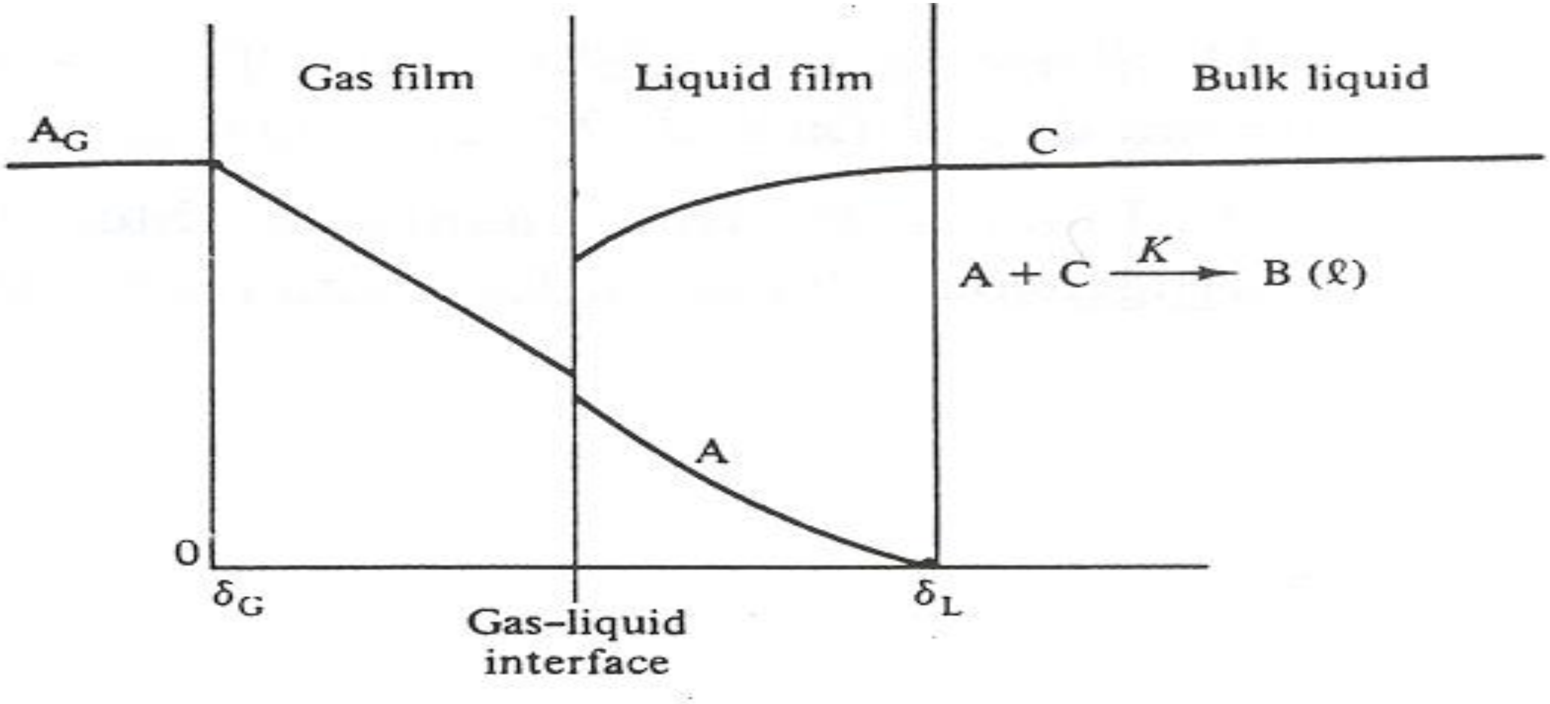
Gas-liquid reactors

- Non-catalytic or homogeneously catalyzed reactions
    - Gas phase
    - Liquid phase (+ homogeneous catalyst)
- Components i gas phase diffuse to the gas-liquid boundary and dissolve in the liquid phase
- Procukt molecules desorb from liquid to gas or remain in liquid

Gas-liquid reactions

- Synthesis of chemicals
- Gas absorption, gas cleaning
- Very many reactor constructions used, depending on the application

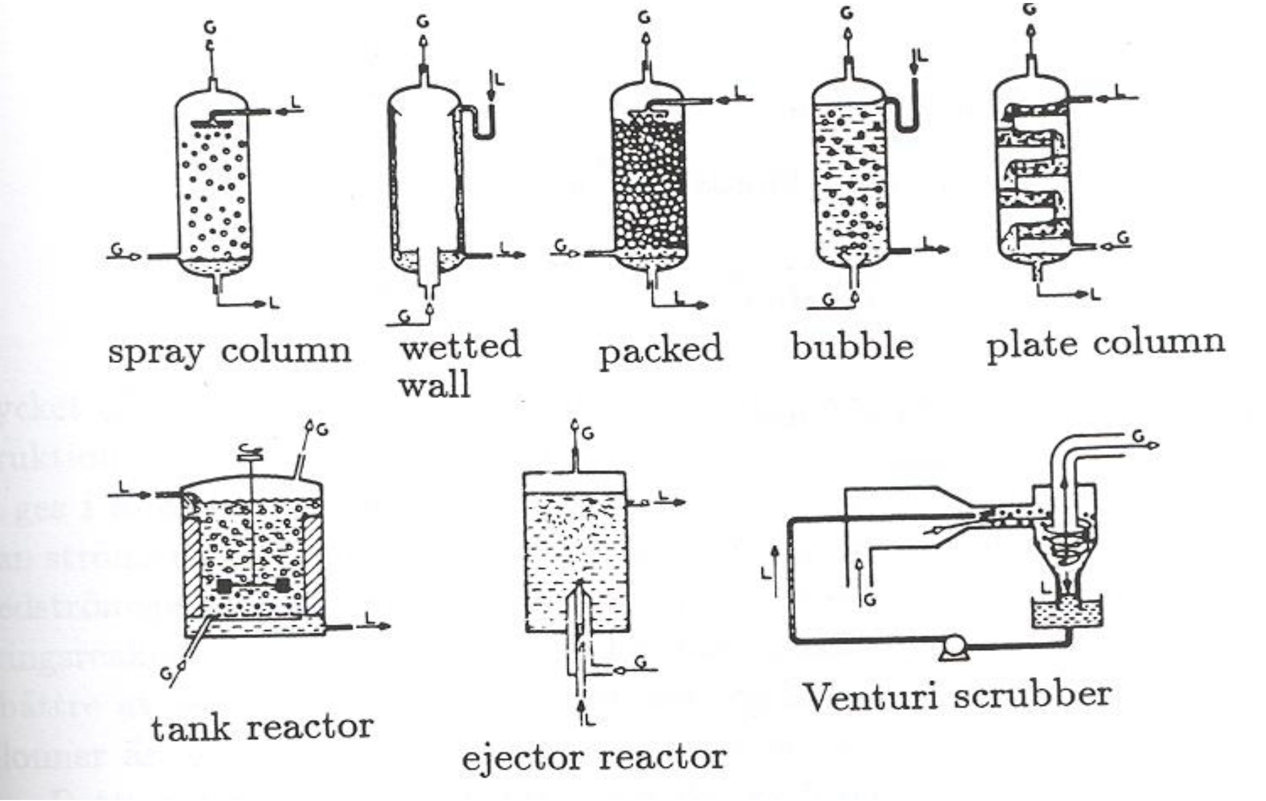
Gas-liquid reaction: basic principle



Gas-liquid reactor constructions

- Spray column
- Wetted wall column
- Packed column
- Plate column
- Bubble columns
- Continuous, semibatch and batch tank reactors
- Gas lift reactors
- Venturi scrubbers

Gas-liquid reactors - overview



spray column

wetted wall

packed

bubble

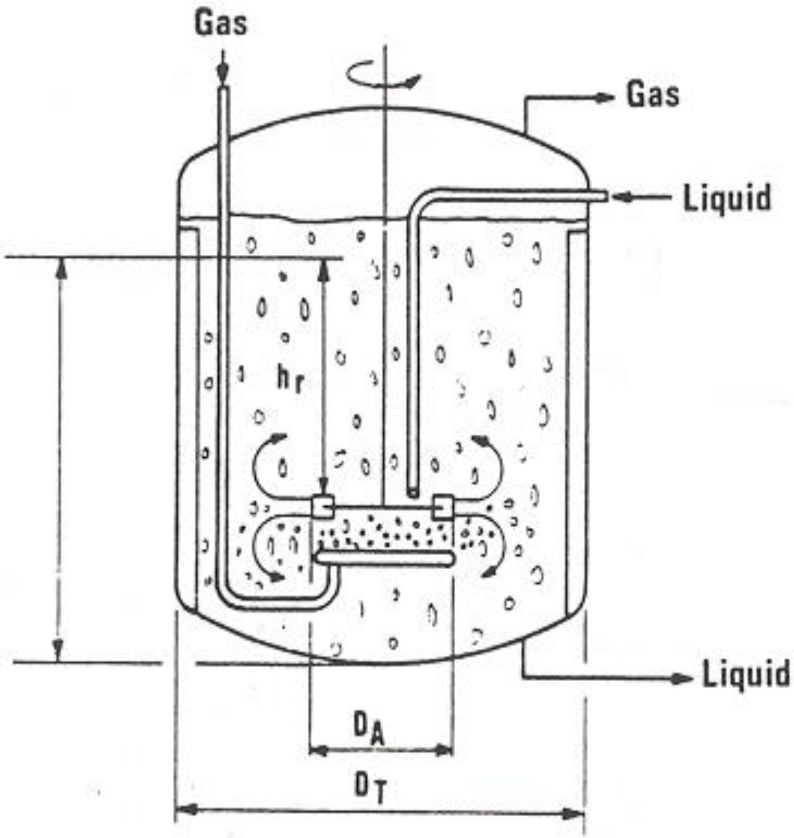
plate column

tank reactor

ejector reactor

Venturi scrubber

Tank reactor



Gas-liquid reactors

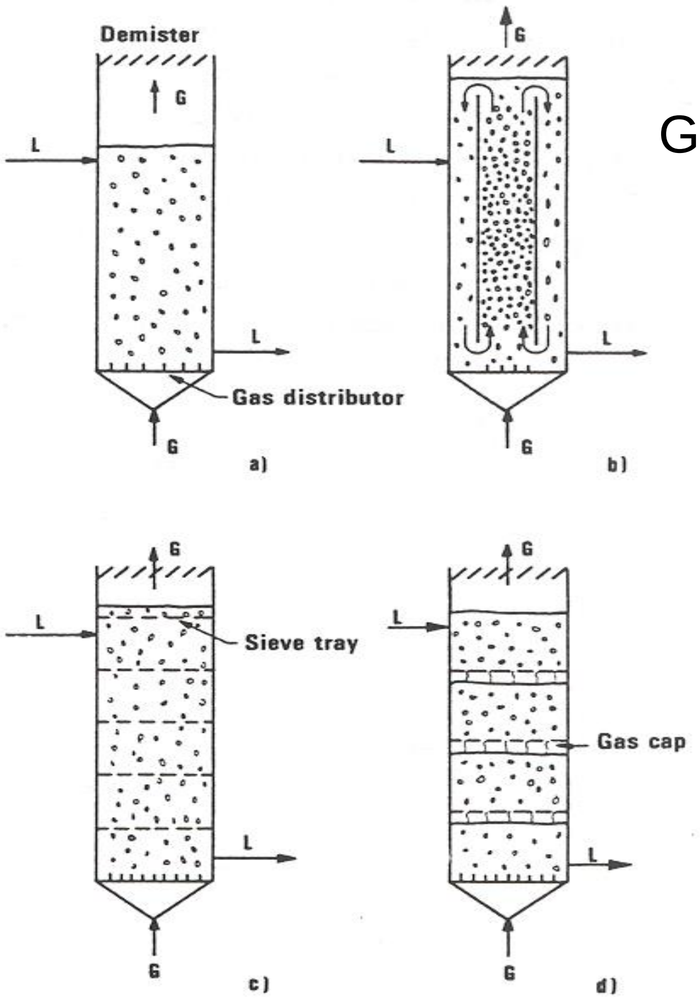
- Packed column
  - Absorption of gases
  - Countercurrent principle: gas upwards, liquid downwards
  - Column packings
    - enable a large gas-liquid contact area
    - made of ceramics, plastics or metal
    - good gas distribution because of packings
    - channeling can appear in liquid phase; can be handled with distribution plates
  - Plug flow in gas and liquid phases

Gas-liquid reactors

- Plate column
  - Absorption of gases
  - Countercurrent
  - Various plates used as in distillation, e.g.
    - Bubble cap
    - Plate column

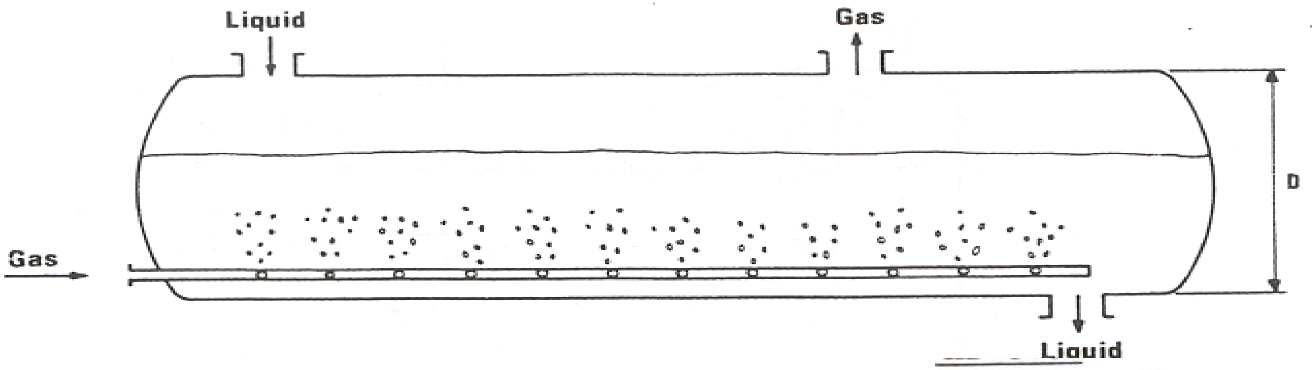
- Packed column
  - Absorption of gases
  - Countercurrent
  - A lot of column packings available; continuous development

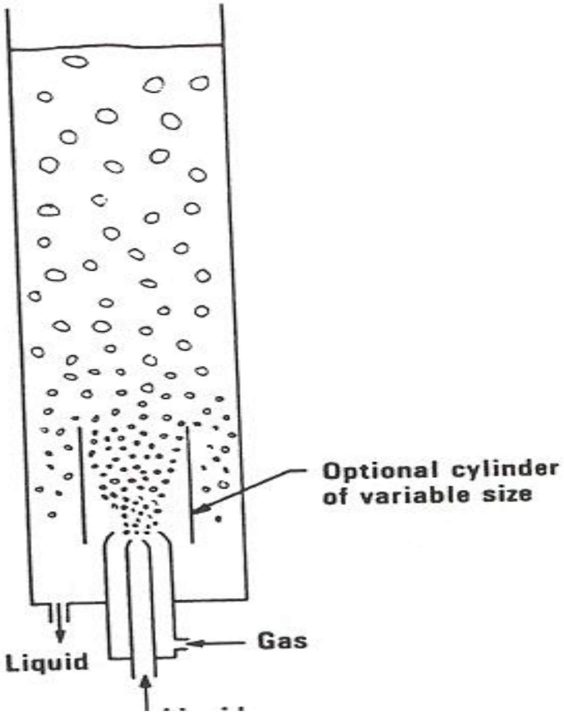
Bubble column



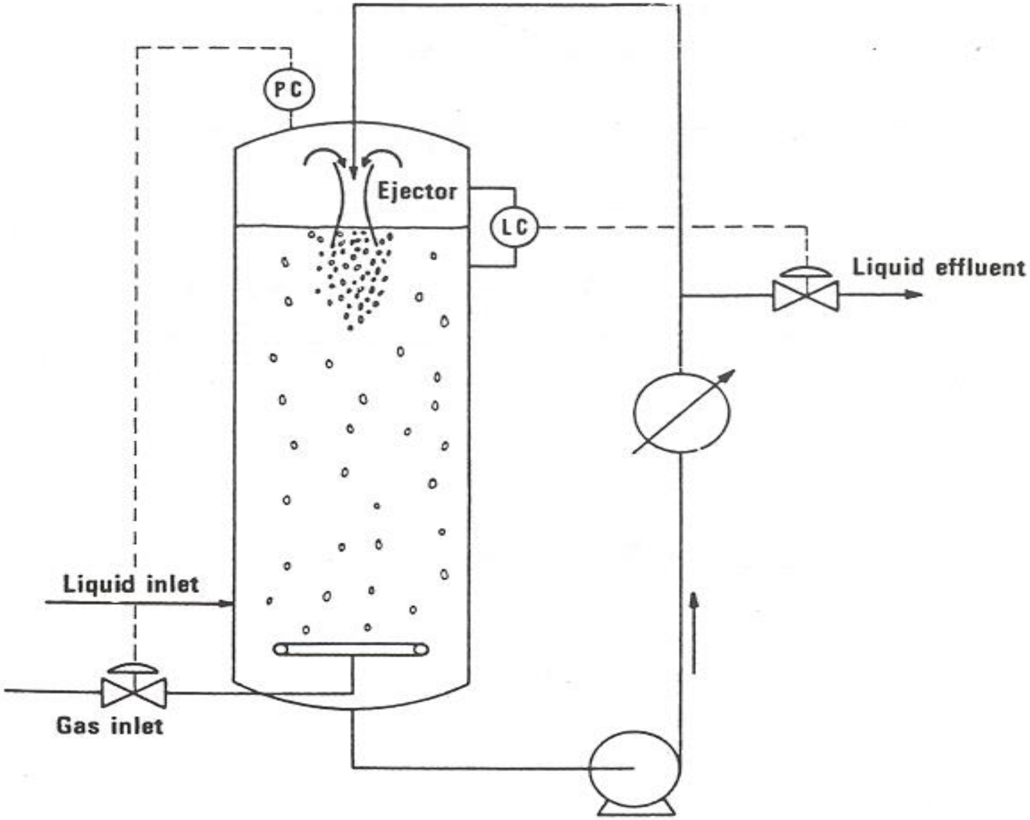
Gas-lift -reactor

Bubble column – design examples

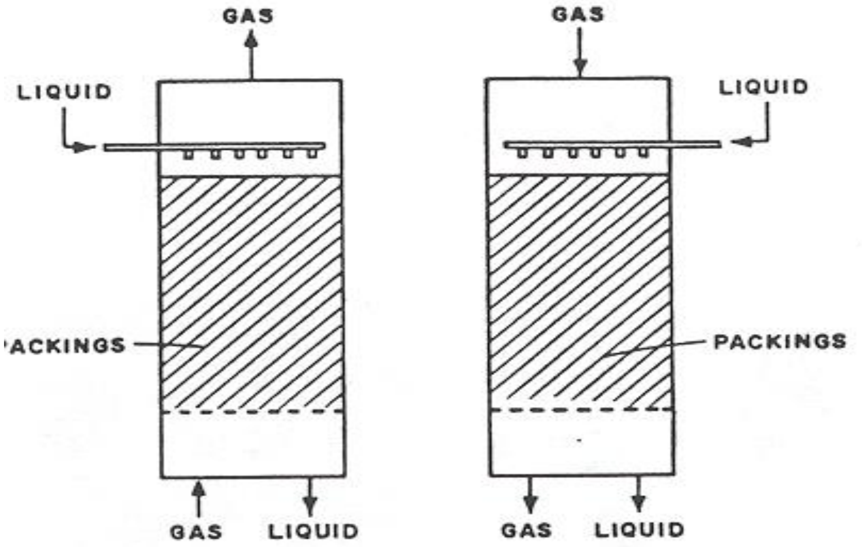




Bubble column



Packed column



(i) COUNTER-CURRENT FLOW

(ii) CO-CURRENT DOWNWARD FLOW

(a) PACKED COLUMN

CONTINUOUS PHASE : GAS
DISPERSED PHASE : LIQUID
PACKING : USUALLY AN INERT MATERIAL

Packings

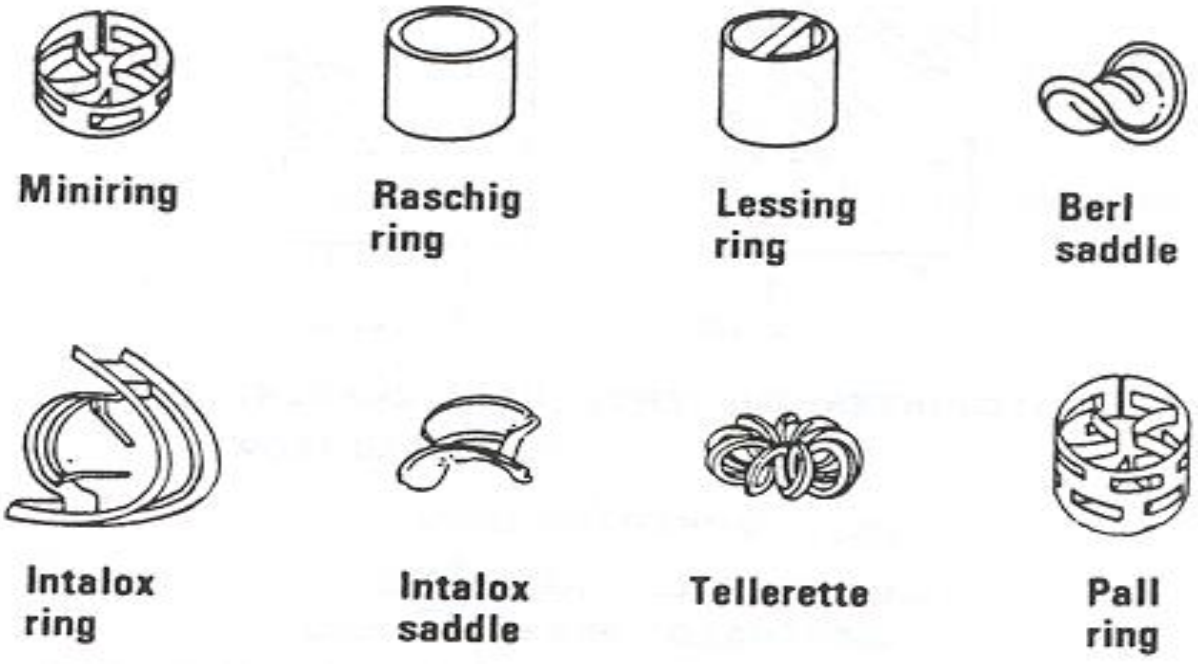
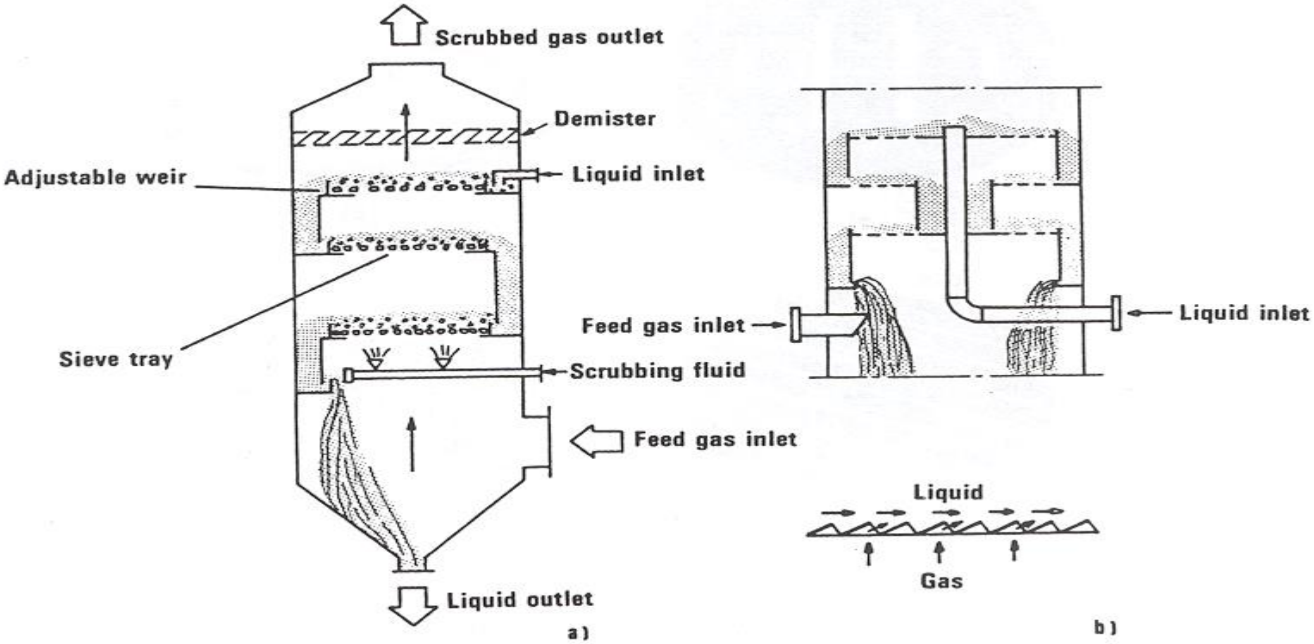

Miniring
Raschig ring
Lessing ring
Berl saddle
Intalox ring
Intalox saddle
Tellerette
Pall ring

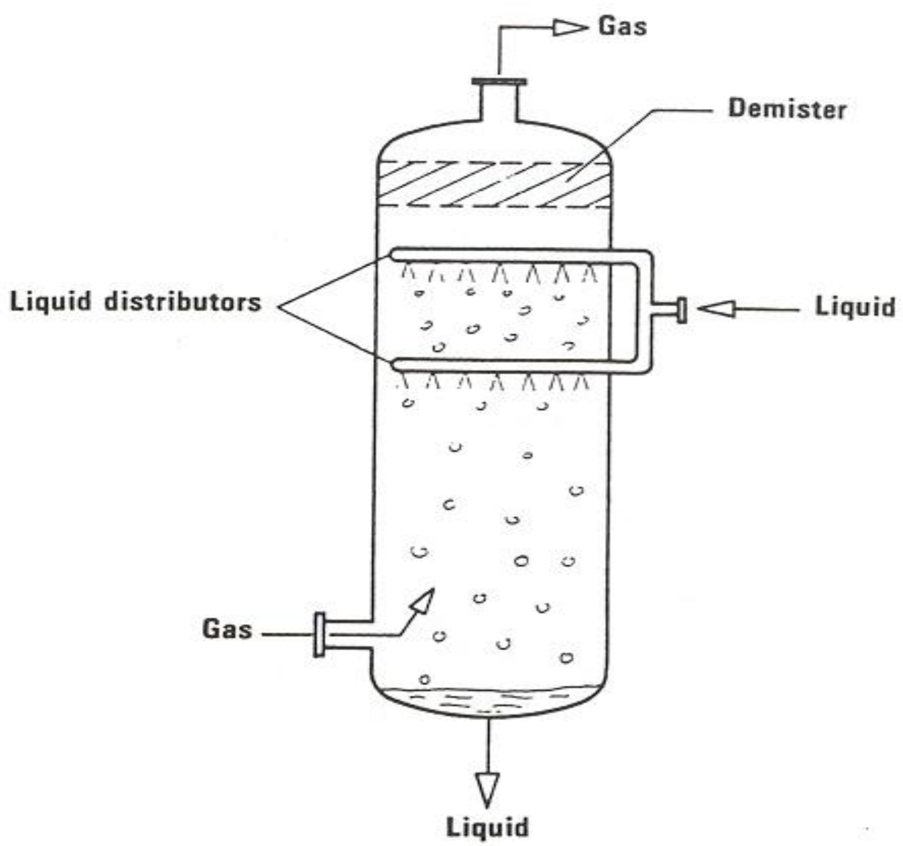
Plate column



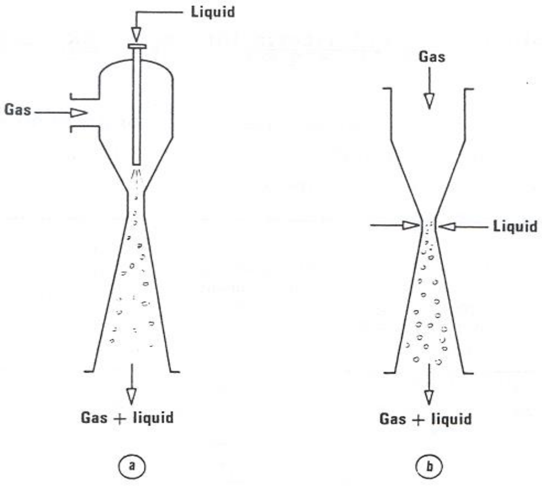
Gas-liquid reactors

- Gas scrubbers
  - Spray tower
    - Gas is the continuous phase
    - In shower !
  - Venturi scrubber
    - Liquid dispergation via a venturi neck
- For very rapid reactions

Spray tower

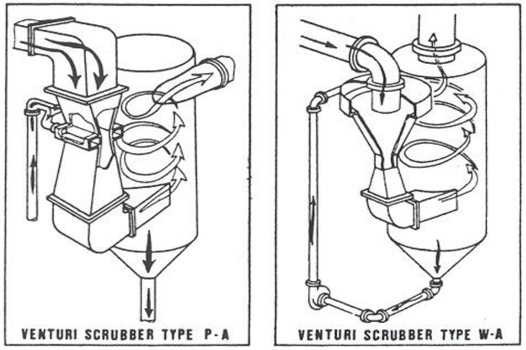


Venturi scrubber



ⓐ Ejector

ⓑ Venturi

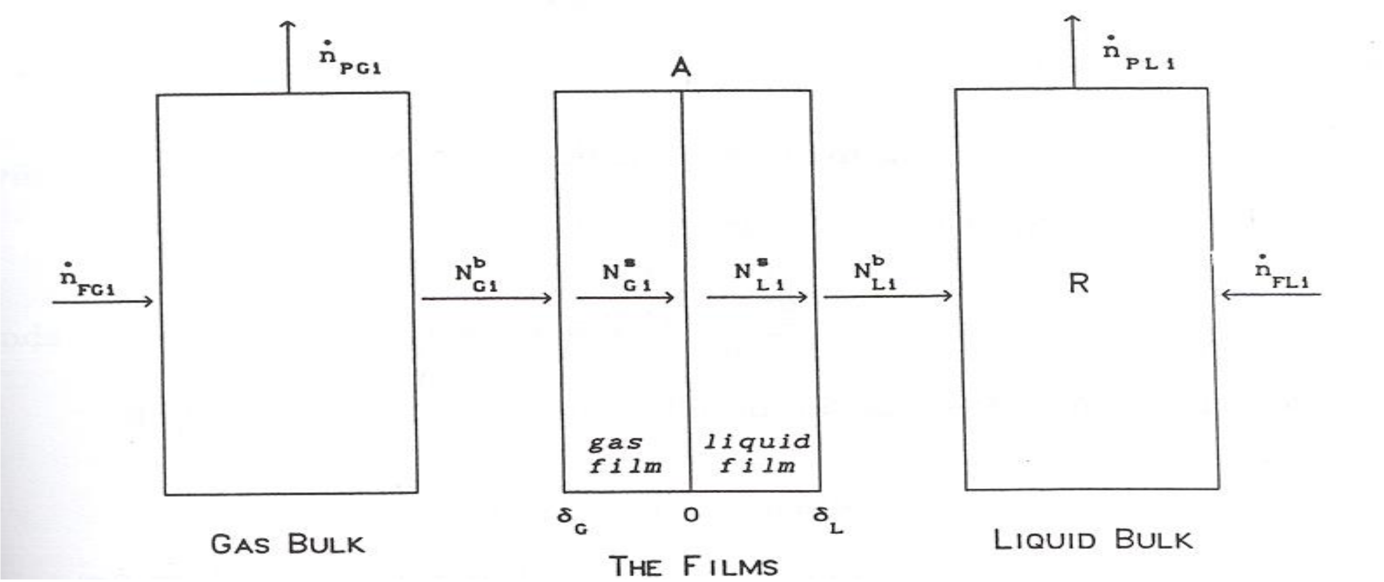


Technological details of Venturi scrubbers.
Type PA, with liquid injection by nozzles.
Type WA, with liquid stripping at neck.

Gas-liquid reactors

- Selection criteria
  - Bubble columns for slow reactions
  - Sckrubbers or spray towers for rapid reactions
  - Packed column or plate column if high reatant conversion is desired

Mass balances



$$N_i A = (\quad)\frac{mol}{m^2 s}(\quad)m^2$$

Gas-liquid reactors
Mass balances

- Plug flow

$$\dot{n}_{Li,in} + N_{Li}^{b}\Delta A + r_i \Delta V_L = \dot{n}_{Li,ut}$$

- Liquid phase $\dfrac{d\,\dot{n}_{Li}}{dV_R} = N_{Li}^{b} a_v + \varepsilon_L r_i$

- Gas phase $\dfrac{d\,\dot{n}_{Gi}}{dV_R} = \pm N_{Gi}^{b} a_v$

- a_v =gas-liquid surface area/reactor volume
- ε_L = liquid hold-up

Gas-liquid reactions
Mass balances

- Complete backmixing

$$\dot{n}_{Li,in} + N_{Li}^{b} A + r_i V_L = \dot{n}_{Li,ut}$$

- Liquid phase $$\frac{\dot{n}_{Li} - \dot{n}_{0Li}}{V_R} = N_{Li}^{b} a_v + \varepsilon_L r_i$$

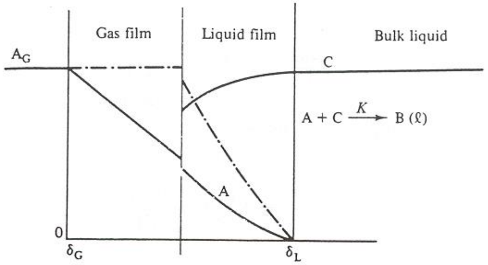
- Gas phase $$\frac{\dot{n}_{Gi} - \dot{n}_{0Gi}}{V_R} = -N_{Gi}^{b} a_v$$
- a_v =gas-liquid surface area/reactor volume
- ε_L = liquid hold-up

Gas-liquid reactors
Mass balances

- Batch reactor
- Liquid phase $$\frac{dn_{Li}}{dt} = \left(N_{Li}^{b} a_v + \varepsilon_L r_i\right) V_R$$
- Gas phase $$\frac{dn_{Gi}}{dt} = -N_{Gi}^{b} a_v V_R$$
- a_v =interfacial area/reactor volume
- ε_L = liquid hold-up

Gas-liquid reactors
- Gas-liquid film

- Fluxes in gas-liquid films
  - N^b_{Li} N^b_{Gi}



- Two-film theory
  - Chemical reaction and molecular diffusion proceed simultaneously in the liquid film with a thickness of δ_L
  - Only molecular diffusion in gas film, thickness δ_G
- Fick's law can be used: $N^b_{Gi} = +D_{Gi}\left(\frac{dc_{Gi}}{dz}\right)_{z=\delta_G}$ $N^b_{Li} = -D_{Li}\left(\frac{dc_{Li}}{dz}\right)_{z=\delta_L}$

Gas-liquid reactors
Gas film

- Gas film, no reaction

$$\left(D_{Gi}\frac{dc_{Gi}}{dz}\right)_{in}A=\left(D_{Gi}\frac{dc_{Gi}}{dz}\right)_{ut}A$$

$$D_{Gi}\frac{d^2c_{Gi}}{dz^2}=0 \qquad N_{Gi}^{b}=k_{Gi}\left(c_{Gi}^{b}-c_{Gi}^{s}\right)$$

- Analytical solution possible
- The flux depends on the mass transfer coefficient and concentration difference

Gas-liquid reactors
Liquid film

- Diffusion and reaction in liquid film:

$$-\left(D_{Li}\frac{dc_{Li}}{dz}\right)_{in}A+r_iA\Delta z=-\left(D_{Li}\frac{dc_{Li}}{dz}\right)_{ut}A$$

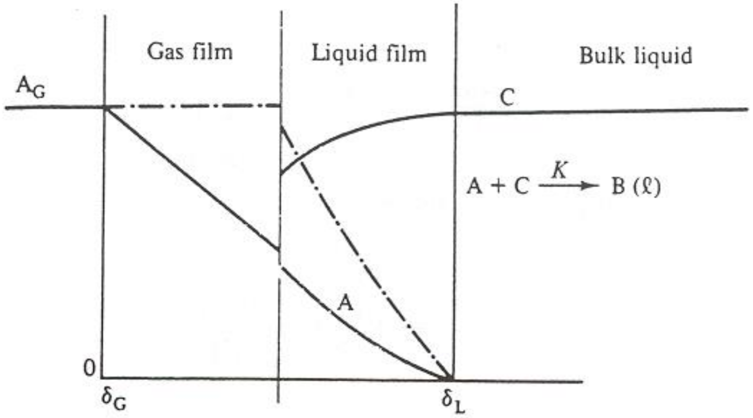
$$D_{Li}\frac{d^2c_{Li}}{dz^2}+r_i=0$$

- Boundary conditions:

$$N_{Gi}^b=N_{Li}\quad vid\quad z=0$$
$$c_{Li}=c_{Li}^b\quad vid\quad z=\delta_L$$

Gas-liquid reactors
Liquid film

- Liquid film
  - Equation can be solved analytically for isothermas cases for few cases of linear kinetics; in other case numerical solution should be used



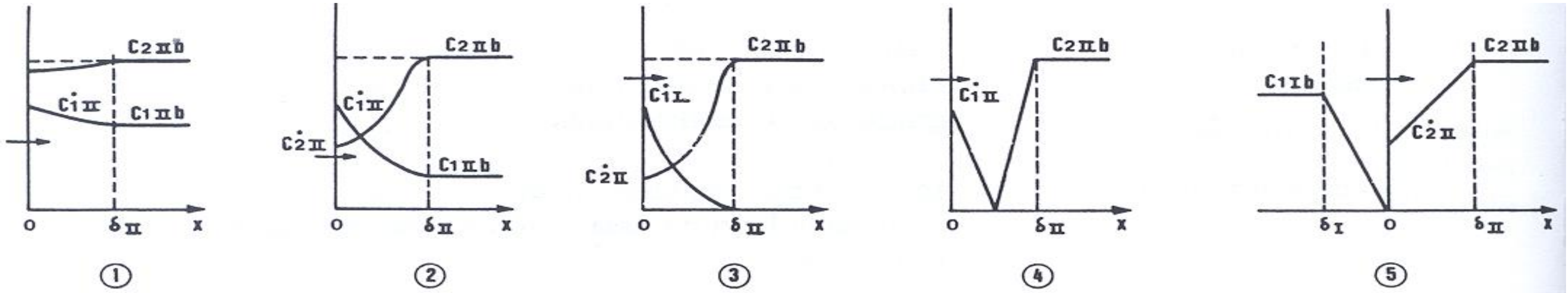
Reaction categories

- Physical absorption
  - No reaction in liquid film, no reaction in liquid bulk
- Very slow reaction
  - The same reaction rate in liquid film and liquid bulk – no concentration gradients in the liquid film, a pseudo-homogeneous system
- Slow reaction
  - Reaction in the liquid film negligible, reactions in the liquid bulk; linear concentration profiles in the liquid film

Reaction categories

- Moderate rates
  - Reaction in liquid film and liquid bulk
- Rapid reaction
  - Chemical reactions in liquid film, no reactions in bulk
- Instantaneous reaction
  - Reaction in liquid film; totally diffusion-controlled process

Concentration profiles in liquid film



Slow reaction

$Ha < 0.3$

Moderate-rate reaction

$0.3 < Ha < 5$

Fast reaction

$Ha > 5$

Instantaneous reaction

$Ha > 5$

and $Ha/\mathcal{N}_2 > 10$

Surface reaction

$Ha > 5$ and $Ha/\mathcal{N}_2 > 10$

and $\frac{C_{2IIb}}{C_{1Ib}} > \frac{k_{1I}\,\nu_2\mathcal{D}_{1I}}{k_{1II}\,\nu_1\mathcal{D}_{2II}}$

Enhancement factor

- Real flux/flux in the presence of pure physical absorption

$$E_A = \frac{N_{LA}^{s}}{\dfrac{c_{GA}^{b} - K_A c_{LA}^{b}}{\dfrac{K_A}{k_{LA}} + \dfrac{1}{k_{GA}}}}$$

- $E_A \geq 1$

Gas-liquid reactors
- very slow reaction

- No concentration gradients in the liquid film
- Depends on the role of diffusion resistance in the gas film

$$K_A = \frac{c_{GA}^{s}}{c_{LA}^{b}} \qquad K_A = \frac{c_{GA}^{b}}{c_{LA}^{b}}$$

$$N_{GA}^{b} = N_{LA}^{b} = k_{GA}\left(c_{GA}^{b} - K_A c_{LA}^{b}\right)$$

Gas-liquid reactors
- slow reaction

- Diffusion resistance both in gas- and liquid- film retards the adsorption, but the role of reactions is negligible in the liquid film

$$N_{GA}^{b} = k_{GA}\left(c_{GA}^{b} - c_{GA}^{s}\right)$$

$$N_{LA}^{b} = k_{LA}\left(c_{LA}^{s} - c_{LA}^{b}\right)$$

$$N_{LA}^{b} = \frac{c_{GA}^{b} - K_{A} c_{LA}^{b}}{\frac{K_{A}}{k_{LA}} + \frac{1}{k_{GA}}}$$

Gas-liquid reactors
- moderate rate in liquid film

- Chemical reactions in liquid film

$$N_{GA}^{b} \neq N_{LA}^{b}$$

$$N_{GA}^{b} = N_{GA}^{s} = N_{LA}^{s}$$

Reaction in liquid film

No reaction in gas film

$$K_A = \frac{c_{GA}^{s}}{c_{LA}^{s}}$$

$$D_{LA}\frac{d^2 c_{LA}}{dz^2} + r_A = 0$$

- The transport equation should be solved numerically

Moderate rate in the liquid film

- Transport equation can be solved analytically only for some special cases:
  - isothermal liquid film – zero or first order kinetics

    Approximative solutions exist for rapid second order kinetics

Moderate rate…

- Zero order kinetics

$$\frac{d^2 c_{LA}}{dz^2} = -\frac{\nu_A k}{D_{LA}}$$

$$N_{LA}^{s} = \frac{c_{GA}^{b} - K_A c_{LA}^{b}(M-1)}{\dfrac{K_A}{k_{LA}} + \dfrac{1}{k_{GA}}}$$

$$M = -\frac{\nu_A k D_{LA}}{2 k_{LA}^{2} c_{LA}^{b}}$$

Moderate rate…

- First order kinetics

$$\frac{d^2 c_{LA}}{dz^2} = -\frac{\nu_A k c_{LA}}{D_{LA}}$$

$$N_{LA}^s = \frac{c_{GA}^b - \dfrac{K_A c_{LA}^b}{\cosh(\sqrt{M})}}{\dfrac{\tanh\sqrt{M}}{\sqrt{M}}\dfrac{K_A}{k_{LA}} + \dfrac{1}{k_{GA}}} \qquad M = -\frac{\nu_A k D_{LA}}{k_{LA}^2} = -\frac{\nu_A k}{D_{LA}}\delta_L^2$$

- Hatta number $Ha=\sqrt{M}$ (compare with Thiele modulus)

Rapid reactions

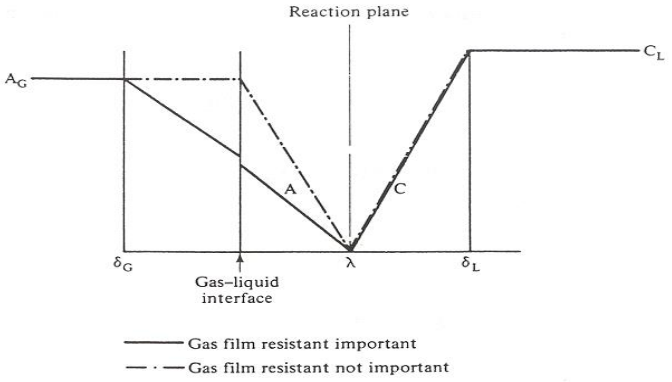
- Special case of reactions with finite rate
- All gas components totally consumed in the film; bulk concentration is zero, $c^{b}_{LA}=0$

Instantaneous reactions

- Components react completely in the liquid film

$$D_{LA}\frac{d^{2}c_{LA}}{dz^{2}}=0$$

- A reaction plane exists



- Reaction plane coordinate

$$z'=\frac{\dfrac{\nu_B\delta_L}{D_{LB}c_{LB}}}{\dfrac{\nu_A}{D_{LA}c_{LA}^{s}}+\dfrac{\nu_B}{D_{LB}c_{LB}^{s}}}$$

Instantaneous reactions

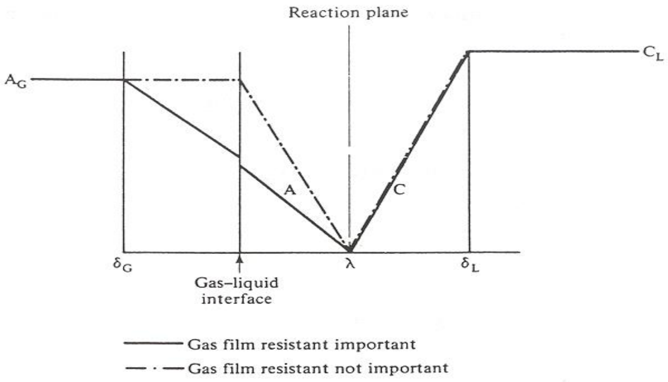
- Enhancement factor:

$$E_A = 1 + \frac{\nu_A D_{LB} c_{LB}^{b} K_A}{\nu_B D_{LA} c_{GA}^{b}}$$

- Flux at the interface:

$$N_{LA}^{s} = \frac{c_{GA}^{b} + \frac{\nu_A D_{LB}}{\nu_B D_{LA}} K_A c_{LB}^{b}}{\frac{K_A}{k_{LA}} + \frac{1}{k_{GA}}}$$

- (



Instantaneous reactions

- Flux

$$N_{LA}^{s}=\frac{c_{GA}^{b}+\dfrac{\nu_A D_{LB}}{\nu_B D_{LA}}K_A c_{LB}^{b}}{\dfrac{K_A}{k_{LA}}+\dfrac{1}{k_{GA}}}$$

- Only diffusion coeffcients affect !
- For simultaneous reactions can several reaction planes appear in the film

Fluxes in reactor mass balances

- Fluxes are inserted in mass balances

$$N_{Gi}^{b} = N_{Gi}^{s} = N_{Li}^{s}$$

- For reactants: $N_{Li}^{b} < N_{Li}^{s}$
- For slow and very slow reactions: (no reaction in liquid film)

$$N_{Li}^{b} = N_{Li}^{s}$$

General approach

- We are left with the model for the liquid film:

$$D_{Li}\frac{d^2 c_{Li}}{dz^2}+r_i=0$$

$$N_{Li}^{b}=-D_{Li}\left(\frac{dc_{Li}}{dz}\right)_{z=\delta_L}$$

Solution of mass balances

- Numerical strategy:
  - Algebraic equations
    - Newton-Raphson method
  - Differential equations, initial value problem (IVP)
    - Backward difference- and SI Runge-Kutta-methods
  - Differential equations, BVP
    - orthogonal collocation or finite differences

Number of equations

- N = number of components in the system

- N eqs for liquid phase; N eqs for gas phase
- N eqs for the liquid film
- Energy balances
  - 1 for gas phase
  - 1 for liquid phase

- 3N+2 equations in total

Mass transfer coefficients

- Flux through the gas film

$$N_{GA}^{b} = N_{GA}^{s} = k_{GA}\left(c_{GA}^{b} - c_{GA}^{s}\right)$$

- Partial pressures often used:

$$N_{GA}^{b} = N_{GA}^{s} = k'_{GA}\left(p_{A} - p_{A}^{s}\right)$$

- Ideal gas law gives the relation: $k_{GA} = k'_{GA} RT$

Gas-liquid equilibria

- Definition

$$K_A = \frac{c_{GA}^s}{c_{LA}^s}$$

- For sparingly soluble gases:

- Relation becomes

$$He_A = \frac{p_A^s}{c_{LA}^s} \qquad He'_A = \frac{p_A^s}{x_{LA}^s}$$

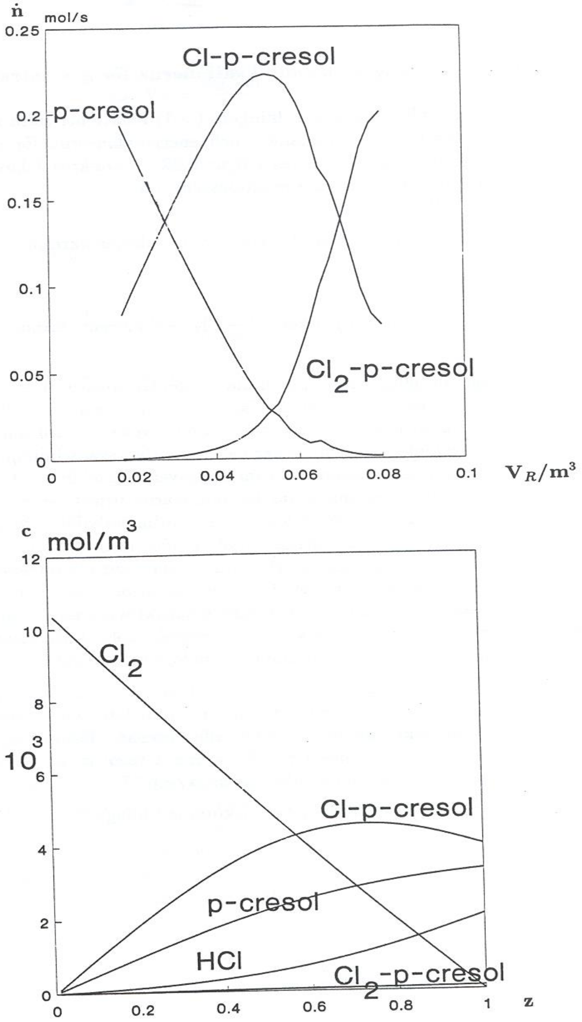
- K_A from thermodynamics; often Henry’s constant is enough

$$K_A = \frac{He_A}{RT}$$

Simulation example

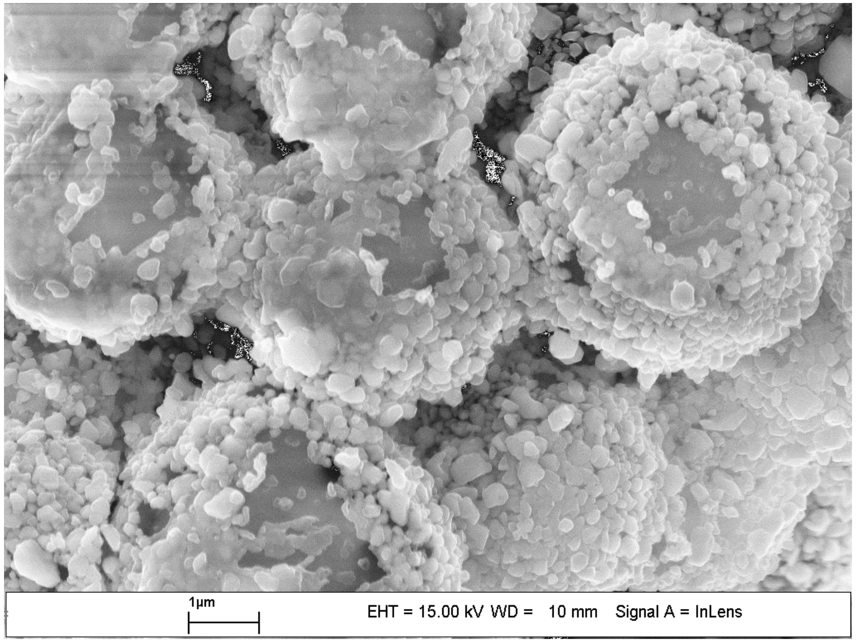
- Chlorination of p-kresol
  - p-cresol + Cl_2 -> monocloro p-kresol + HCl
  - monocloro p-kresol + Cl_2 -> dichloro p-kresol + HCl
- CSTR
  - Newton-Raphson-iteration
- Liquid film
  - Orthogonal collocation

Chlorination of para-cresol in a CSTR



Fluid-solid reactions

- Three main types of reactions:
    - Reactions between gas and solid
    - Reactions between liquid and solid
    - Gas-liquid-solid reactions



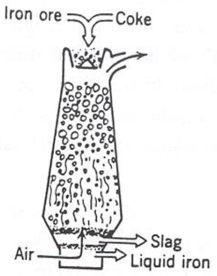
Fluid-solid reactions

- The size of the solid phase
  - Changes:
    - Burning oc charcoal or wood
  - Does not change:
    - oxidation av sulfides, e.g. zinc sulphide --> zinc oxide

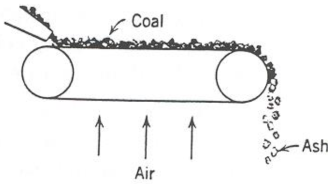
Reactors for fluid-solid reactions

- Reactor configurations
  - Fluidized bed
  - Moving bed
  - Batch, semibatch and continuous tank reactors (liquid and solid, e.g. CMC production, leaching of minerals)

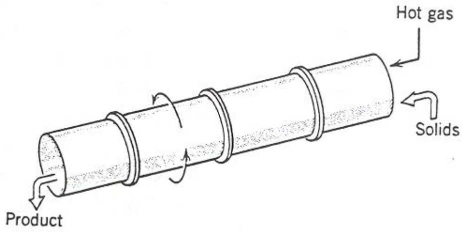
Processes and reactors



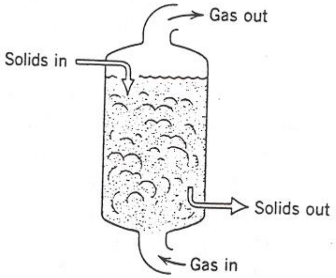
(*a*) Blast furnace



(*b*) Moving feeder for coal furnaces



(*c*) Rotary dryer for heat-sensitive materials



(*d*) Fluidized-bed reactor

(*e*) Ion exchange bed

Fluid-solid reaction modelling

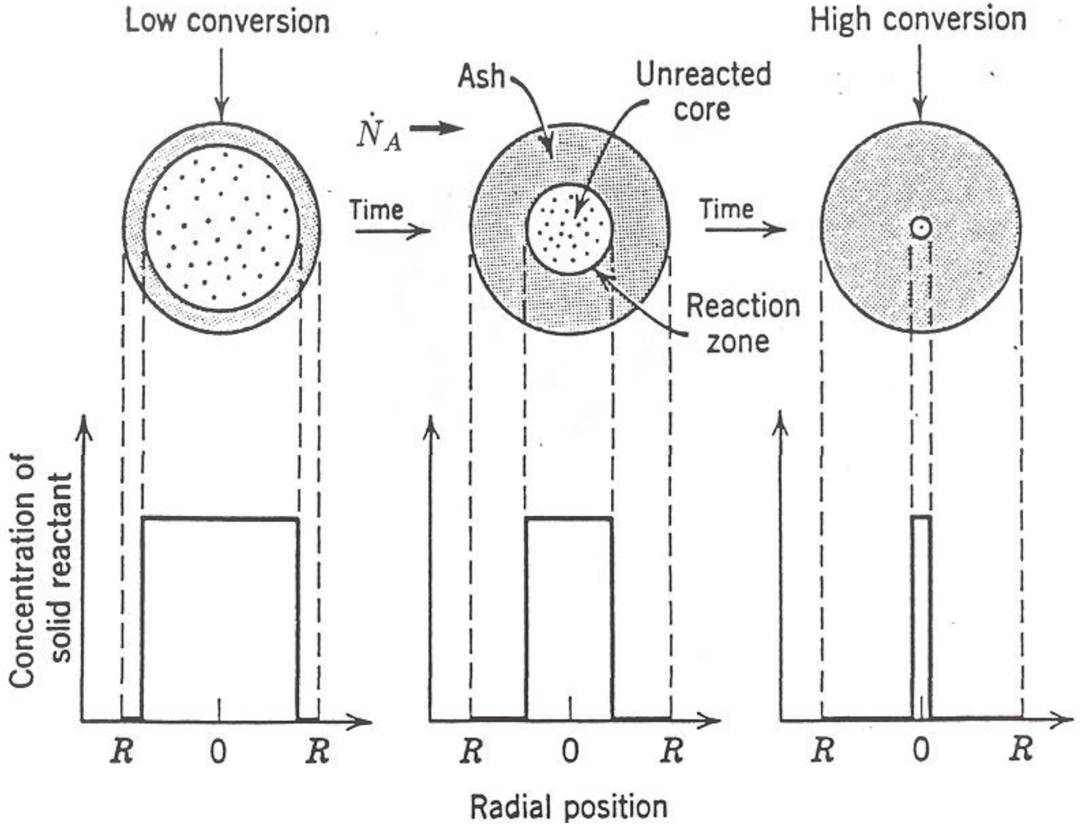
- Mathematical models used
  - Porous particle model
    - Simultaneous chemical reaction and diffusion throughout the particle
  - Shrinking particle model
    - Reaction product continuously removed from the surface
  - Product layer model (shrinking core model)
    - A porous product layer is formed around the non-reacted core of the solid particle
  - Grain model
    - The solid phase consists of smaller non-porous particles (rasberry structure)

Fluid-solid reactions

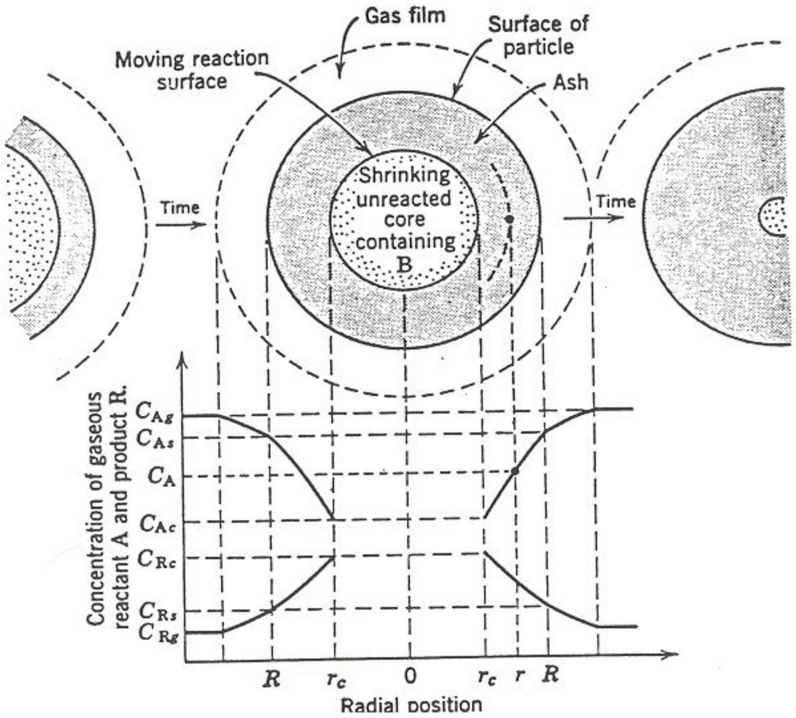
- Solid particles react with gases in such a way that a narrow reaction zone is formed

- Shrinking particle model can thus often be used even for porous particles
- Grain model most rrealistic but mathematically complicated

Product layer

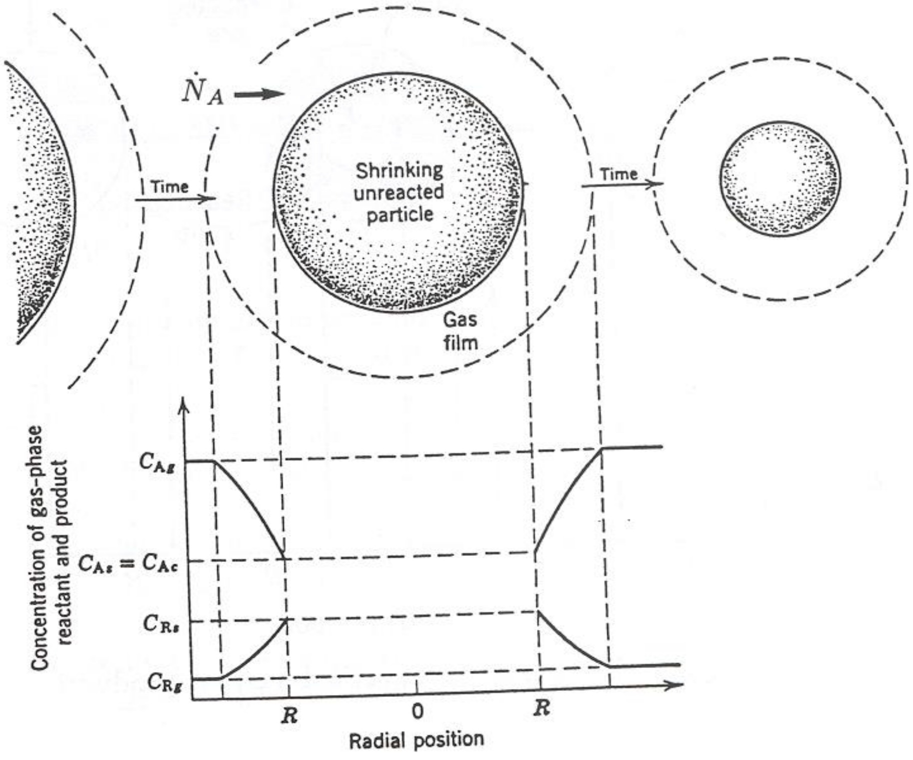


Product layer

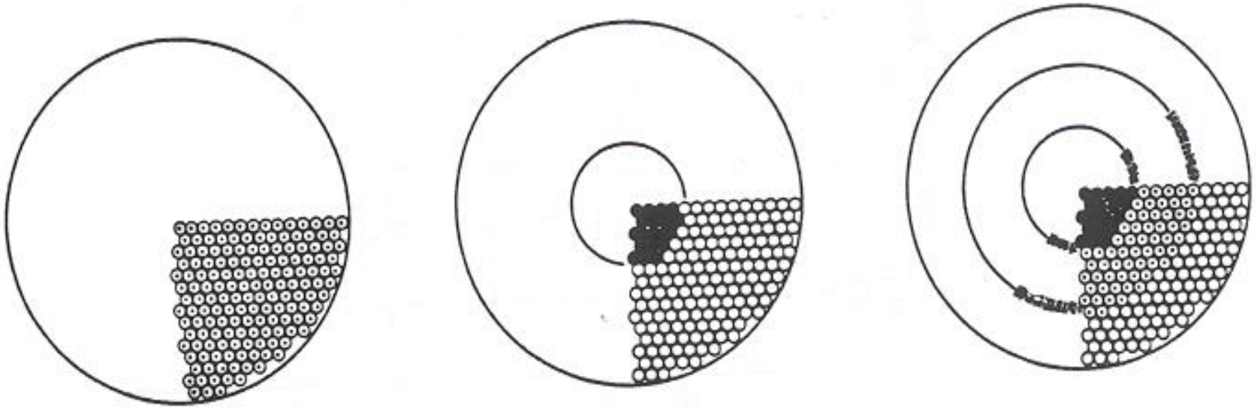


Concentration profiles in the product layer

Shrinking particle



Grain model



Fluid-solid reactions

- Particle with a porous product layer
  - Gas or liquid film around the product layer
  - Porous product layer
  - The reaction proceeds on the surface of non-reacted solid material
    - Gas molecules diffuse through the gas film and through the porous product layer to the surface of fresh, non-reacted material

Fluid-solid reactions

- Reaction between A in fluid phase and B in solid phase

$$RA = ()\frac{mol}{m^2 s}()m^2$$

- R=reaction rate, A=particle surface area
- Generated B= Accumulated B

$$\frac{dr}{dt} = \frac{M}{x_B \rho_P} \nu_B R\left(c^s\right)$$

Fluid-solid reactions

- Diffusion through the porous product layer (spherical particle)

$$D_{EA}\left(\frac{d^2 c_A}{dr^2} + \frac{2}{r}\frac{dc_A}{dr}\right) = 0$$

- Solution gives $N_A = D_{eA}(dc_A/dr)$:

$$N_A = \frac{D_{EA}\left(c_A^b - c_A^s\right)}{r\left(1 - \frac{r}{R}\left(1 - \frac{1}{Bi_M}\right)\right)} = -\nu_A R(c^s)$$

Fluid-solid reactions

- Fick's law is applied for the diffusion in the product layer gives the particle radius

$$\frac{dr}{dt} = \frac{M}{x_B \rho_p} \frac{\nu_B D_{eA}\left(c_A^b - c_A^s\right)}{\left(-\nu_A\right) r \left(1 - \frac{r}{R}\left(1 - \frac{1}{Bi_{AM}}\right)\right)}$$

- Surface concentration is obtained from

$$\frac{D_{ei}\left(c_i^b - c_i^s\right)}{r\left(1 - \frac{r}{R}\left(1 - \frac{1}{Bi_{iM}}\right)\right)} = -\nu_i R(c^s)$$

Fluid-solid reactions

- For first-order kinetics an analytical solution is possible

- Four cases – rate limiting steps
  - Chemical reaction
  - Diffusion through product layer and fluid film
  - Diffusion through the product layer
  - Diffusion through the fluid film

Fluid-solid reactions

- Reaction time (t) and total reaction time (t_0) related to the particle radius (r)
- Limit cases
  - Chemical reaction controls the process – Thiele modulus is small -> Thiele modulus small
  - Diffusion through product layer and fluid film rate limiting -> Thiele modulus large

Reaktorer med reaktiv fast fas

- Diffusion through the product layer much slower than diffusion through the fluid -> $Bi_{AM}=\infty$

- Diffusion through fluid film rate limiting -> $Bi_{AM}=0$

Fluid-solid reactions

- Shrinking particle
  - Phase boundary
  - Fluid film around particles
- Product molecules (gas or liquid) disappear directly from the particle surface
- Mass balance

In via diffusion through the fluid film + generated = 0

Fluid-solid reactions

- First order kinetics
  - Surface reaction rate limiting
  - Diffusion through fluid film rate limiting

- Arbitrary kinetics
  - A general solution possible, if diffusion through the fluid film is rate limiting

Semibatch reactor

- An interesting special case
  - Semibatch reactor
    - High throughflow of gas so that the concentrations in the gas phase can be regarded as constant; used e.g. in the investigation of gas-solid kinetics (thermogravimetric equipment)
    - Complete backmixing locally
    - simple realtions between the reaction time and the particle radius obtained

Reaction time and particle radius

- Thiele modulus, $\varphi=-v_A kR/D_{eA}$ and Biot number, $Bi_M=k_{GA}R/D_{eA}$

$$\frac{t}{t_0}=\frac{6(1-(r/R)+3\phi(1-(r/R)^2)-2\phi(1-(r/R)^3)(1-1/Bi_M)}{6+\phi(1+2/Bi_M)}$$

- Special cases – large Thiele modulus φ;
- control by product layer and fluid film

$$\frac{t}{t_0}=\frac{3(1-(r/R)^2)-2(1-(r/R)^3)(1-1/Bi_M)}{1+2/Bi_M}$$

Fluid-solid reactions

- **Product layer model**

- Large Thiele modulus, $\varphi = -v_A kR/D_{eA}$ and large Bi - control by product layer

$$\frac{t}{t_0} = 1 - 3(r/R)^2) + 2(r/R)^3$$

- Large Thiele modulus, $\varphi = -v_A kR/D_{eA}$ and small Bi - control by film

$$\frac{t}{t_0} = 1 - (r/R)^3$$

Fluid-solid reactions

- **Product layer model**

- Small Thiele modulus, $\varphi=-v_A kR/D_{eA}$ and large Bi - control by chemical reaction

$$\frac{t}{t_0}=1-(r/R)$$

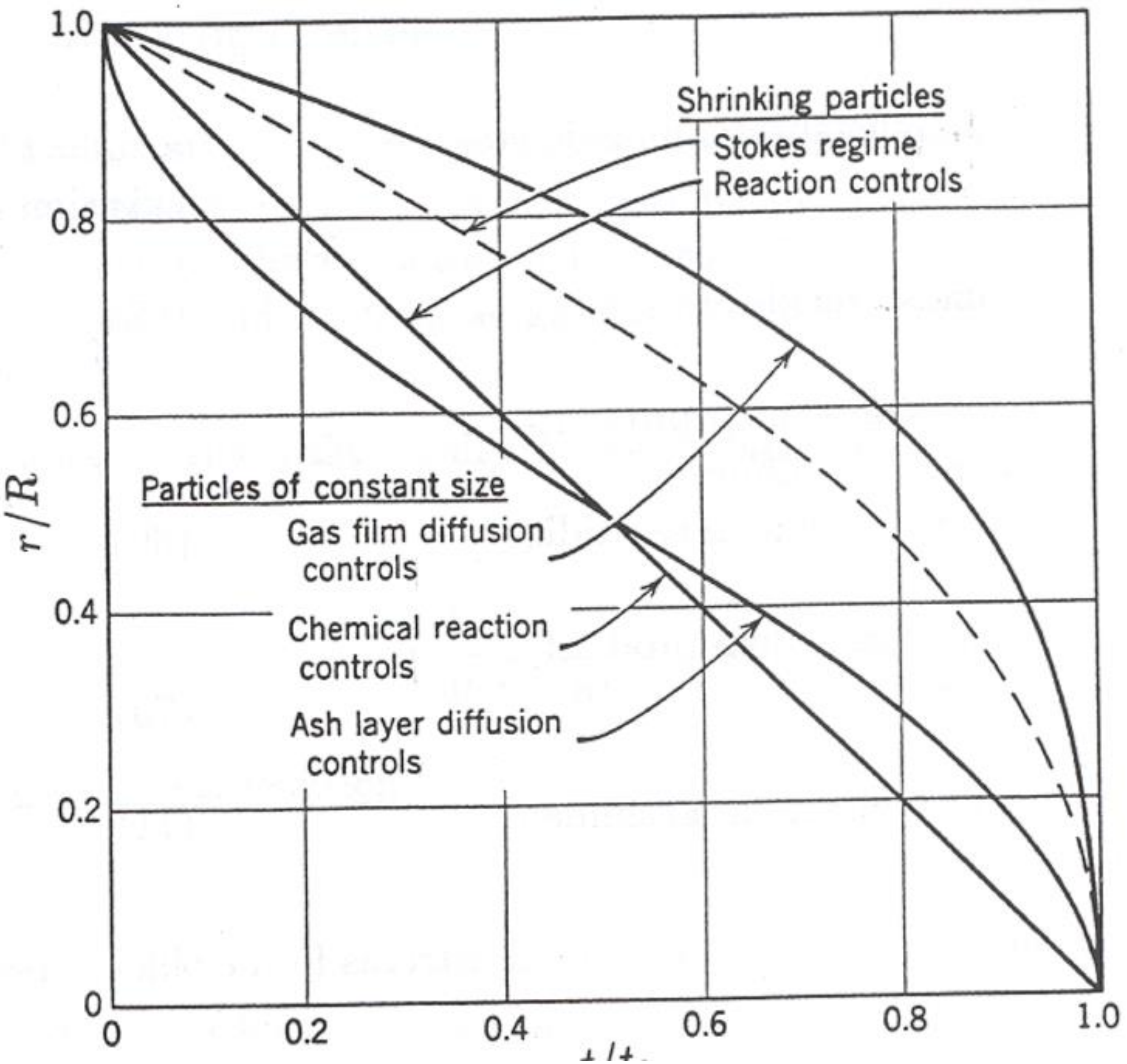
Fluid-solid reactions

- **Shrinking particle model**
- Small Bi - control by film diffusion

$$\frac{t}{t_0} = 1 - (r/R)^2$$

- Large Bi - control by chemical reaction

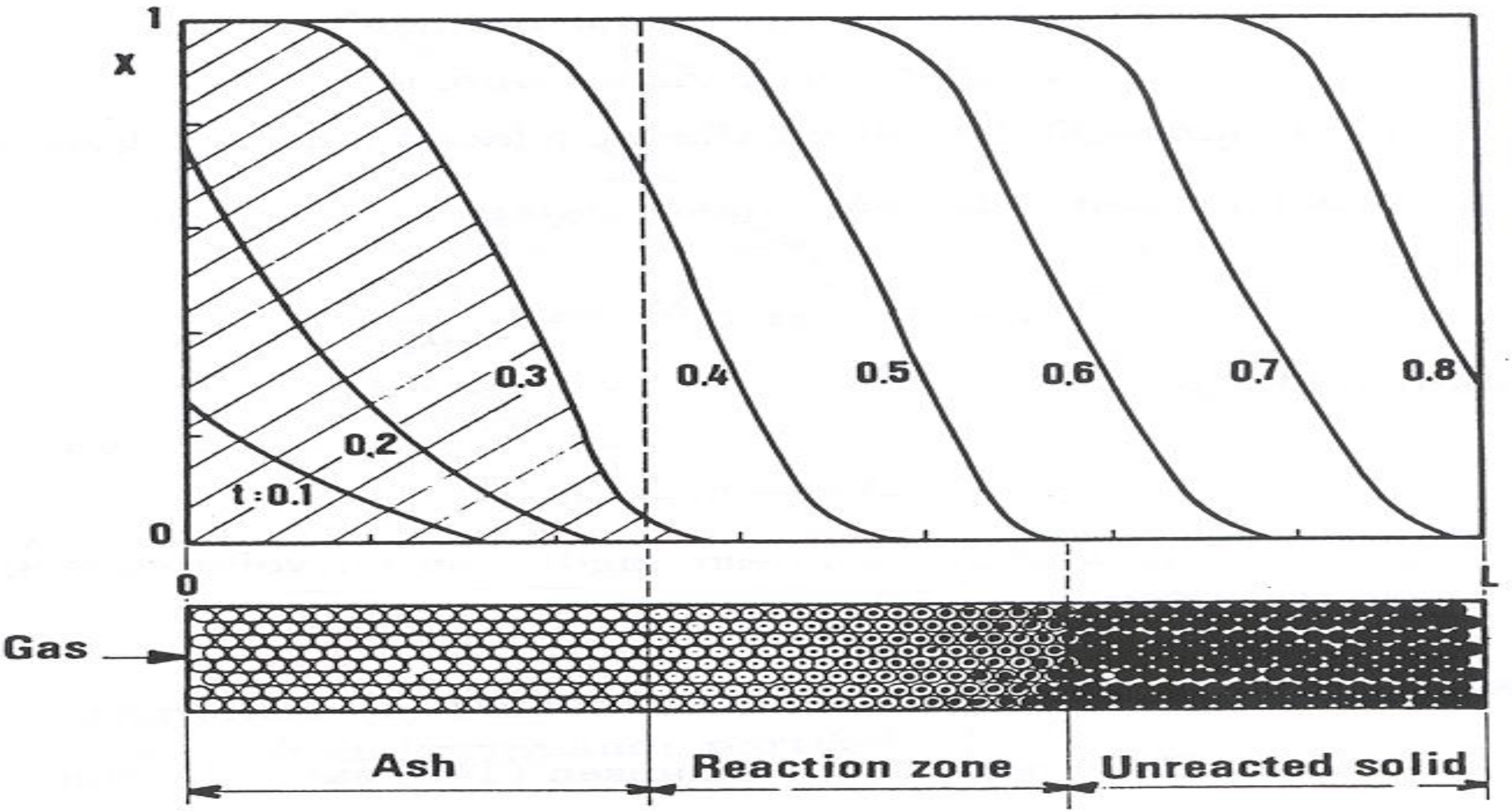
$$\frac{t}{t_0} = 1 - (r/R)$$


1.0
0.8
0.6
0.4
0.2
0
r/R
0
0.2
0.4
0.6
0.8
1.0
Shrinking particles
Stokes regime
Reaction controls
Particles of constant size
Gas film diffusion controls
Chemical reaction controls
Ash layer diffusion controls

Packed bed

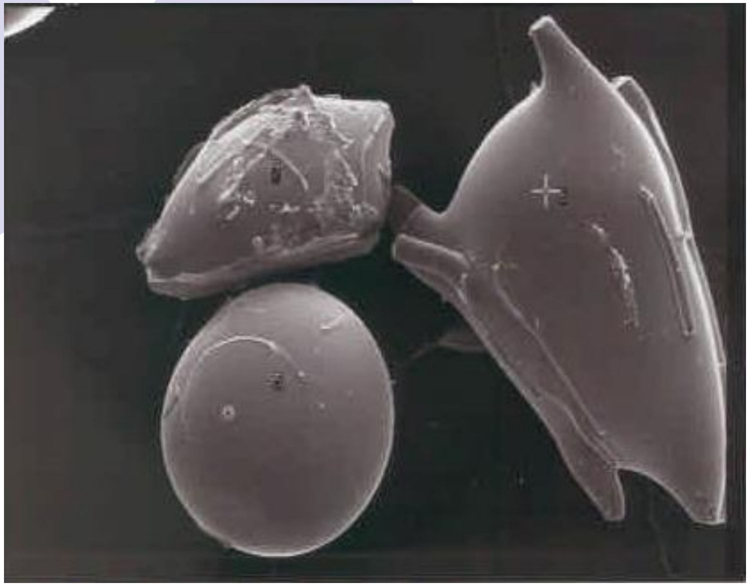
- Packed bed – operation principle
  - Gas or liquid flows through a stagnant bed of particles, e.g. combustion processes or ion exchangers
  - Plug flow often a sufficient description for the flow pattern
  - Radial and axial dispersion effects neglected

Simulation of a packed bed



Fluid-solid reactions: the roughness of even surfaces

Tapio Salmi and Henrik Grénman



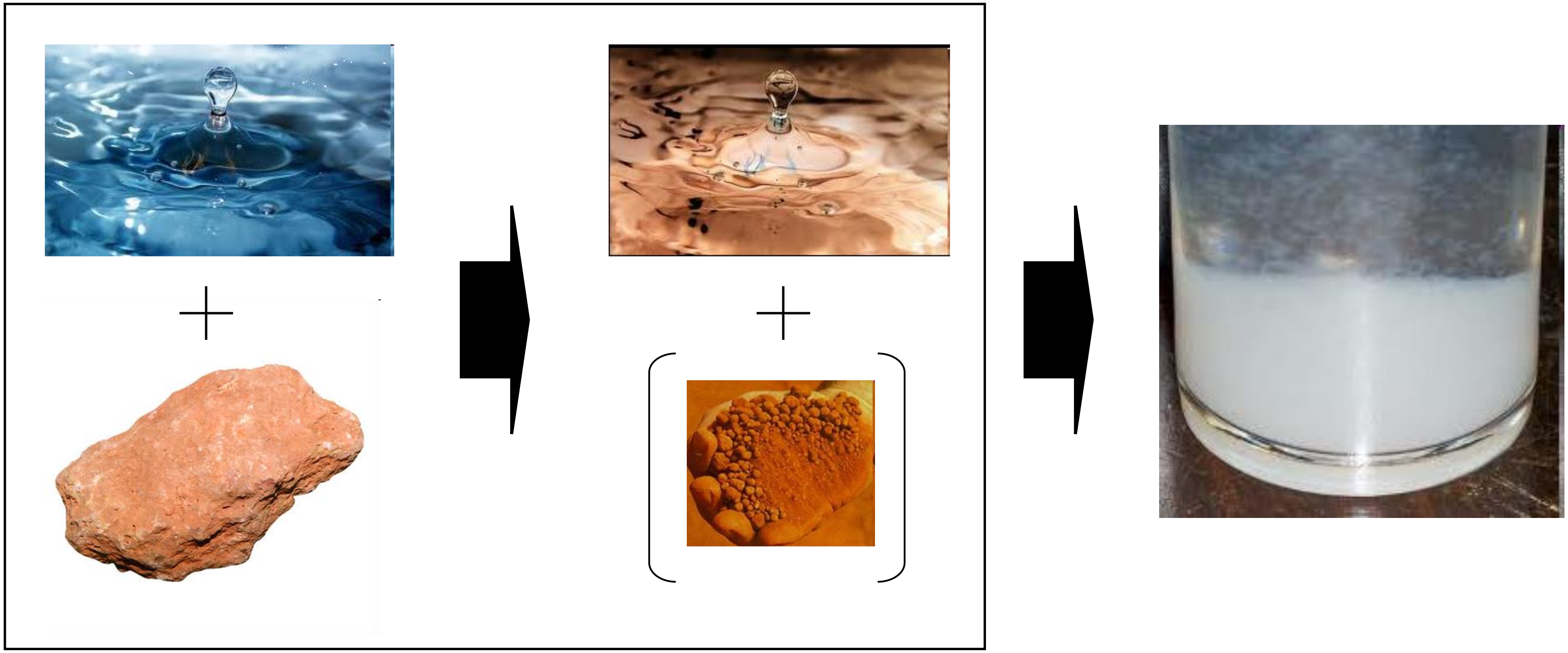
Outline

- Background of solid-liquid reactions

- New methodology for solid-liquid kinetic modeling
  - Description of rough particles
  - General product layer model
  - Particle size distribution

- Conclusions

Solid-liquid reaction kinetics



- The aim is to develop a mathematical model for the dissolution kinetics

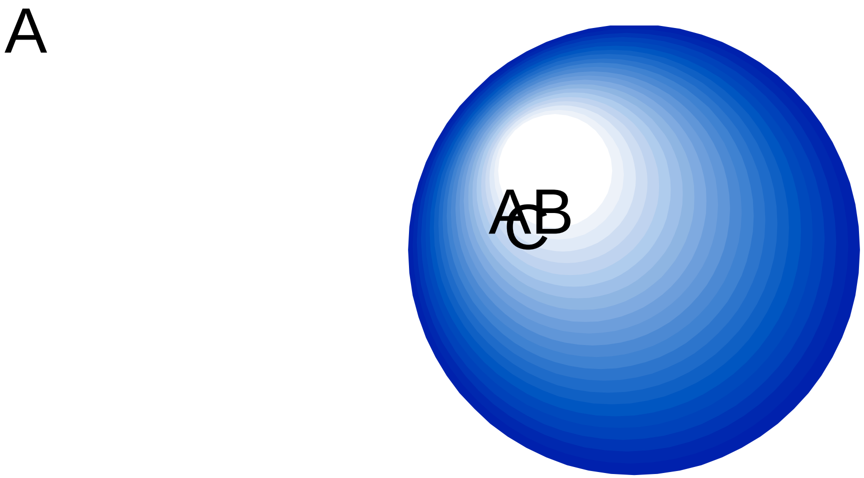
Why modeling is useful?

- Modeling helps in effective process and equipment design as well as control
- Empirical process development is slow in the long run
- The optimum is often not achieved through empirical development, at least in a reasonable time frame

What influences the kinetics

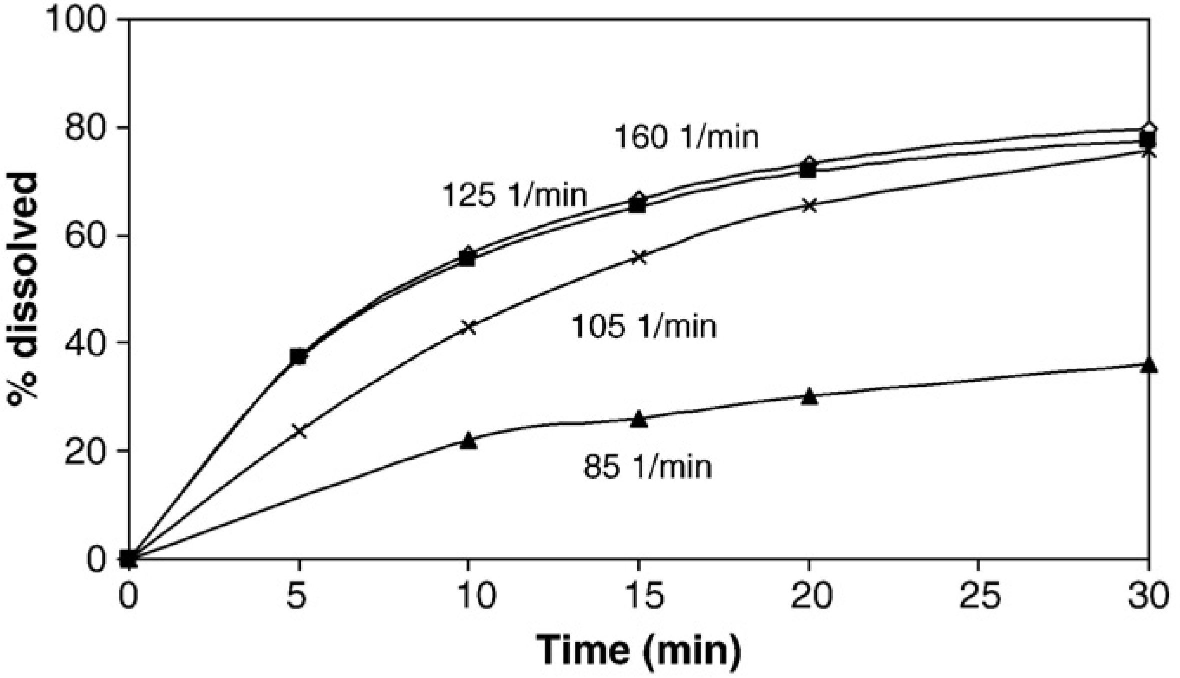
$$A + B \rightarrow AB \rightarrow C \text{ (I)}$$

- Reaction rate depends on
  - Mass transfer
    - External
    - Internal (often neglected)
  - Intrinsic kinetics (the “real” chemical rates



Practical influence of mass transfer

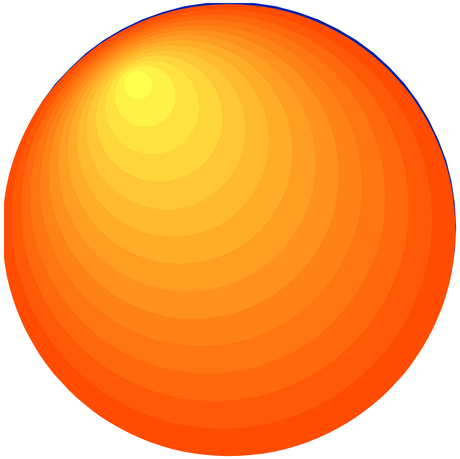
- External mass transfer resistance can be overcome by agitation



- It is important to recognize what you actually are measuring

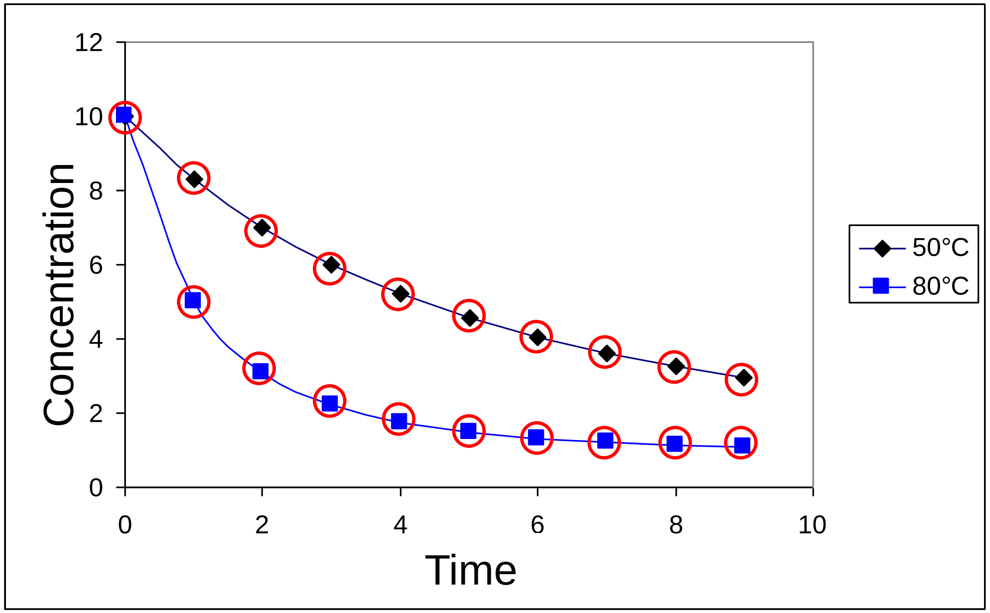
What influences the kinetics

- Reaction rate depends on
  - Surface area of solid
    - Morphological changes
  - Reactive surface sites on solid
    - Heterogeneous solids
  - Possible phase transformations in solid phase
  - Equilibrium considerations
    - Complex chemistry in liquid phase

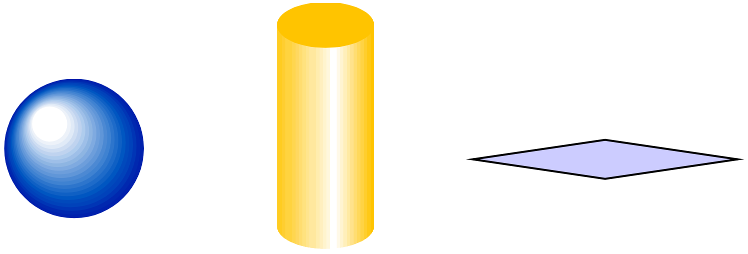


Traditional methodology

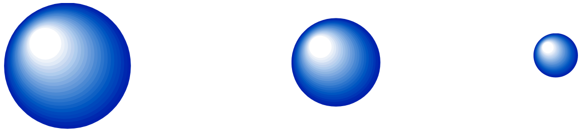
The conversion is followed by measuring the solid or liquid phase



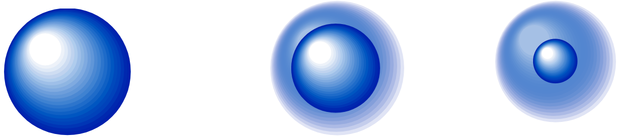
Traditional hypothesis in modeling solid-liquid reactions



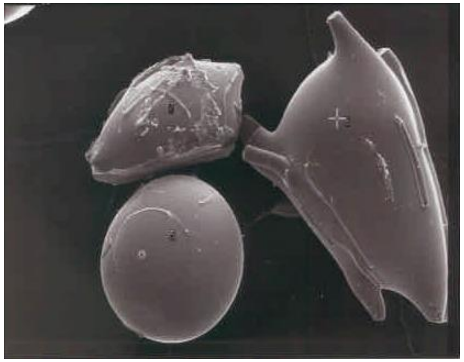
Sphere Cylinder Slab

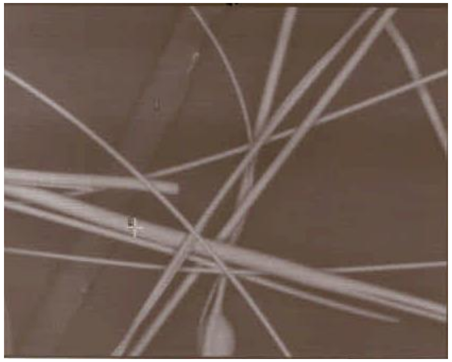


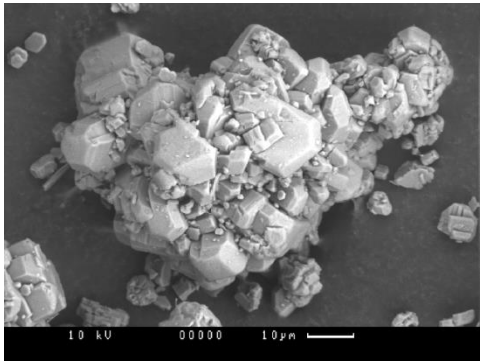
Shrinking particle



Shrinking core







Traditional kinetic modeling – screening models from literature

- The kinetics depends on the surface area (*A*) of the particles

$$kt = 1 - (1-\alpha)^{1/3}$$

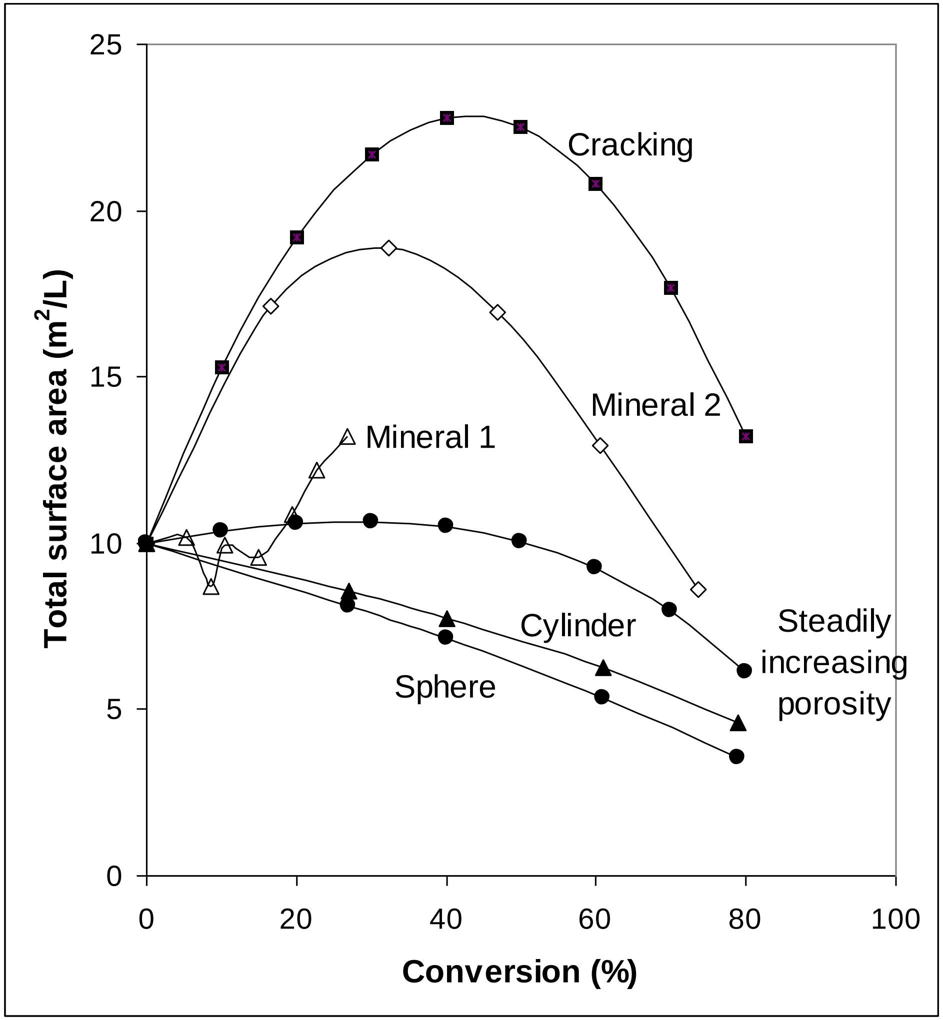
$$\frac{dc_{solid}}{dt} = -kA_{particles}c_{liquid}^{\alpha}$$

- Because of the difficulties associated with measuring the surface area on-line, the change is often expressed with the help of the conversion

- Experimental test plots are used to determine the reaction mechanism

nr	$g(\alpha)$	$f(c_S)$	Type of model
1	$-\ln(1-\alpha)$	c_S/c_{0S}	First-order kinetics
2	$(1-\alpha)^{-1/2} - 1$	$(c_S/c_{0S})^{3/2}$	Three-halves-order kinetics
3	$(1-\alpha)^{-1}$	$(c_S/c_{0S})^{2}$	Second-order kinetics
4	$1 - (1-\alpha)^{1/2}$	$(c_S/c_{0S})^{1/2}$	One-half-order kinetics; two-dimensional advance of the reaction interface
5	$1 - (1-\alpha)^{1/3}$	$(c_S/c_{0S})^{2/3}$	Two-thirds-order kinetics; three-dimensional advance of the reaction interface
6	$1 - (1-\alpha)^{2/3}$	$(c_S/c_{0S})^{1/3}$	One-thirds-order kinetics; film diffusion
7	$[1 - (1-\alpha)^{1/3}]^2$	$(c_S/c_{0S})^{2/3}/(1 - (c_S/c_{0S})^{1/3})$	Jander; three-dimensional
8	$1 - 2\alpha/3 - (1-\alpha)^{2/3}$	$(c_S/c_{0S})^{1/3}/(1 - (c_S/c_{0S})^{1/3})$	Crank-Ginstling-Brounshtein, mass transfer across a nonporous product layer
9	$[1/(1-\alpha)^{1/3} – 1]^2$	$(c_S/c_{0S})^{5/3}/(1 - (c_S/c_{0S})^{1/3})$	Zhuravlev-Lesokhin-Tempelman, diffusion, concentration of penetrating species varies with α
10	$[1 - (1-\alpha)^{1/2}]^2$	$(c_S/c_{0S})^{1/2}/(1 - (c_S/c_{0S})^{1/2})$	Jander; cylindrical diffusion
11	$1/(1-\alpha)^{1/3} - 1$	$(c_S/c_{0S})^{4/3}$	Dickinson, Heal, transfer across the contacting area
12	$1-3(1-\alpha)^{2/3}+2(1-\alpha)$	$(c_S/c_{0S})^{1/3}/(1 - (c_S/c_{0S})^{1/3})$	Shrinking core, product layer (different form of Crank-Ginstling-Brounshtein)

Surface area of solid phase



- The change in the total surface area of the solid depends strongly on the morphology of the particles

- Models based on ideal geometries can be inadequate for modeling non-ideal cases

- The particle morphology can be implemented into the model with the help of a shape factor

New methodology for general shapes

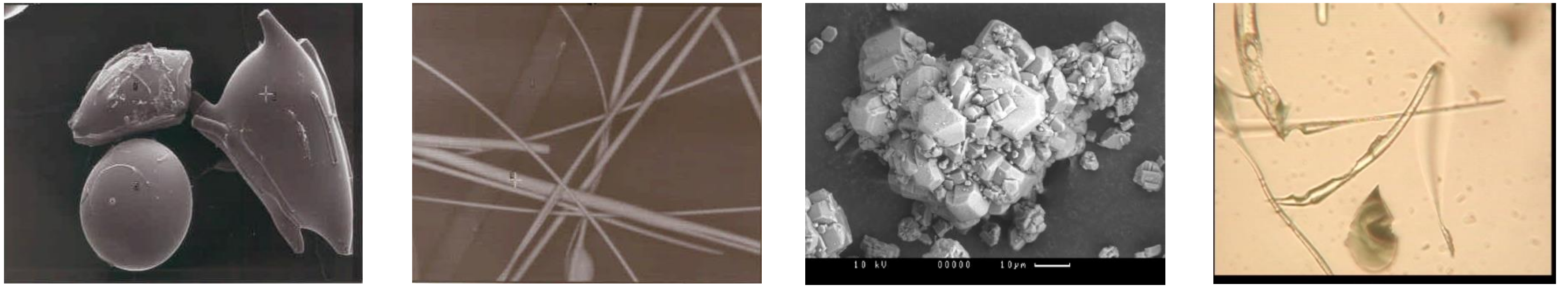
- The morphology can be flexibly implemented with the help of a shape factor (*a*)

Reaction rate: $$\frac{dc_{solid}}{dt} = -kA_{particles}c_{liquid}^{\alpha}$$

Reaction rate: $$\frac{dc_{solid}}{dt} = -kc_{particles}^{1-x}c_{liquid}^{\alpha}$$

Shape factor: $$\boxed{a = \frac{A_P}{V_P}R_0}$$

Geometry	**Shape factor (*a*)**	**x= 1/a**	**1-x**
Slab	1	1	0
Cylinder	2	½	1/2
Sphere	3	1/3	2/3
Rough, porous particle	high value	→0	→1



Geometry	**Shape factor (*a*)**	**x= 1/a**	**1-x**
Slab	1	1	0
Cylinder	2	½	1/2
Sphere	3	1/3	2/3
Rough, porous particle	high value	→0	→1

Often kinetics is closer to first order!

The roughness is always there, σ=1 m^2/g is not a perfect sphere!

- Detailed considerations give a relation
  between area (A),
  specific surface area (σ),
  amount of solid (n),
  initial amount of solid(n_0),
  and molar mass (M);
  a=shape factor

$$A = \sigma M n_0^{1/a} n^{1-1/a}$$

New methodology

- The solid-liquid reaction mechanism should be considered from chemical principles, exactly like in organic chemistry!

$$\frac{dc_{prod}}{dt} = k\underbrace{c_{particle}^{1-x}}_{\text{Solid contribution}}\underbrace{f(c_{liquid})}_{\text{Liquid contribution}}$$

The dissolution of zink with ferric iron

$ZnS(s) + Fe^{3+} \leftrightarrow I_1$ (I)

$I_1 + Fe^{3+} \leftrightarrow I_2$ (II)

$I_2 \leftrightarrow S(s) + 2\ Fe^{2+} + Zn^{2+}$ (III)

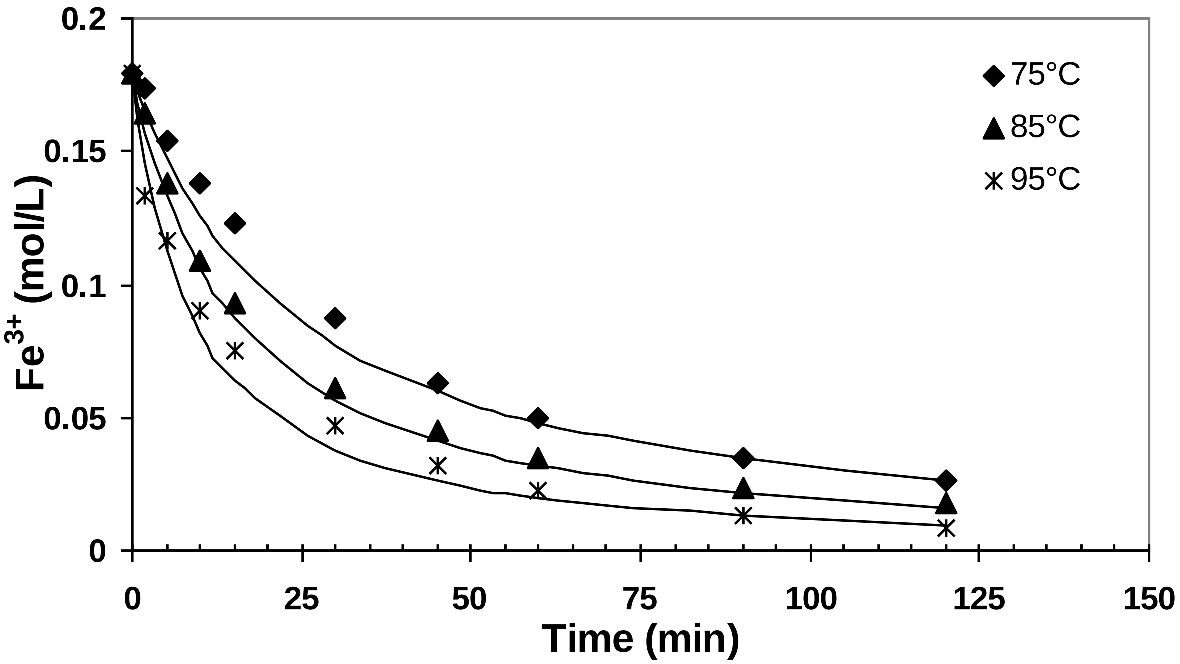
$ZnS(s) + 2Fe^{3+} \leftrightarrow S(s) + 2\ Fe^{2+} + Zn^{2+}$

The mechanism gave the following rate expression

$$r = \frac{k(c_{FeIII}{}^2 - c_{FeII}{}^2 c_{ZnII} / K)}{D}$$

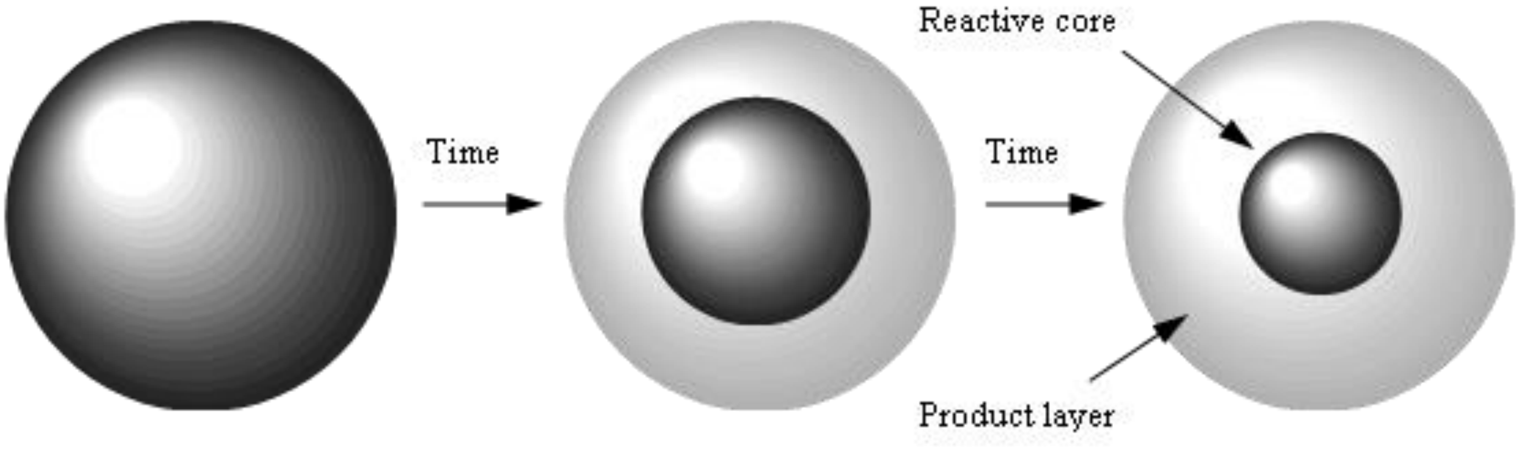
The dissolution of zink with ferric iron

The reaction order is not 2/3 but clearly higher!



Wrong reaction order in the kinetic model is the worst mistake!

General product layer model



General product layer model in a nutshell

$$\frac{(a-2)D_{ei}(c_{Li}{}^{b}-c_{Li}{}^{s})}{R(1-(1-(a-2)/Bi_{Mi})(r/R)^{a-2})(r/R)}+\sum_{k=1}^{S}\nu_{ik}R_k(c_{Li}{}^{s})=0$$

$$D_{ei}\left(\frac{d^2c_i}{dr^2}+\frac{(a-1)}{r}\frac{dc_i}{dr}\right)=0$$

$$N_i=-D_{ei}CR^{1-a}=-k_{Li}(c_{Li}{}^{b}-c_{Li}{}^{*})$$

$$N_i=\frac{-(a-2)D_{ei}(c_{Li}{}^{b}-c_{Li}{}^{s})}{R(1-(1-(a-2)/Bi_{Mi})(r/R)^{a-2})(r/R)}$$

$$N_iA=\sum_{k=1}^{S}\nu_{ik}R_k(c_{Li}{}^{s})$$

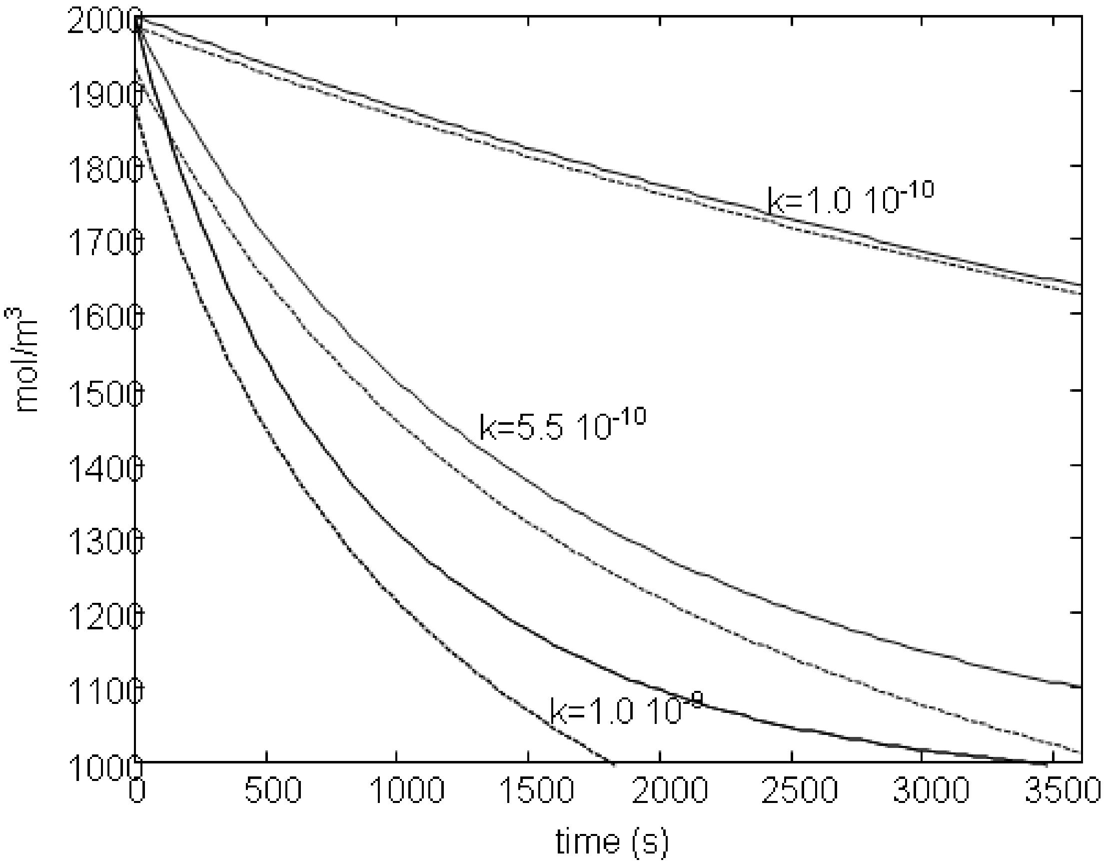
$$\frac{dn_i}{dt}=\sum_{k=1}^{S}\nu_{ik}R_kA$$

$$\frac{dc_j}{dt}=\frac{\nu_j\sigma M}{x_{0j}}c_{0j}{}^{x}c_j{}^{1-x}r$$

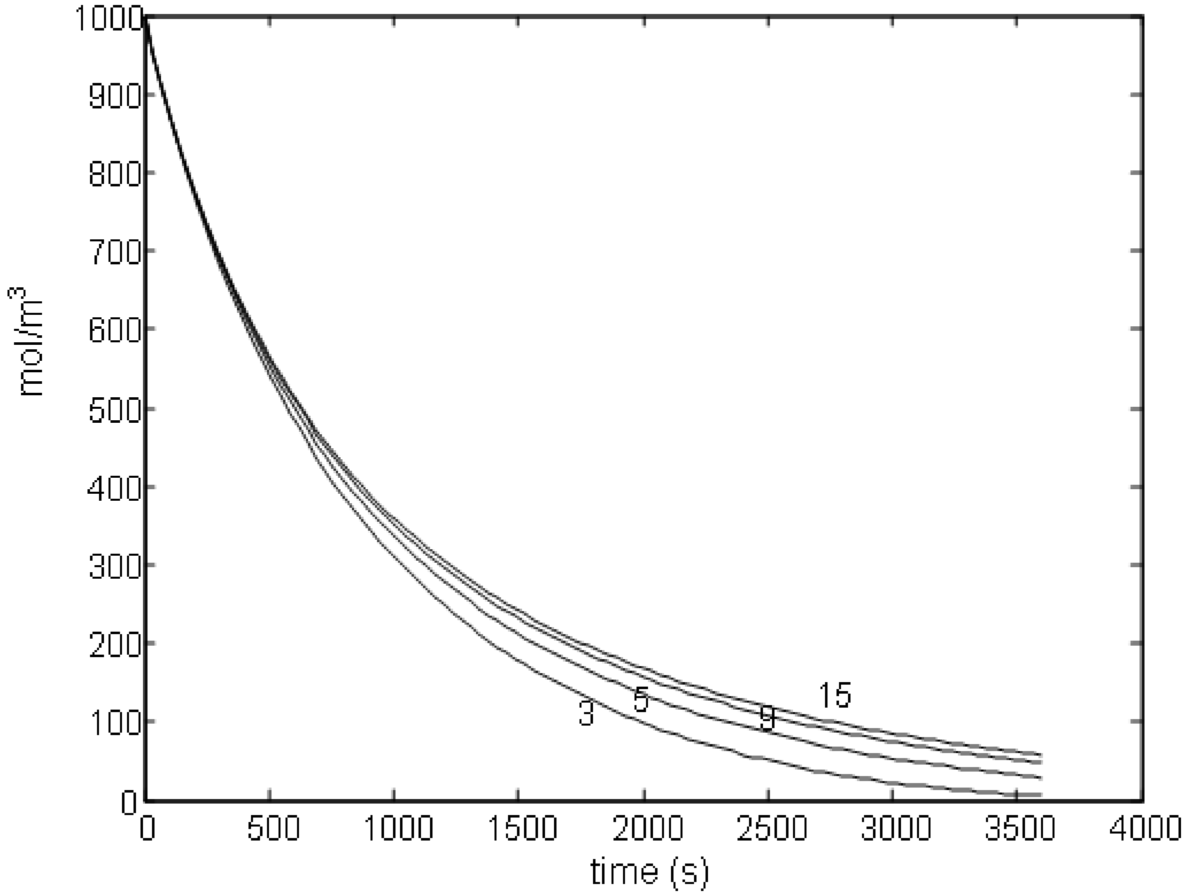
$$\frac{dc_i}{dt}=\frac{\nu_i\sigma M}{x_{0j}}c_{0j}{}^{x}c_j{}^{1-x}r$$

$$r=f(c_{LiS})$$

Comparison of shrinking particle and product layer model



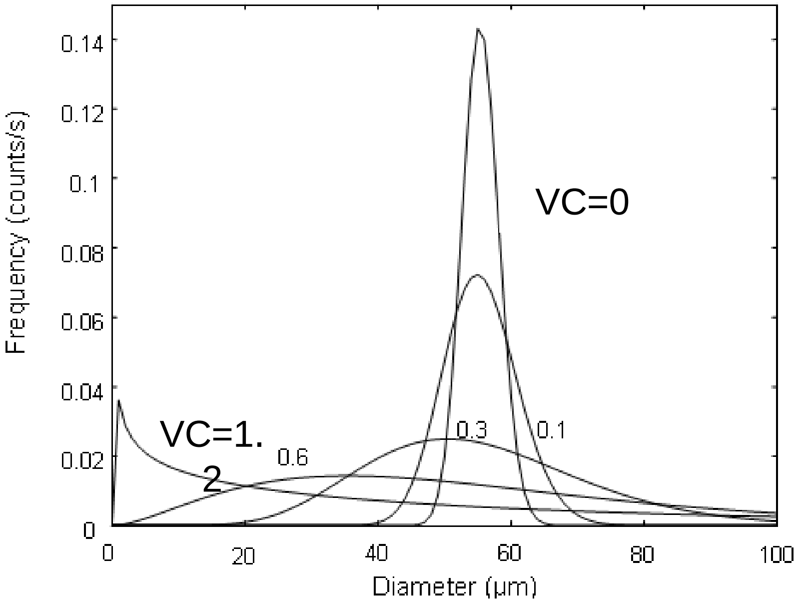
Effect of shape factor

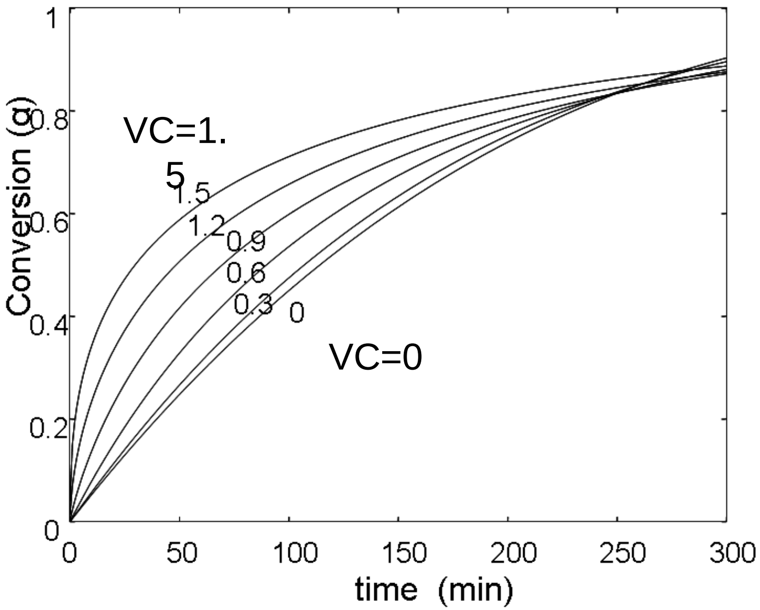


Particle size distribution

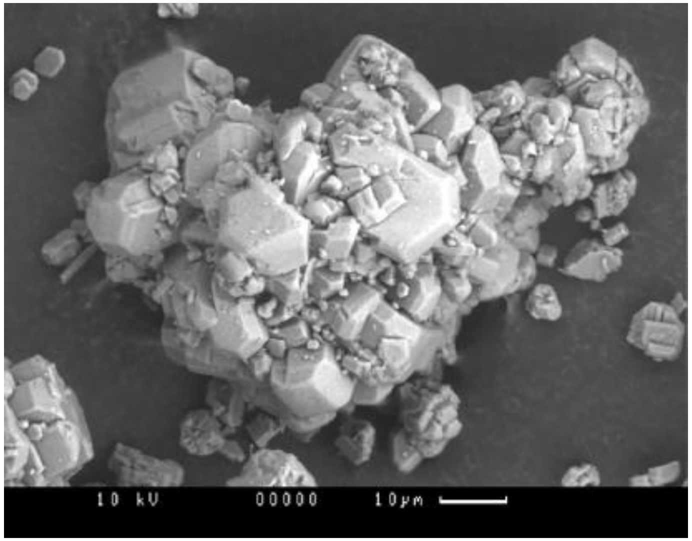
- If the particle size distribution deviates significantly from the Gaussian distribution, erroneous conclusions can be drawn about the reaction mechanism

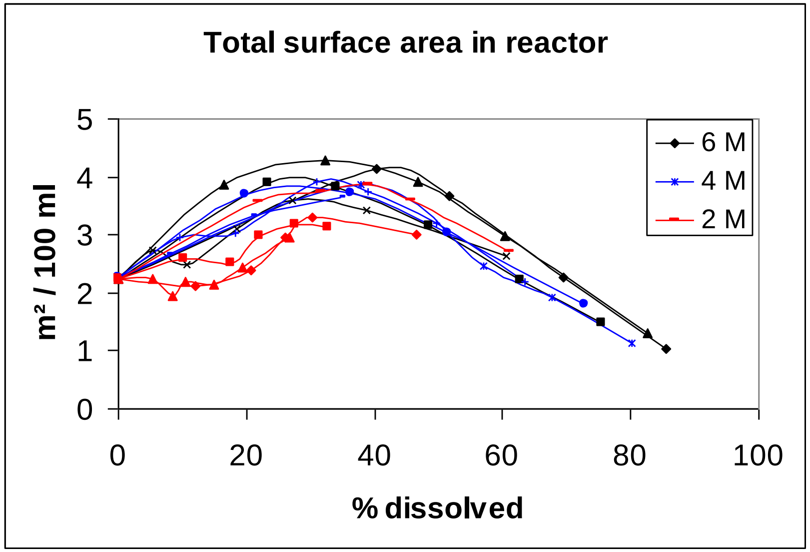
VC = standard deviation / mean particle size




Shrinking sphere

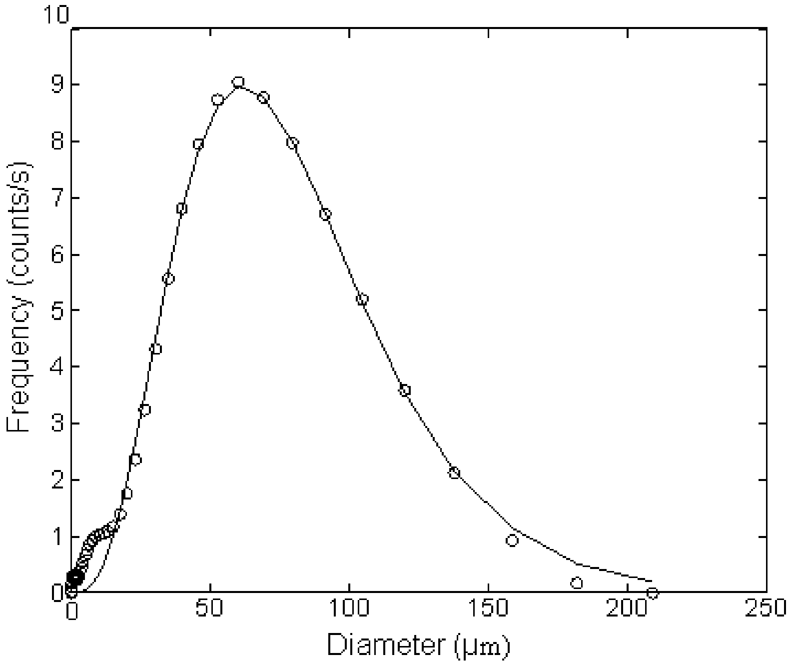
Implementing the particle size distribution into modeling





- Gibbsite is rough/porous and cracks during dissolution
- The surface area goes through a maximum, non-ideal behavior

Implementing the particle size distribution into modeling



$$f(x) = x^{k_{SP}-1} \frac{e^{-x/\theta}}{\theta^{k}\Gamma(k_{SP})}$$

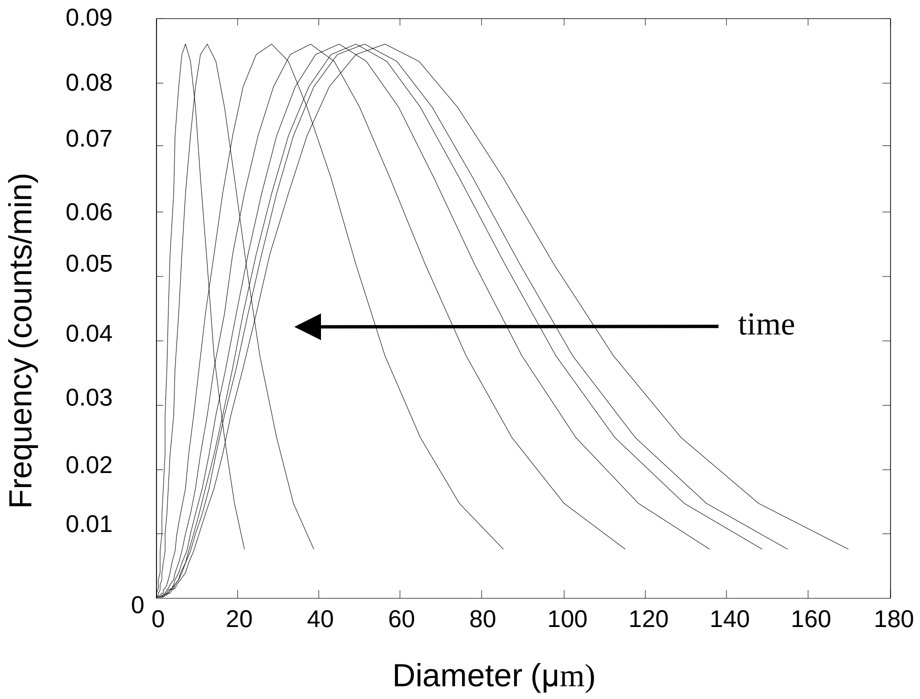
$$\Gamma(k_{SP}) = \int_{0}^{\infty} t^{k_{SP}-1} e^{-t} dt$$

$$Var(x) = k_{SP}\theta^{2} \qquad E(x) = k_{SP}\theta$$

- The Gamma distribution is fitted to the fresh particle size distribution and the distribution is divided into fractions

- The shape parameter (k) and the scale parameter (θ) are kept constant

Implementing the particle size distribution into modeling



$$\frac{c_t}{c_0} = \frac{m_t}{m_0} = \frac{V_t}{V_0} = X = 1 - \alpha$$

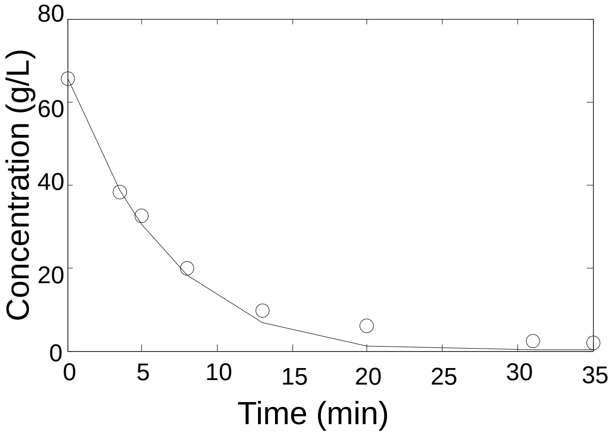
$$r_{i,t} = r_{i,0}\sqrt[a]{X}$$

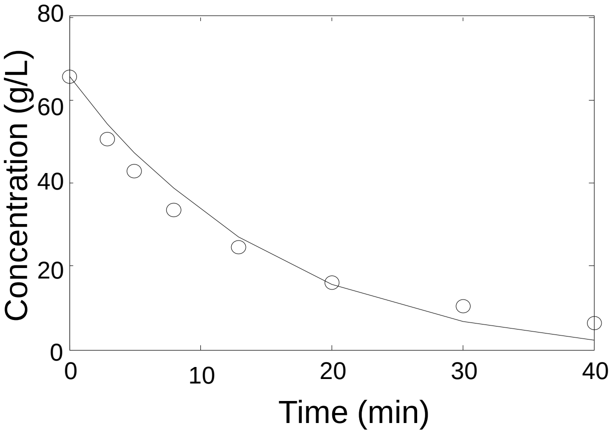
$$a = \frac{A_P}{V_P} R_0 \qquad A_{r_i,tP} = \frac{aV_{r_i,tP}}{r_{i,tP}}$$

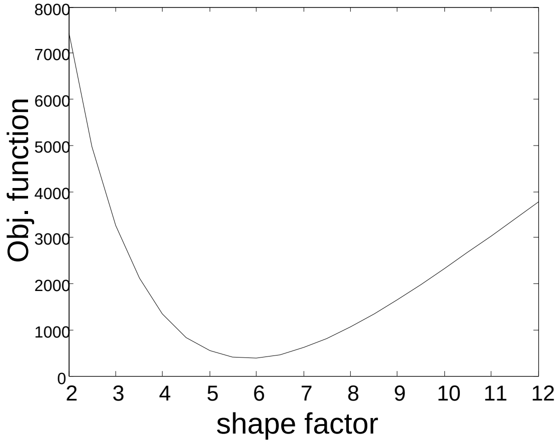
- A new radius is calculated for each fraction and each fraction is summed to obtain the new surface area in the reactor

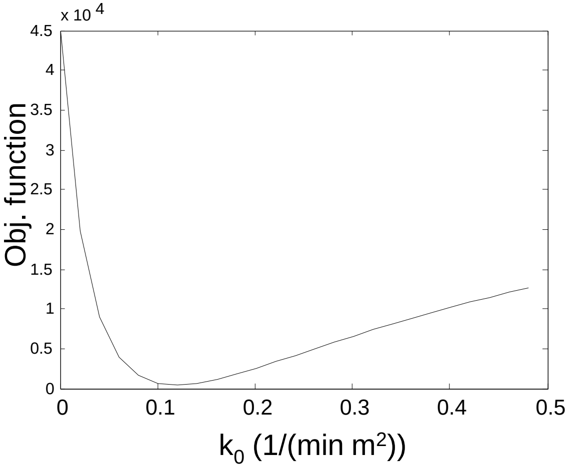
- The new surface area is implemented into to rate equation

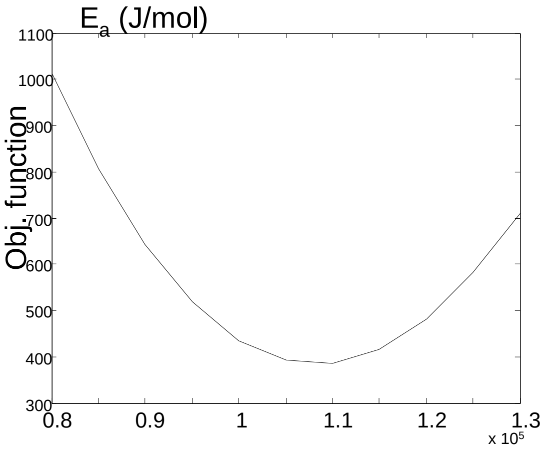
The fit of the model and sensitivity analysis

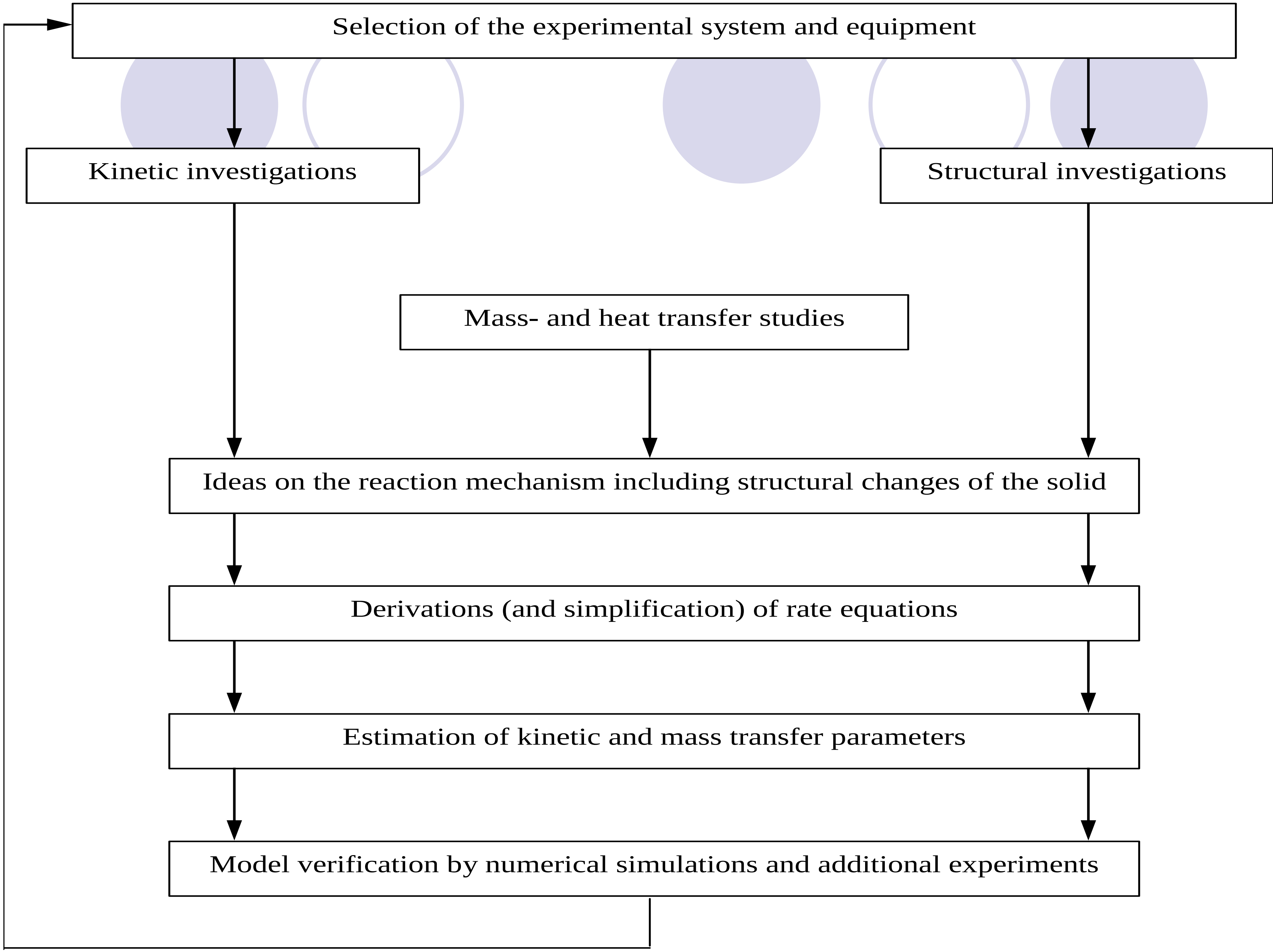












Selection of the experimental system and equipment

Kinetic investigations

Structural investigations

Mass- and heat transfer studies

Ideas on the reaction mechanism including structural changes of the solid

Derivations (and simplification) of rate equations

Estimation of kinetic and mass transfer parameters

Model verification by numerical simulations and additional experiments

Conclusions

- Modeling is an important tool in developing new processes as well as optimizing existing ones
- Solid-liquid reactions are in general more difficult to model than homogeneous reactions
- Traditional modeling procedures have potholes, which can severely influence the outcome
- Care should be taken in drawing the right conclusions about the reaction mechanisms

Things to consider in modeling

- Some important factors:
  1. Be sure about what you actually are measuring
  2. Evaluate if the particle size distribution needs to be taken into account (*VC*<0.3)
  3. If the morphology is not ideal use a shape factor to describe the change in surface area (surface area, density and conversion measurements needed)
  4. Use sensitivity analysis to see if your parameter values are well defined

Some relevant publications

- Salmi, Tapio; Grénman, Henrik; Waerna, Johan; Murzin, Dmitry Yu. Revisiting shrinking particle and product layer models for fluid-solid reactions - From ideal surfaces to real surfaces.Chemical Engineering and Processing 2011, 50(10), 1076-1084.
- Salmi, Tapio; Grénman, Henrik; Bernas, Heidi; Wärnå, Johan; Murzin, Dmitry Yu. Mechanistic Modelling of Kinetics and Mass Transfer for a Solid-liquid System: Leaching of Zinc with Ferric Iron. Chemical Engineering Science 2010, 65(15), 4460-4471.
- Grénman, Henrik; Salmi, Tapio; Murzin, Dmitry Yu.; Addai-Mensah, Jonas. The Dissolution Kinetics of Gibbsite in Sodium Hydroxide at Ambient Pressure. Industrial & Engineering Chemistry Research 2010, 49(6), 2600-2607.
- Grénman, Henrik; Salmi, Tapio; Murzin, Dmitry Yu.; Addai-Mensah, Jonas. Dissolution of Boehmite in Sodium Hydroxide at Ambient Pressure: Kinetics and Modelling. Hydrometallurgy 2010, 102(1-4), 22-30.
- Grénman, Henrik; Ingves, Malin; Wärnå, Johan; Corander, Jukka; Murzin, Dmitry Yu.; Salmi, Tapio. Common potholes in modeling solid-liquid reactions – methods for avoiding them. Chemical Engineering Science (2011), 66(20), 4459-4467.
- Grénman, Henrik; Salmi, Tapio; Murzin, Dmitry Yu.. Solid-liquid reaction kinetics – experimental aspects and model development. Rev Chem Eng 27 (2011): 53–77

Mechanistic modelling of kinetics and mass transfer for a solid-liquid system: Leaching of zinc with ferric iron

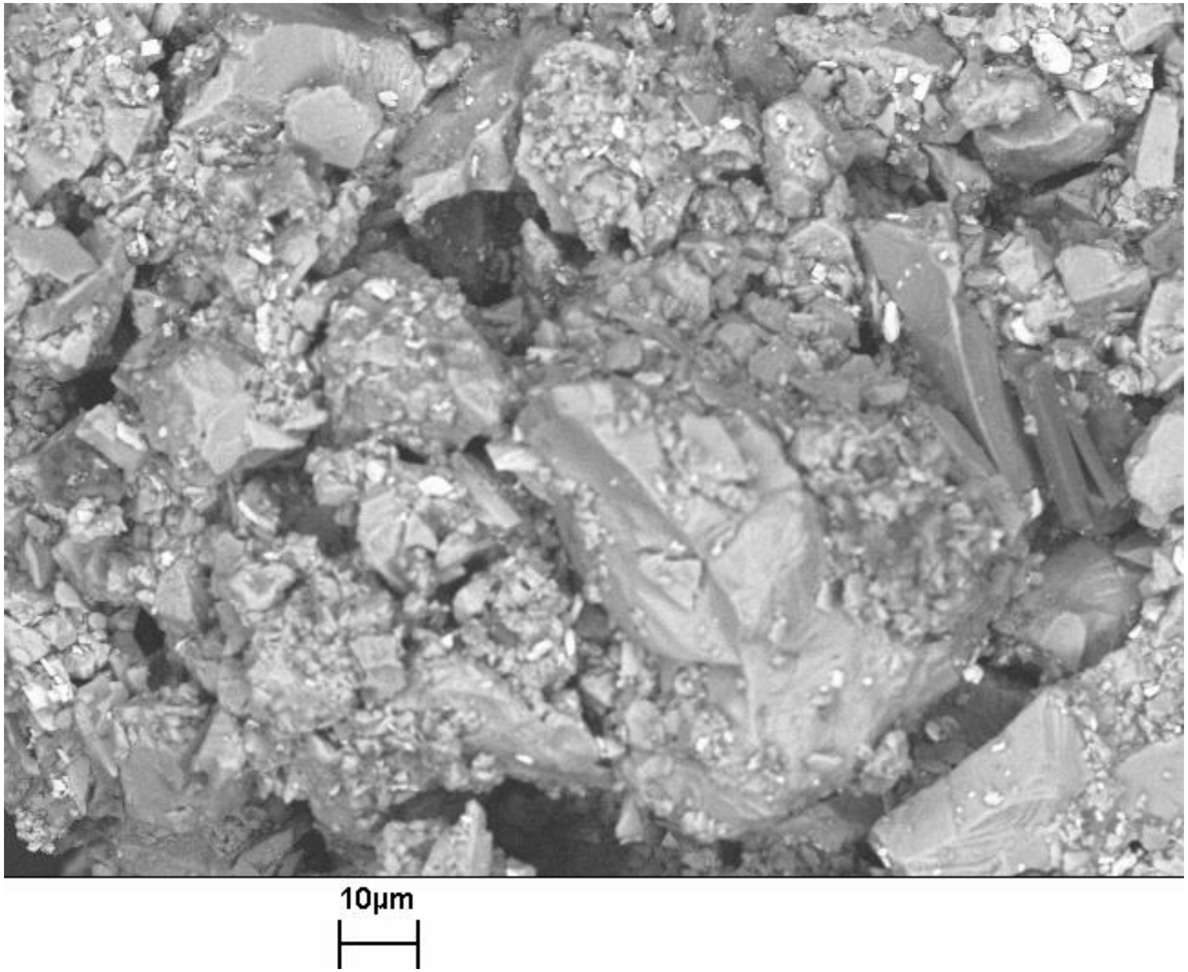
Tapio Salmi, Henrik Grénman, Heidi Bernas,
Johan Wärnå, Dmitry Yu. Murzin

Laboratory of Industrial Chemistry and Reaction Engineering,
Process Chemistry Centre,
Åbo Akademi, FI-20500 Turku/Åbo, Finland

Reaction system

$ZnS(s) + Fe2(SO_4)_3 \leftrightarrow S(s) + 2FeSO_4 + ZnSO_4$

SEM



Experimental system

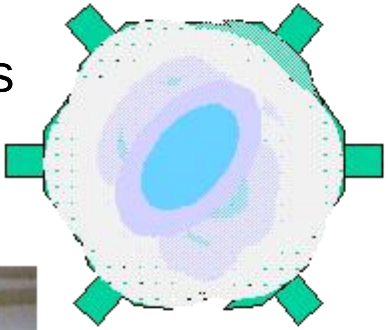
- Isothermal batch reactor
- Turbine impeller
- Ultrasound input
- SIA – analysis of Fe^{3+}

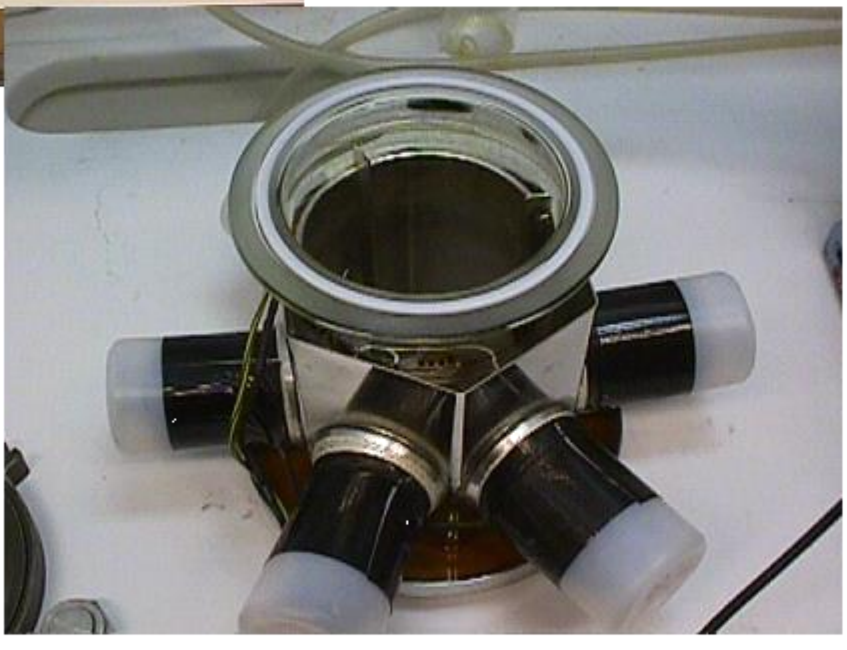
Experimental data of Bernas (Markus) & Grénman

Markus et al, Hydrometallurgy 73 (2004) 269-282,
Grénman et al, Chemical Engineering and Processing 46 (2007) 862-869

Multi-transducer ultradound reactor

6 transducers





Generator (0-600W)

20 kHz

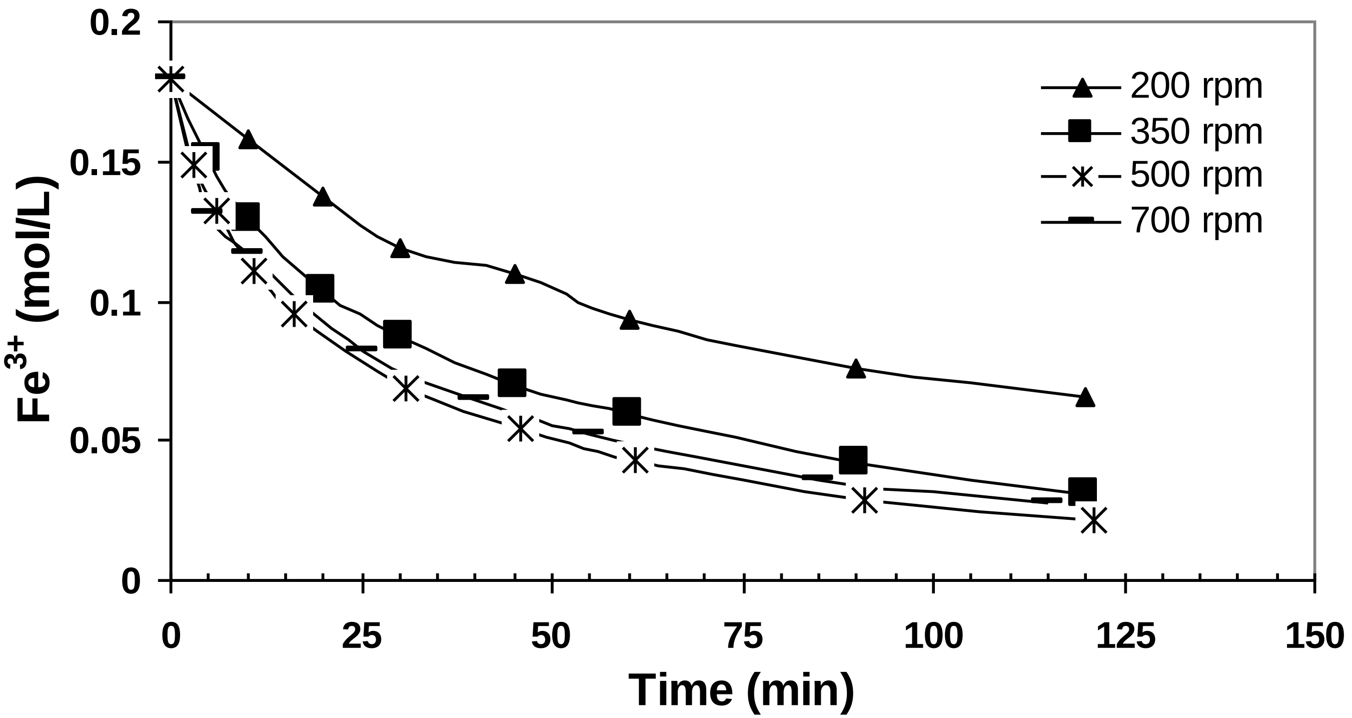
Reactor pot inserted

A time-variable

power input

Experimental results - Stirring speed

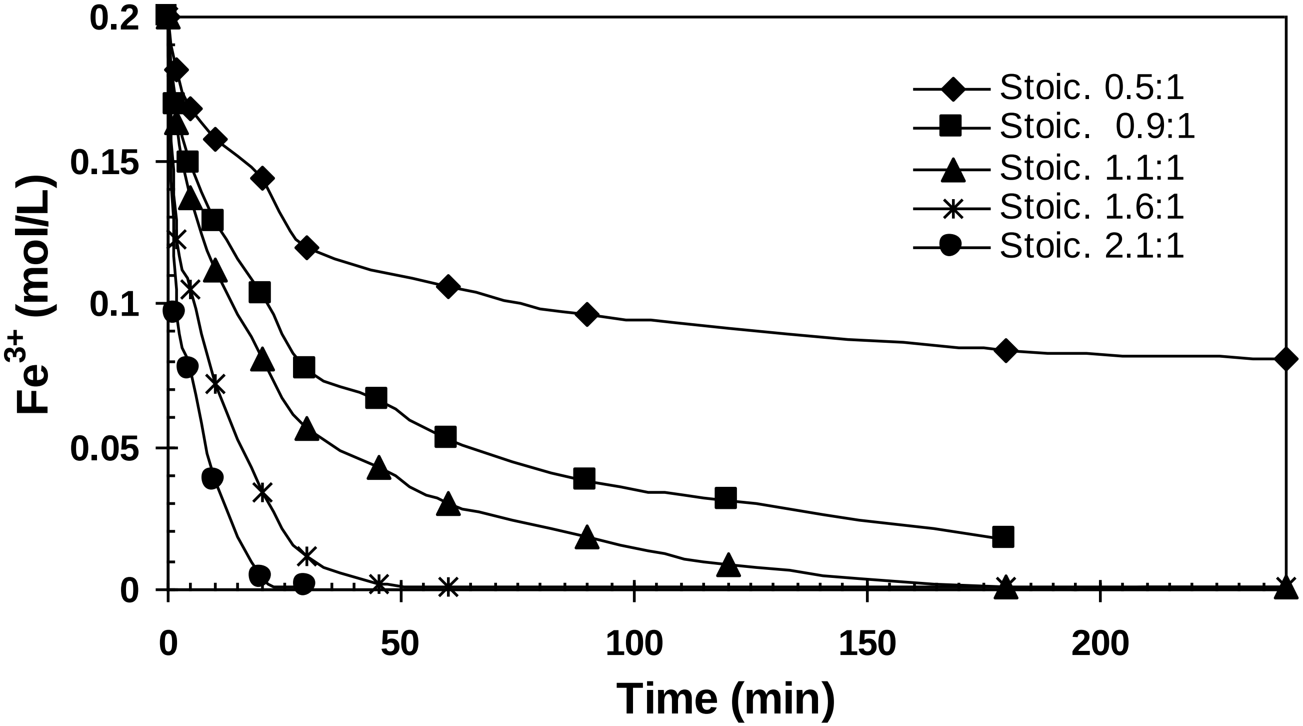
T = 85°C , Sphalerite : Fe^{3+} = 1.1:1



The effect of the stirring speed on the leaching kinetics.

Experimental results

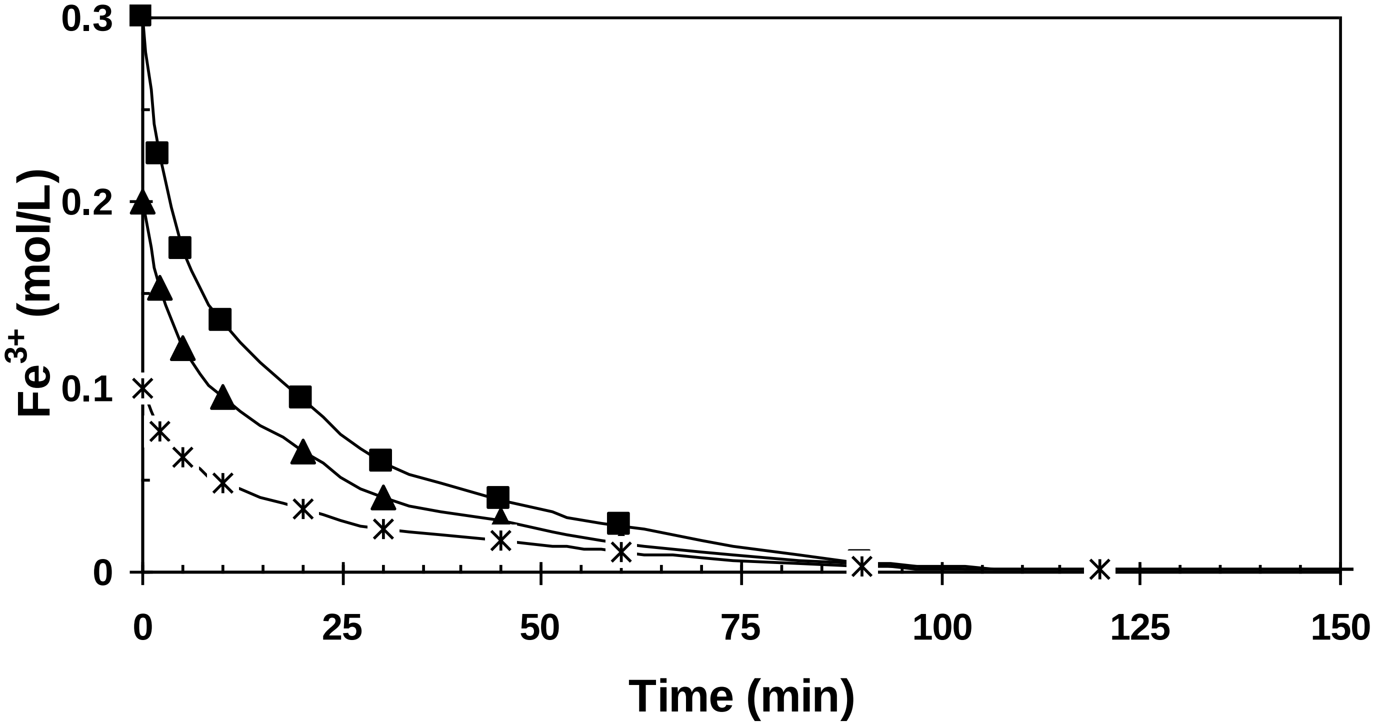
$T = 85°C, \quad C_{0Fe(III)} = 0.2\ mol/L$



The effect of the zinc sulphide concentration on the leaching kinetics.

Experimental results

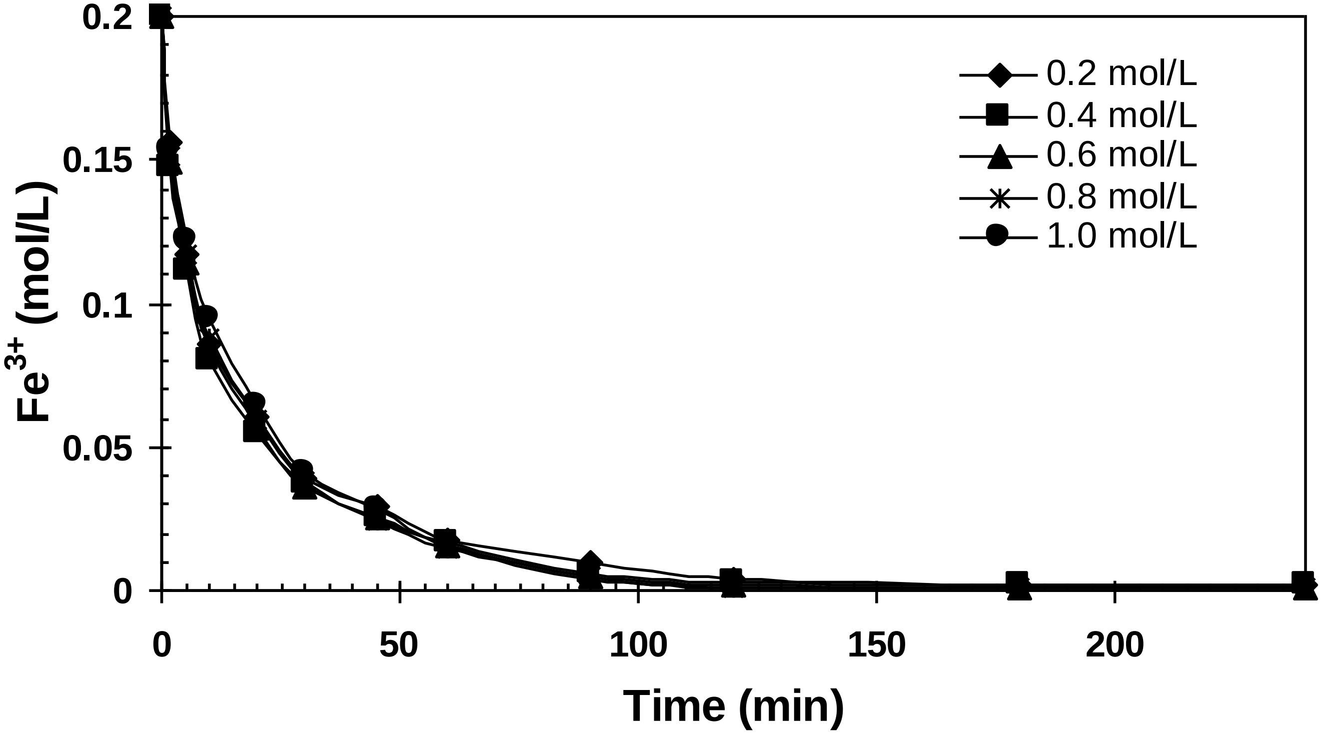
T = 95°C, Sphalerite : Fe^{3+} = 1.1:1



The effect of the ferric ion concentration on the leaching kinetics.

Experimental results

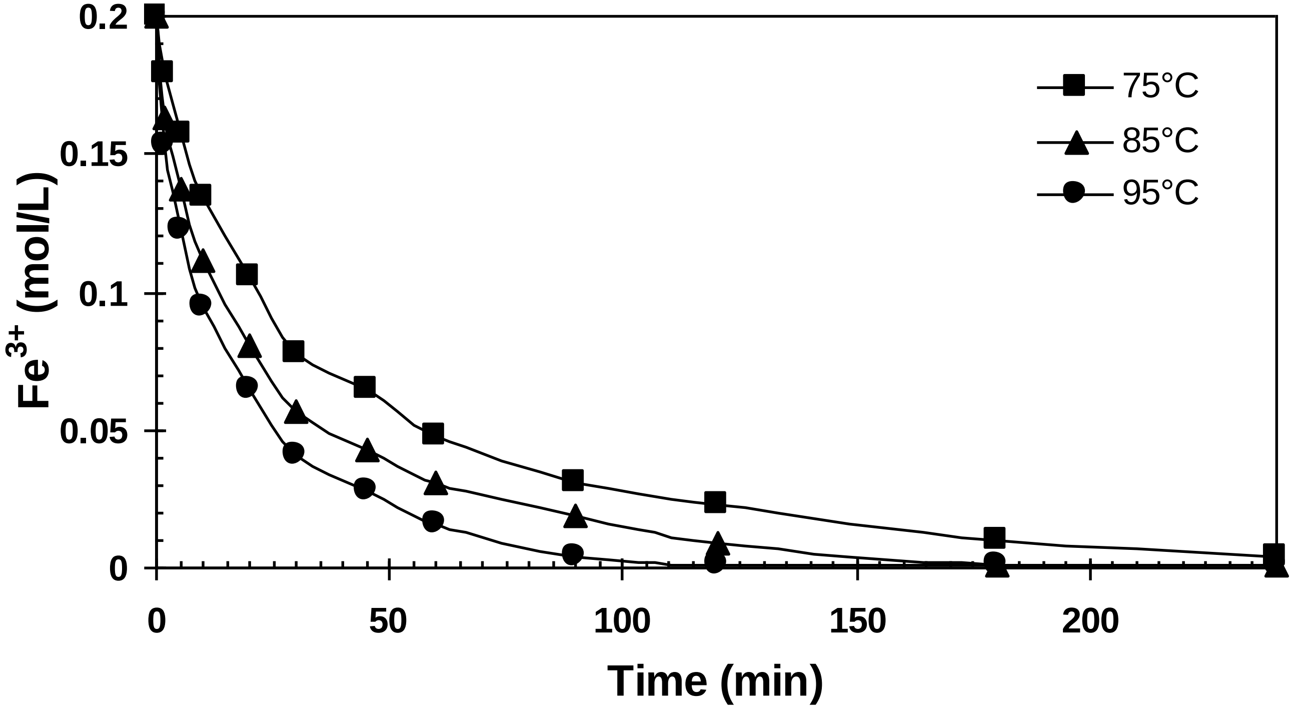
T = 95°C,   Sphalerite : Fe^{3+} *= 1.1:1*



The effect of sulphuric acid on the leaching kinetics.

Experimental results - Temperature effect

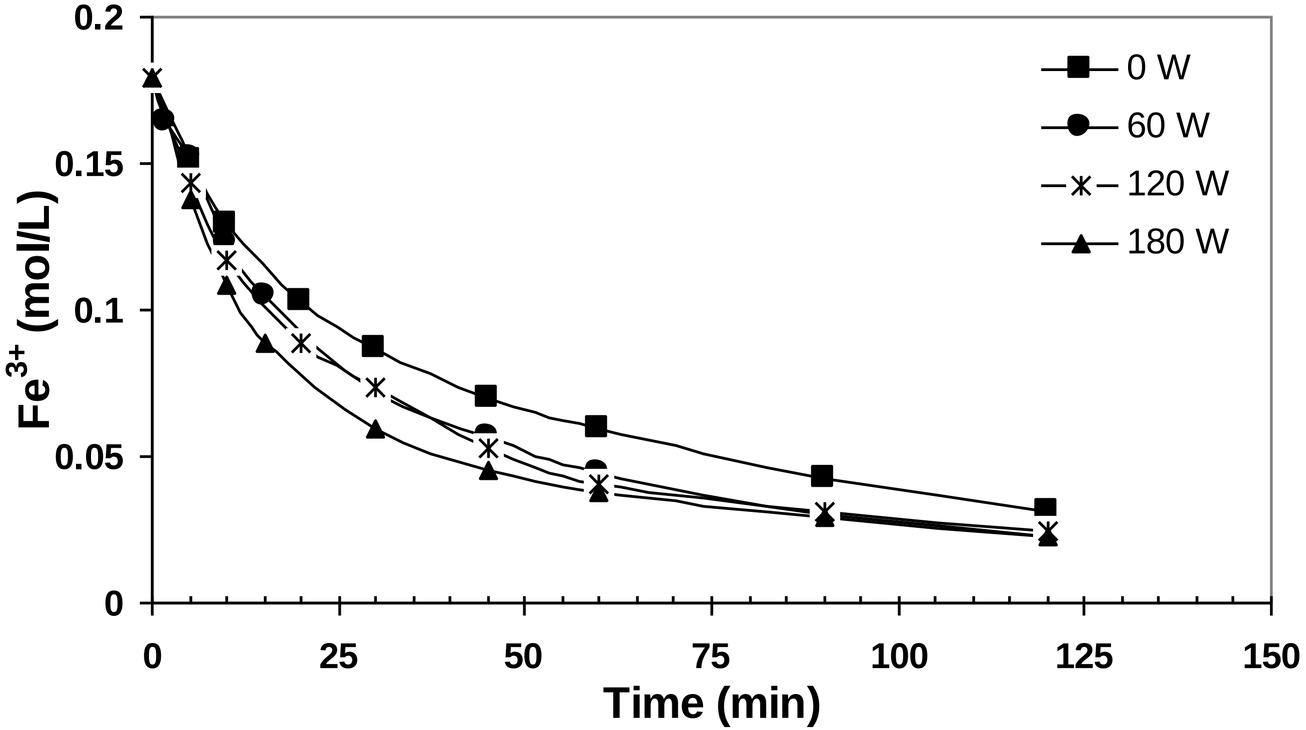
Sphalerite : Fe^{3+} *= 1.1:1*



The effect of temperature on the leaching kinetics.

Experimental results - Ultrasound effect

T = 85°C Stirring rate 350 rpm



The effect of ultrasound on the leaching kinetics.

Reaction mechanism and rate equations

- Surface reaction

- Stepwise process

  (first reacts one Fe^{3+}, then the second one!)

- Rough particles

Three-step surface reaction mechanism

$ZnS(s) + Fe^{3+} \leftrightarrow I_1$ (I)

$I_1 + Fe^{3+} \leftrightarrow I_2$ (II)

$I_2 \leftrightarrow S(s) + 2\,Fe^{2+} + Zn^{2+}$ (III)

$ZnS(s) + 2Fe^{3+} \leftrightarrow S(s) + 2\,Fe^{2+} + Zn^{2+}$

rates of steps (I-III)

$$r_1 = a_1 - a_{-1} c_{I1}$$

$$r_2 = a_2 c_{I1} - a_{-2} c_{I2}$$

$$r_3 = a_3 c_{I2} - a_{-3}$$

$$a_1 = k_{+1} c_{FeIII}$$

$$a_{-1} = k_{-1}$$

$$a_2 = k_{+2} c_{FeIII}$$

$$a_{-2} = k_{-2}$$

$$a_3 = k_{+3}$$

$$a_{-3} = k_{-3} c_{FeIII}^2 c_{ZnII}$$

c_{I1}, c_{I2} and c_{I3} = surface concentrations of the intermediates.

Development of rate equations

Pseudo-steady state hypothesis *Rate equation*

$$r_1 = r_2 = r_3 = r$$

$$r = \frac{a_1 a_2 a_3 - a_{-1} a_{-2} a_{-3}}{a_{-1} a_{-2} + a_{-1} a_3 + a_2 a_3}$$

Back-substitution of $a_1 \ldots . a_{-3}$ gives

$$r = \frac{k_{+1} k_{+2} k_{+3} c_{FeIII}{}^2 - k_{-1} k_{-2} k_{-3} c_{FeII}{}^2 c_{ZnII}}{D}$$

$$D = k_{-1} k_{-2} + k_{-1} k_{+3} + k_{+2} k_{+3} c_{FeIII}$$

$$r = \frac{k(c_{FeIII}{}^2 - c_{FeII}{}^2 c_{ZnII} / K)}{D}$$

Rate equations

Final form

$$r = \frac{k_1 c_{FeIII}{}^2}{\beta + c_{FeIII}}$$

where $\beta = (k_{-1}k_{-2}+k_{-1}k_{+3})/(k_{+2}k_{+3})$

An alternative rate equation

$$r = \frac{k_1 c_H c_{FeIII}{}^2}{\beta c_H + c_{FeIII}}$$

NOT VALID FOR THIS CASE!

Area & Shape factor

Development of a general approach

The surface area (A) can be expressed with a generalized equation

$$A = \frac{aM}{\rho_P R_0} n_0{}^x n^{1-x}$$

n = amount of solid
n_0= initial amount of solid
Shape factor ($a=1/x$)

$$a = \frac{A_P}{V_P} R_0 \qquad a / R_0 = \frac{\sigma m_{0P}}{V_{0P}} = \sigma\rho_P \qquad A = \sigma M n_0{}^{1/a} n^{1-1/a}$$

Area & Shape factor

Geometry	Shape factor (a)	x	1-x
Slab	1	1	0
Cylinder	2	1/2	1/2
Sphere	3	1/3	2/3
Irregular, ‘rough’ particle	high value	0	1

Reaction order can vary between 0 and 1!

Mass balance for batch reactor

$$\frac{dc_{ZnS}}{dt} = \frac{\nu_{ZnS}\sigma M}{x_{0ZnS}} c_{ZnS} r$$

$$\frac{dc_{FeIII}}{dt} = \frac{\nu_{FeIII}\sigma M}{x_{0ZnS}} c_{ZnS} r$$

$$r' = \frac{\gamma e^{-E_a / RT} c_{ZnS} c_{FeIII}^{2}}{\beta + c_{FeIII}}$$

, *where* $\gamma=(k_1\sigma M / x_{0ZnS})$

$$\frac{dc_i}{dt} = \nu_i r'$$

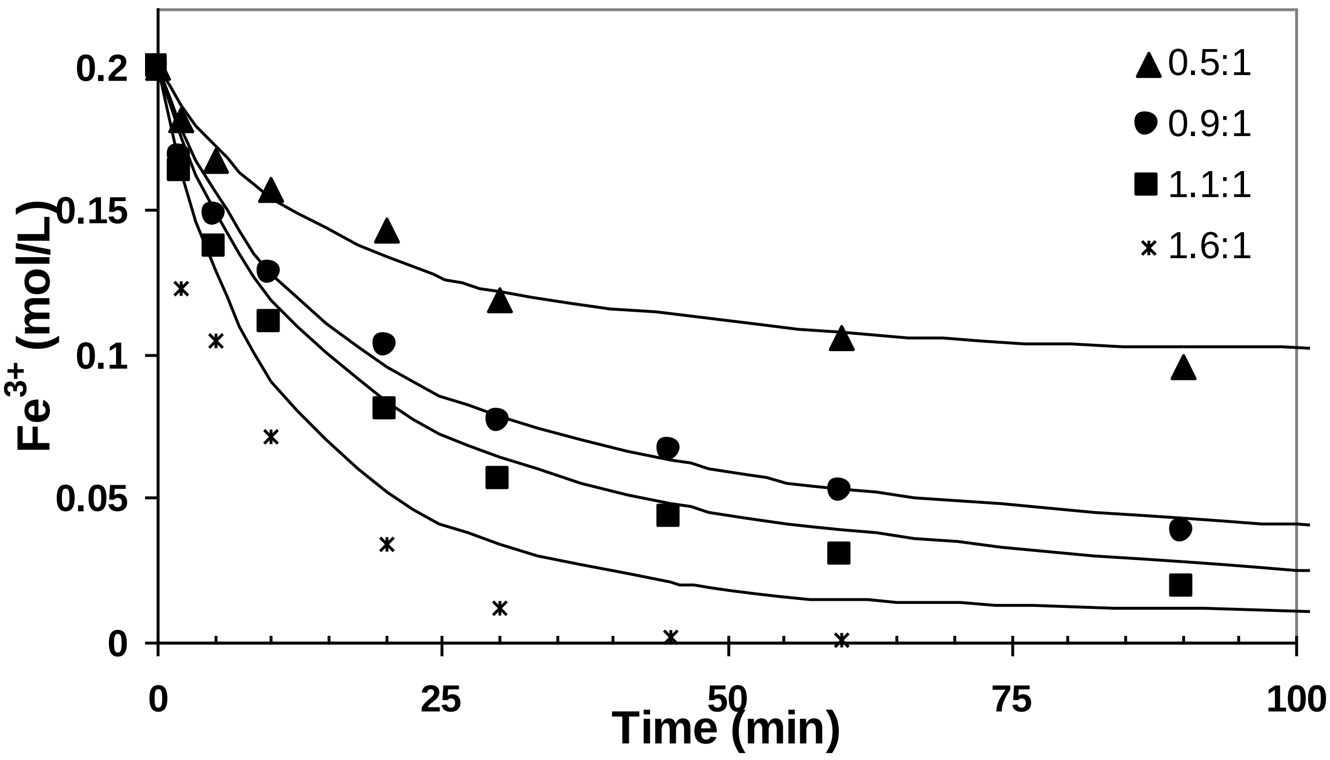
Parameter estimation

Nonlinear regression applied on intrinsic kinetic data

Estimated Parameter		**Parameter value**	**Est. Std. Error %**
γ	(L / mol min)	0.331	4.5
E_a	(J / mol)	53200	4.8
β	(mol / L)	0.2	24.9

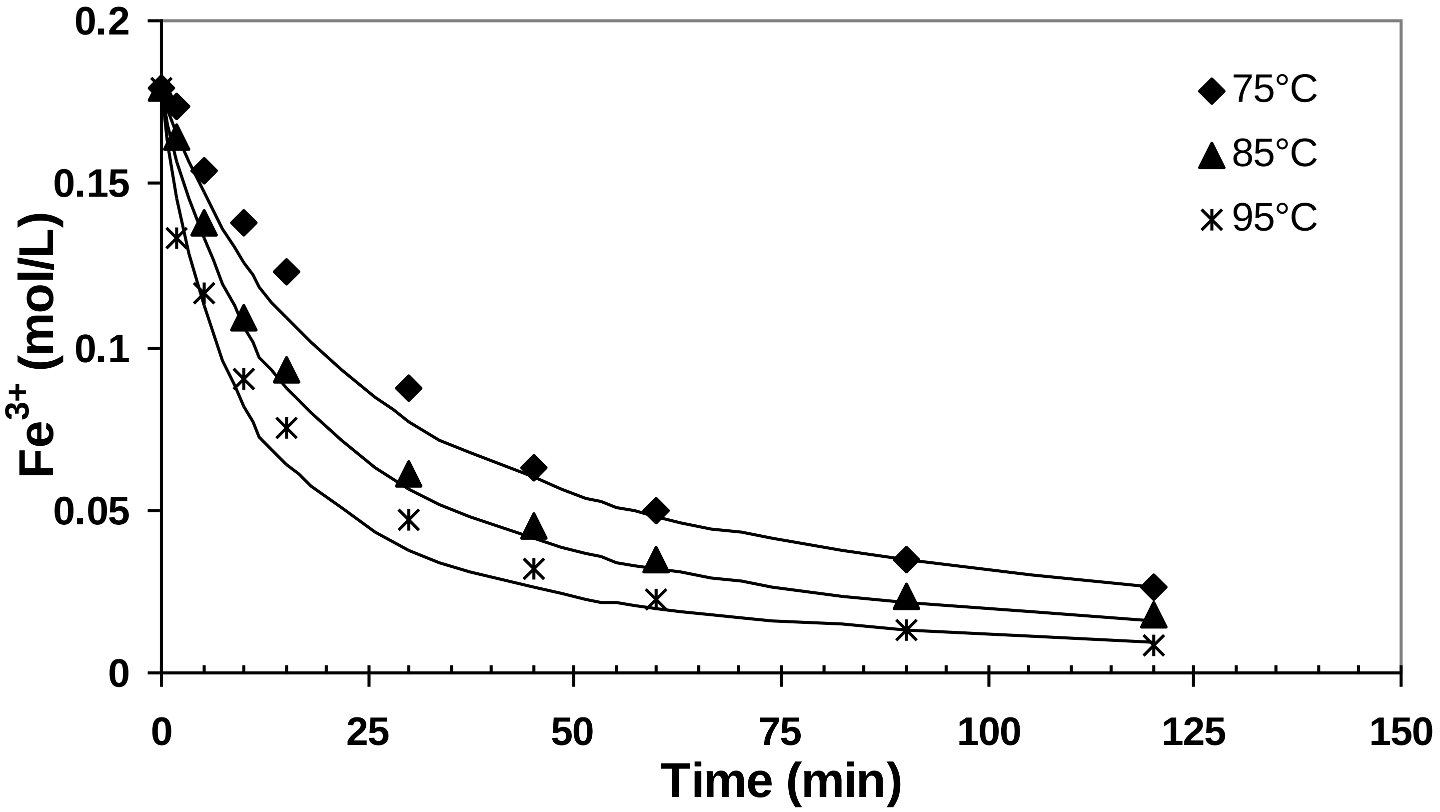
Intrinsic kinetics - *Model fit*

T = 85°C



The effect of the ratio sphalerite : FeIII on the kinetics

Intrinsic kinetics - *Model fit*



Temperature effect on the kinetics.

Mass transfer limitations in Batch reactor

$$N_{Li}{}^{s}A+\nu_i rA=0$$

where $r_i=\nu_i r$ The mass transfer term ($N_{Li}{}^{s}$) is described by Fick's law

$$k_{Li}(c_i-c_i{}^{*})=\frac{-\nu_i k_1 c_i{}^{*2}}{\beta+c_i{}^{*}}$$

$\beta' = \beta/c_i$, $\gamma' = (-\nu_i k_1 c_i/k_{Li})$, $y = c_i{}^{*}/c_i$

The solution becomes

$$c_i{}^{*}/c_i=\frac{2\beta'}{\sqrt{(\beta'-1)^2+4(\gamma'+1)\beta'}+\beta'-1} \Rightarrow r=\frac{k_1 c_{FeIII}{}^{*2}}{\beta+c_{FeIII}{}^{*}}$$

Liquid-solid mass transfer coefficient

General correlation

$$Sh = a + b\,\mathrm{Re}^{1/2}\,Sc^{1/3}$$

$$\mathrm{Re} = \left(\frac{\varepsilon d^{4}}{\upsilon^{3}}\right)^{1/3}$$

$$Sc = \upsilon / D_i$$

$$Sh = k_{Li} d / D_i$$

$$k_{Li} = \frac{D_i}{d}\left(a + b\left(\frac{\varepsilon d^{4}}{\upsilon^{3}}\right)^{1/6}\left(\frac{\upsilon}{D_i}\right)^{1/3}\right)$$

$$k_{Li} = \frac{D_i}{d_0 z^{1/3}}\left(a + b\left(\frac{\varepsilon d_0{}^{4} z^{4/3}}{\upsilon^{3}}\right)^{1/6}\left(\frac{\upsilon}{D_i}\right)^{1/3}\right)$$

where $z=c_{ZnS}/c_{0ZnS}$*. The index (i) refers to Fe(III) and Fe(II)*

Correlations in rate equation

$$k_{Li} = \frac{D_i}{d_0 z^{1/3}}\left(2 + b' z^{2/9}\right)$$

$$b' = b(\varepsilon\, d_0^{\,4} / \upsilon^{\,3})^{1/6} (\upsilon / D_i)^{1/3}$$

IF $b' z^{2/9}$ *>> 2 under stirring,*

$$k_{Li} = \frac{D_i b'}{d_0 z^{1/9}} = \frac{b''}{z^{1/9}}$$

$$\gamma' = -\nu_{FeIII}\, x_{0ZnS}\, \gamma\, c_{FeIII} z^{1/9} / (\sigma M b''_{FeIII})$$

$$\gamma' = \frac{-\nu_{FeIII}\, \gamma c_{FeIII}\, \omega}{(c_{0ZnS} / c_{ZnS})^{1/9}}$$

$$\omega = x_{0ZnS}\, d_0^{1/3} / (\sigma M b (\varepsilon / \upsilon)^{1/6} D_{FeIII}^{2/3})$$

The surface concentration:

The rate:

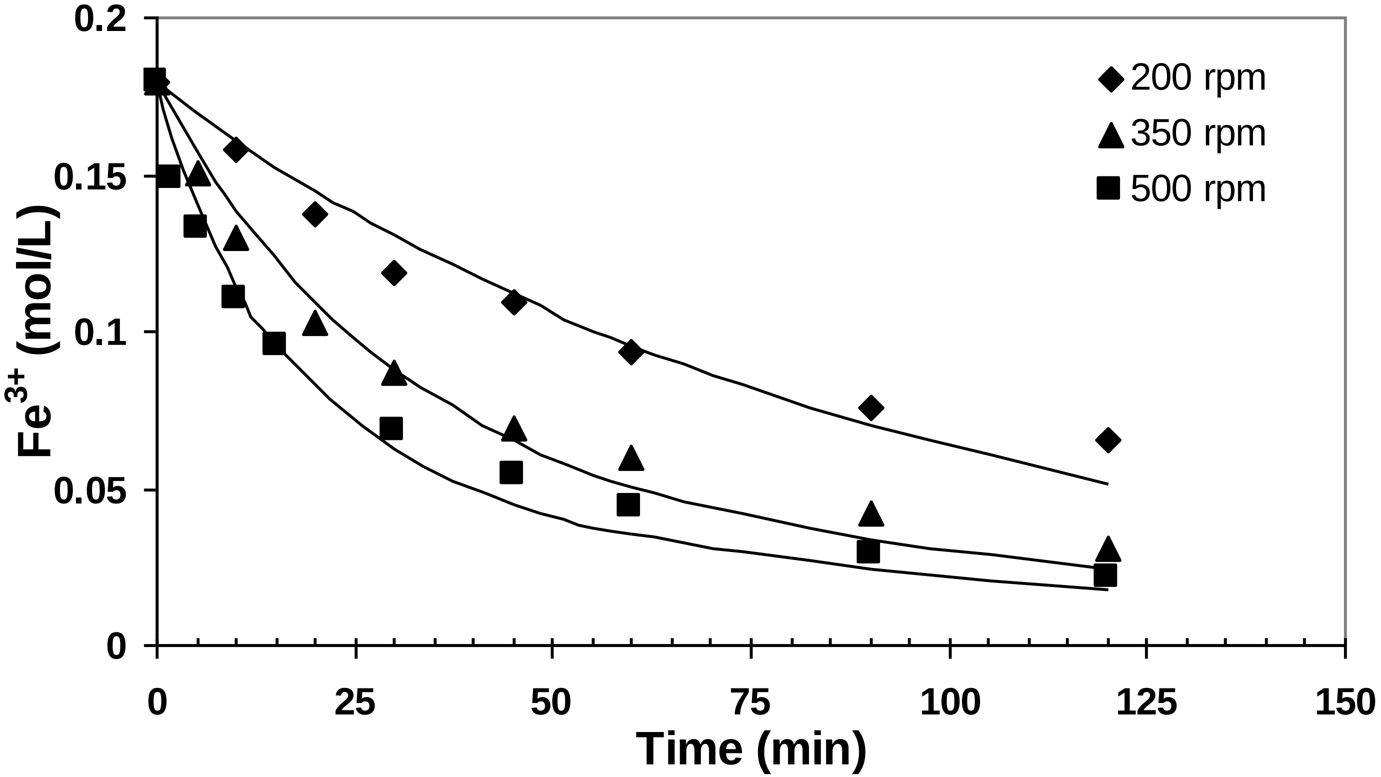
$$c_{FeIII}{}^* = \frac{2\beta c_{FeIII}}{\sqrt{(\beta - c_{FeIII})^2 + 4(\gamma' + 1)\beta c_{FeIII}} + \beta - c_{FeIII}}$$

$$r' = \frac{\gamma c_{ZnS}\, c_{FeIII}{}^{*2}}{\beta + c_{FeIII}{}^*}$$

Determination of mass transfer parameter (ω)

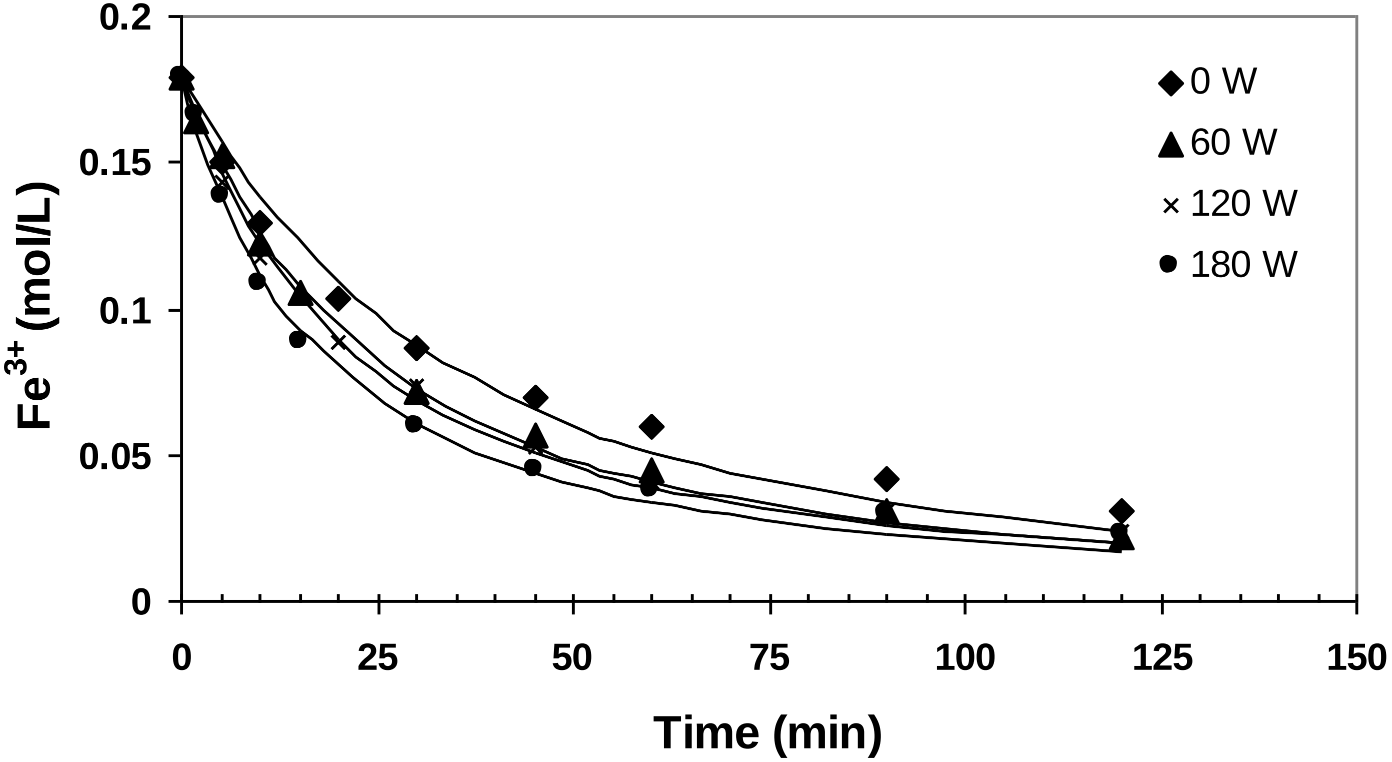
Agitation rate & US effect		**ω (mol min / m^3)**
200 rpm		50
350 rpm		14
500 rpm		2.4
350 rpm	**US 0 W**	14
350 rpm	**US 60 W**	6.8
350 rpm	**US 120 W**	5.8
350 rpm	**US 180 W**	1.67

Modelling of kinetics and mass transfer



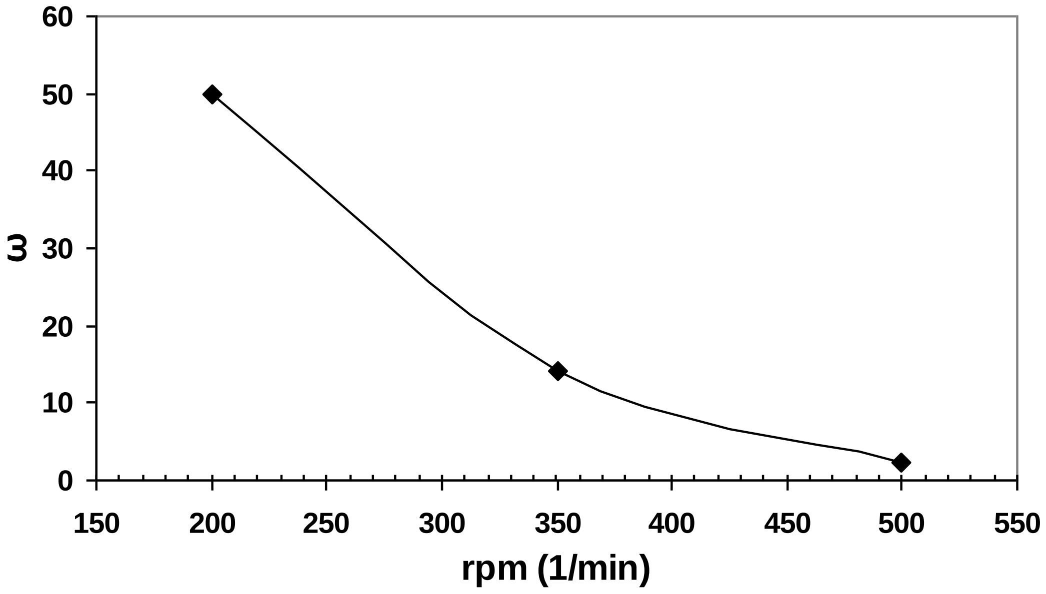
External mass transfer limitations – modelling of individual mass transfer parameters at different agitation rates.

Modelling of kinetics and mass transfer

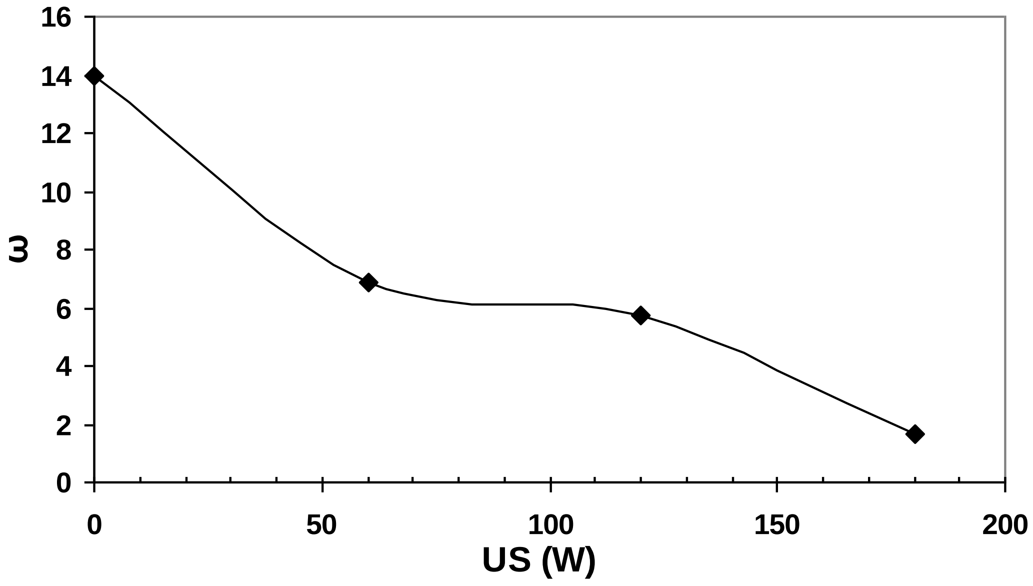


External mass transfer limitations – modelling of individual mass transfer parameters at different ultrasound inputs.

Mass transfer parameter

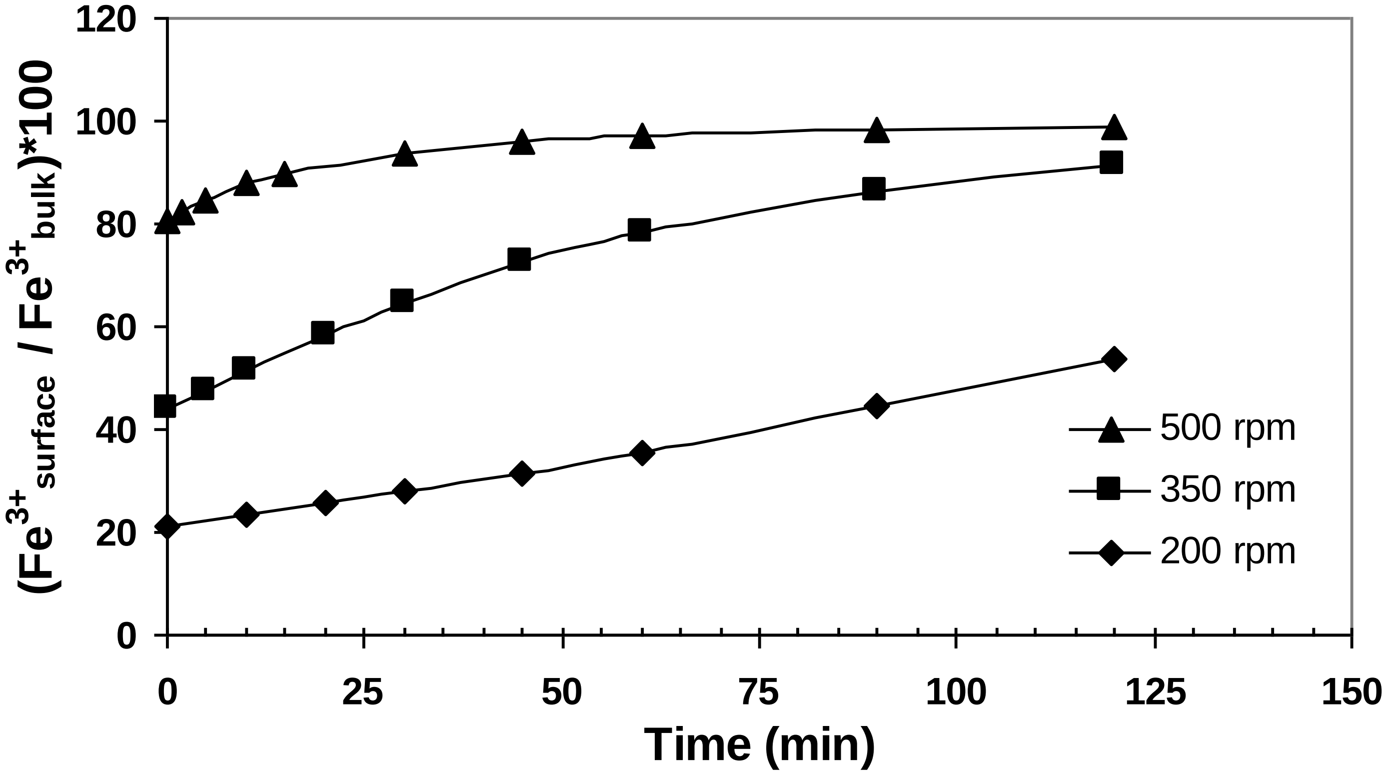


Normal agitation



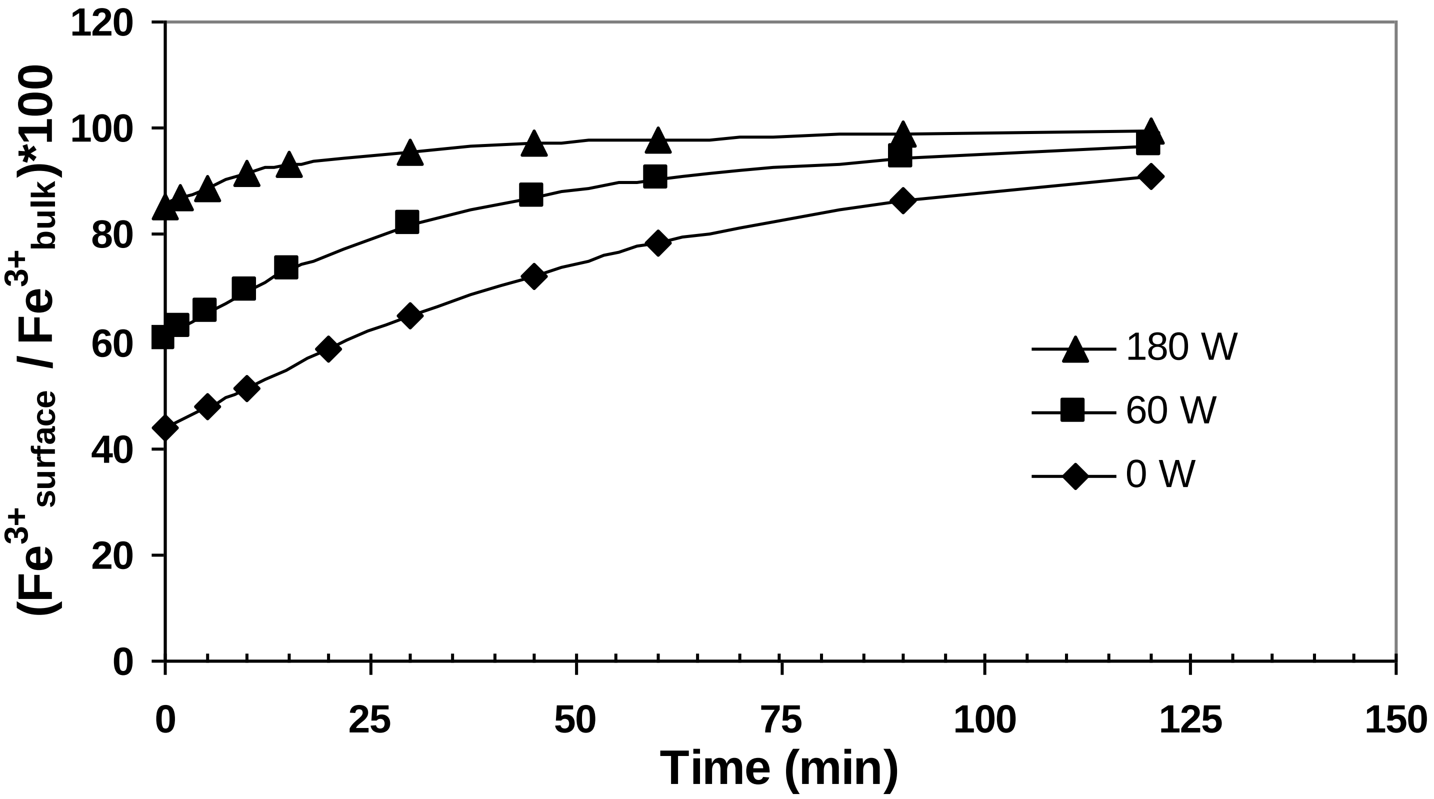
Ultrasound

The real impact of mass transfer limitations



The difference in the model based surface concentrations and measured bulk concentrations of Fe3+ at different stirring rates.

The real impact of mass transfer limitations



The difference in the model based surface concentrations and measured bulk concentrations of Fe3+ at different ultrasound inputs.

Conclusions

- A new kinetic model was proposed
- A general treatment of smooth, rough and porous surfaces was developed
- The theory of mass transfer was implemented in the model
- Model parameters were estimated
- The model works

Modelling and simulation of porous, reactive particles in liquids: delignification of wood

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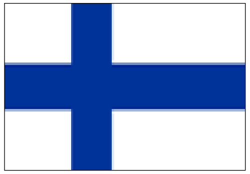
Typical view of Finland



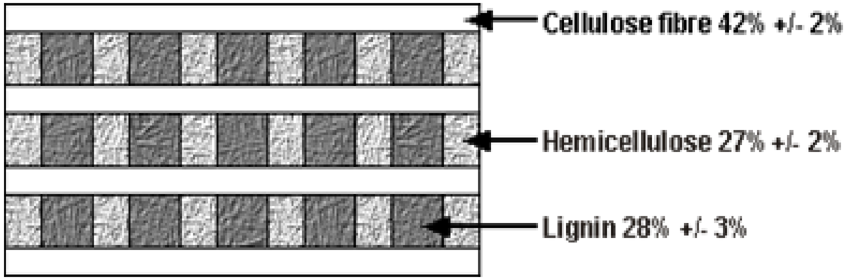
338000 km^2 of
which 70% forest

Papermaking

- **Wood chips**
- This is where paper making begins.
- A typical wood chip measures 40 x 25 x 10 mm.

Wood

- Each chip comprises water, cellulose wood fibres and the binding agent lignin.



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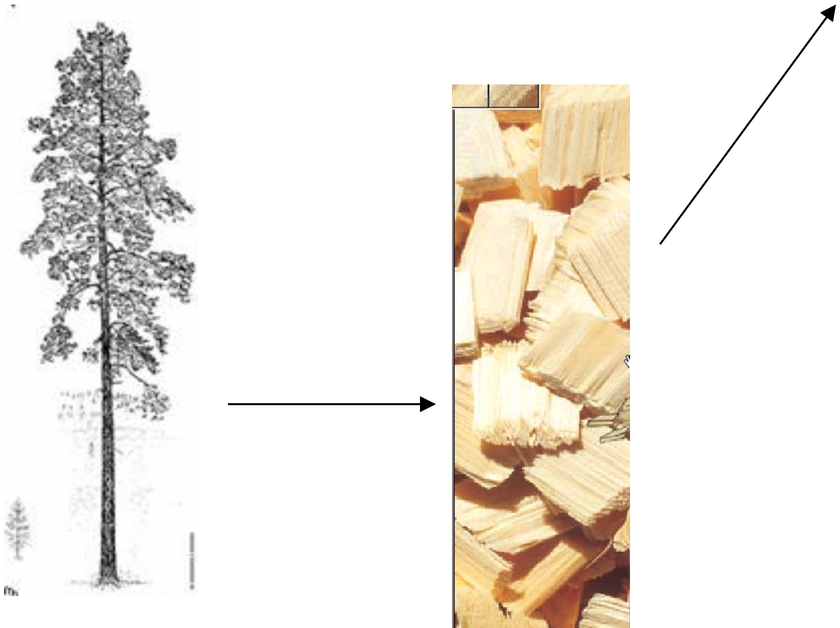
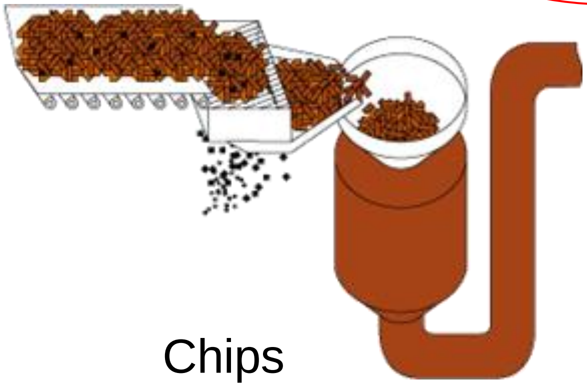
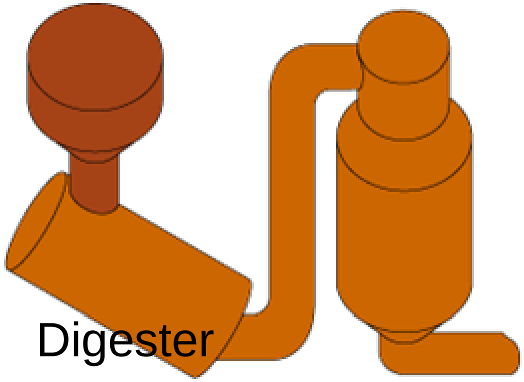


Pulp

- To make paper, we need to first make pulp, which is the process of breaking the wood structure down into individual fibers

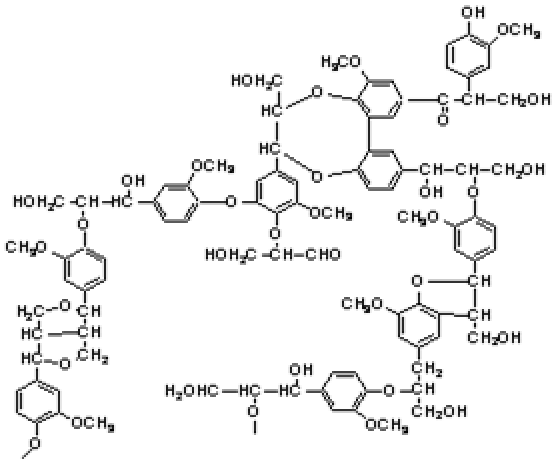

Chips


Digester

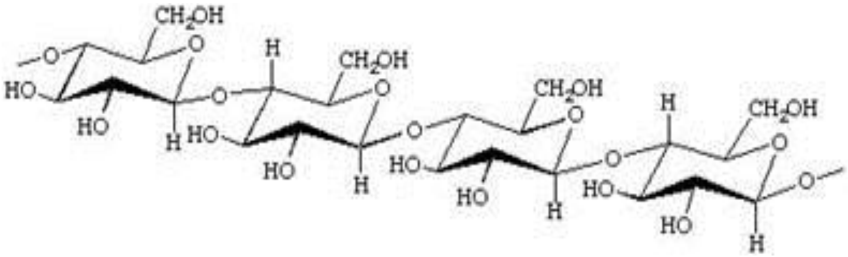
Reactions

The reactions in chemical pulping are numerous. Typical pulping chemicals are NaOH and NaHS

Part of Lignin molecule



cellulose



Overall process:

Lignin+Cellulose+Carbohydrates+Xylanes+OH+HS -> Dissolved components

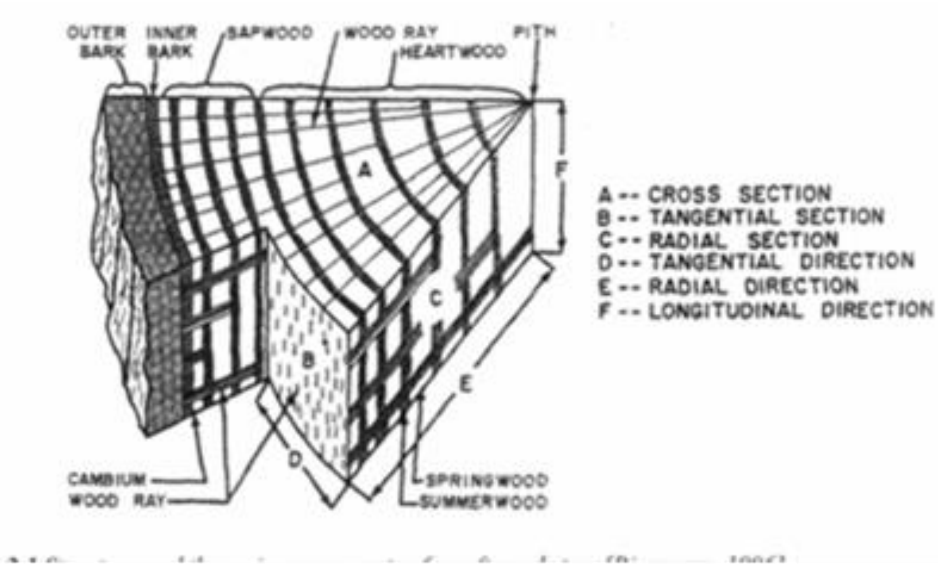
Kinetic modelling of wood delignification

- Purdue model (Smith et.al. (1974) Christensen et al. 1983), 5 pseudocomponents
- Gustafson et al. 1983, 2 wood components Lignin and Carbohydrate, 3 stages
- Andersson 2003, 15 pseudocomponents

- Very few models available!

Wood chip structure

- Wood material is built up of fibres
- We can expect different diffusion rates in the fibre direction and in the opposite direction to the fibres.



Existing models

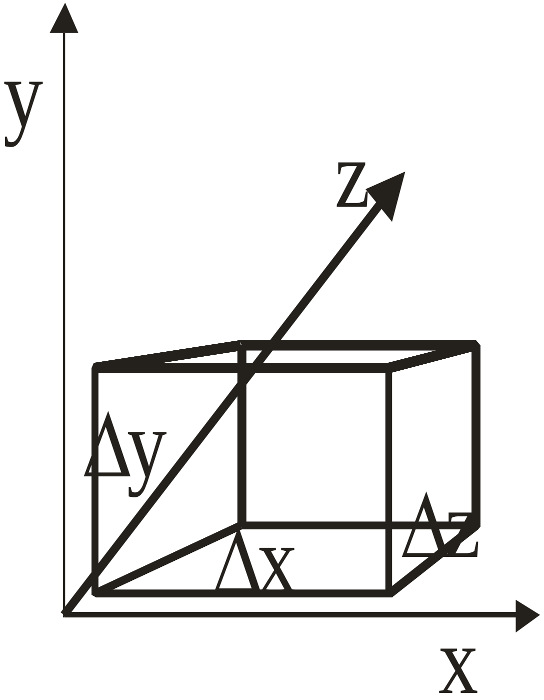
- The existing models for delignification of wood consider a 1 dimensional case with equal diffusion rates in all directions
- Is a 2- or 3-dimensional model needed ?

Characteristics of our model

- Time dependent dynamic model
- Complex reaction network included
- Mass transfer via diffusion in different directions
- Structural changes of the wood chip included
- All wood chips of equal size
- Perfectly mixed batch reactor assumed

Mathematical model,volume element

- 3D –model for a wood chip



$$(N_{ix}A_{yz})_{\mathrm{in}} + (N_{iy}A_{xz})_{\mathrm{in}} + (N_{iz}A_{xy})_{\mathrm{in}} + r_i' \Delta V =$$
$$(N_{ix}A_{yz})_{out} + (N_{iy}A_{xz})_{out} + (N_{iz}A_{xy})_{out} + \frac{dn_i}{dt}$$

Mass balance for a wood chip

$$\frac{dc_i}{dt} = \frac{D_i}{\varepsilon_p(t)}\left(\varepsilon_x' \frac{d^2 c_i}{dx^2} + \varepsilon_y' \frac{d^2 c_i}{dy^2} + \varepsilon_z' \frac{d^2 c_i}{dz^2}\right) + \frac{r_i'}{\varepsilon_p(t)}$$

Porosity

$$\varepsilon_p(t) = \sqrt[3]{\varepsilon_x' \varepsilon_y' \varepsilon_z'}$$

$$\varepsilon_x' = \frac{\varepsilon_x}{\tau_{px}}$$

Boundary conditions

The concentrations outside the wood chip are locally known

$$c_\mathrm{i}=c_\mathrm{Li}$$

at the centre of the chip (symmetry)

$$dc_i/\mathrm{d}x=dc_i/\mathrm{d}y=dc_i/\mathrm{d}z=0$$

Reactor model

Batch reactor model, ideal flow

$$\frac{dc_{Li}}{dt} = N_{ix}a_{yx} + N_{iy}a_{xz} + N_{iz}a_{xy} + r_i$$

Fluxes from wood chip

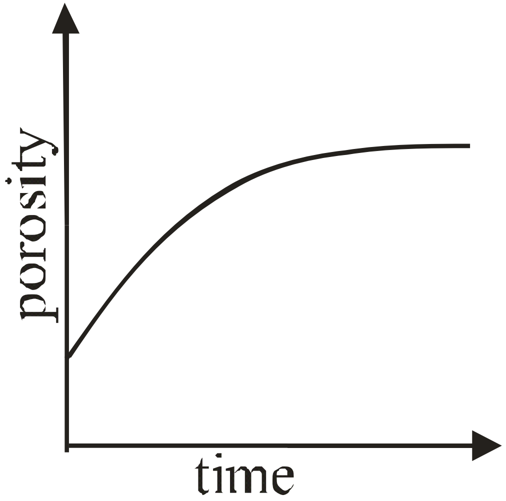
$$N_{ix} = -\varepsilon_x' D_i \left(\frac{dc_i}{dx} \right)_{x=Lx}$$

$$N_{ix} = -\varepsilon_y' D_i \left(\frac{dc_i}{dy} \right)_{y=Ly}$$

$$N_{iz} = -\varepsilon_z' D_i \left(\frac{dc_i}{dz} \right)_{z=Lz}$$

Structural changes of the wood chip

Generally one can state that the porosity of the chip increases during the process, since lignin and hemicelluloses are dissolved



Change of porosity as a function of the lignin conversion

$$\eta_l = \frac{c_{0l} - c_l}{c_{0l}} = 1 - \frac{c_l}{c_{0l}}$$

$$\epsilon_p = \epsilon_{0p} + \left(\epsilon_\infty - \epsilon_{0p}\right)\left(1 - \left(1 - \eta_l\right)^{\alpha'}\right)$$

Kinetic models

Andersson model, 12 wood pseudocomponents

$$r_i = k_1 \left(c_{OH}^{\alpha} c_{HS}^{\beta} + k_2 \right) W_i$$

Purdue model (Christensen et al), 5 wood pseudocomponents

$$\frac{-dC}{dt} = \left[k_i^{'} \cdot \left(OH^{-} \right) + k_i^{''} \cdot (OH^{-})^{a} \cdot (HS^{-})^{b} \right] \cdot (C - C_0)$$

Gustafsson model, 2 wood components, 3 stages

Initial stage, >22% Lignin,

Bulk stage , 22% > Lignin > 2%

Residual stage < 2% Lignin

$$\frac{dL}{dt} = 36.2 \cdot T^{0.5} \cdot e^{\frac{-4807.69}{T}} \cdot L \qquad \frac{dC}{dt} = 2.53 \cdot [OH]^{0.11} \cdot \frac{dL}{dt}$$

$$\frac{dL}{dt} = \left[e^{35.19 - \frac{17200}{T}} \cdot [OH] + e^{29.23 - \frac{14400}{T}} \cdot [OH]^{0.5} \cdot [S]^{0.4} \right] \cdot L$$

$$\frac{dL}{dt} = e^{19.64 - \frac{10804}{T}} \cdot [OH]^{0.7} \cdot L$$

Diffusion models

McKibbins

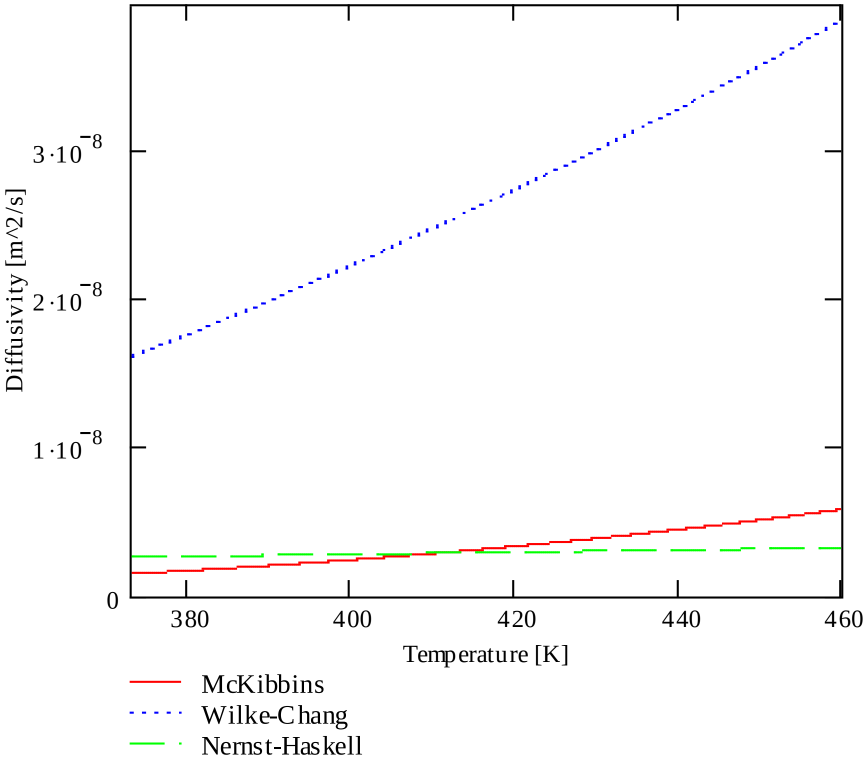
$$D_{NaOH,H_2O} = 5.667\cdot 10^{-8}\cdot\sqrt{T}\cdot e^{\frac{-4870}{1.9872T}}$$

Wilke-Chang

$$D_{AB} = \frac{7.4\cdot 10^{-12}\cdot\sqrt{\phi\cdot M_B}\cdot T}{\mu_B\cdot V_A{}^{0.6}}$$

Nernst-Haskel (infinite dillution)

$$D^o = 8.931\cdot 10^{-14}\cdot T\cdot\left(\frac{\lambda_+^0\cdot\lambda_-^0}{\lambda_+^0+\lambda_-^0}\right)\cdot\left(\frac{z_+ + z_-}{z_+\cdot z_-}\right)$$



Kappa number

The progress of delignification is by pulp professionals described by the Kappa number

$$\kappa = 500\frac{L}{L+CH}+5$$

L = Lignin on wood, CH = Carbohydrates on wood

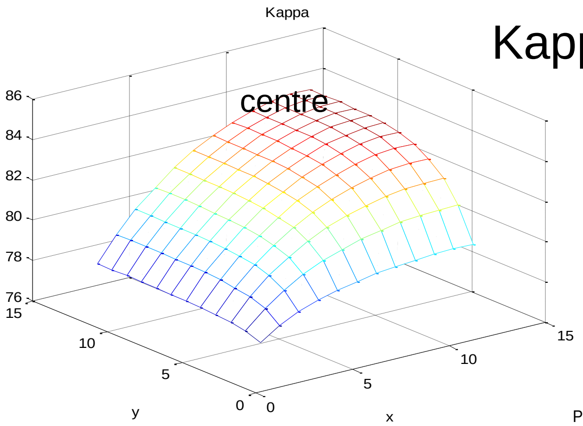
Numerical approach

- Discretizing the partial differential equations (PDEs) with respect to the spatial coordinates (*x*, *y*, *z*).

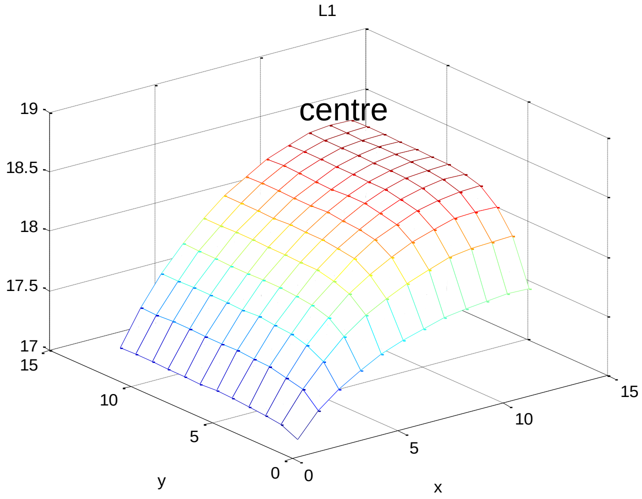
- Central finite difference formulae were used to approximate the spatial derivatives
- Thus the PDEs were transformed to ordinary differential equations (ODEs) with respect to the reaction time with the use of the powerful finite difference method.

- The created ODEs were solved with the backward difference method with the software LSODES

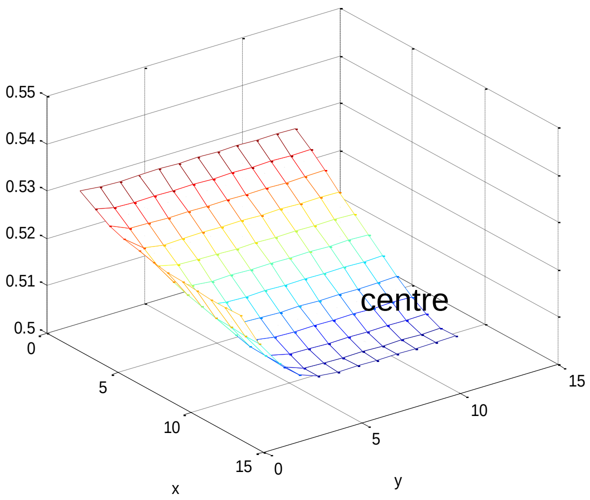
Simulation results, profiles inside wood chip



Kappa value



Lignin content

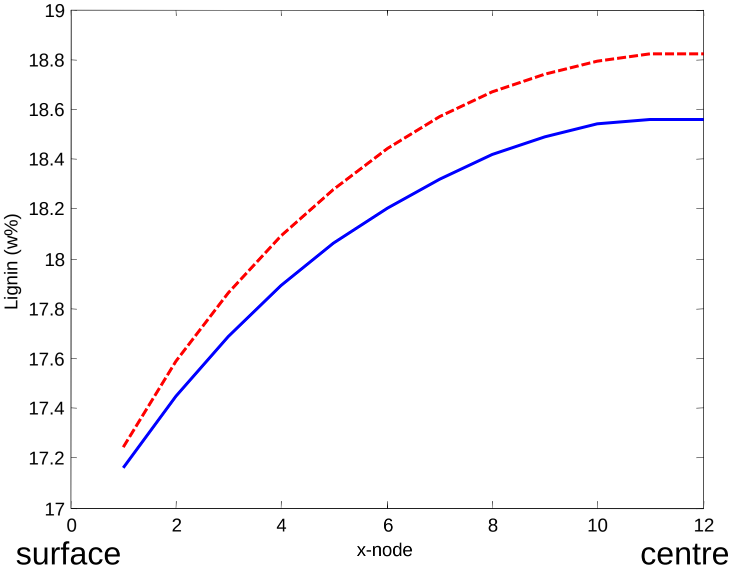


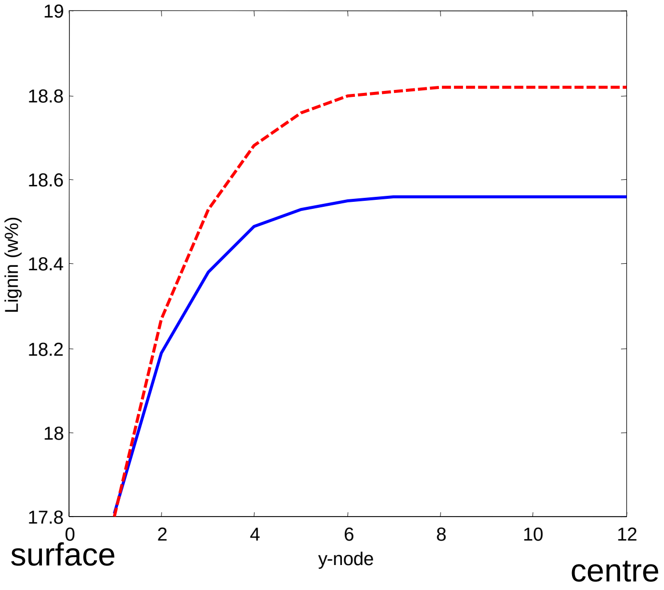
Porosity

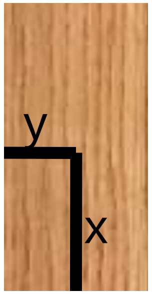
T=170 ºC

$C_{0,NaOH}$=0.5 mol/l

The impact of 2-D model



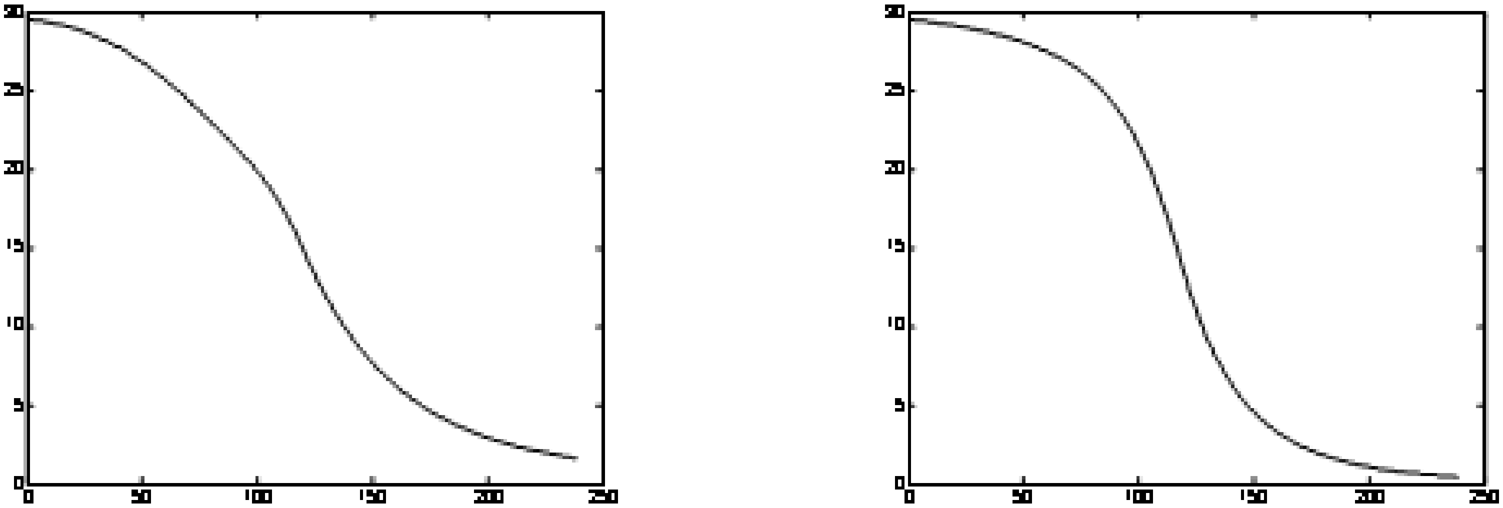




Red line, different diffusion rates in x and y directions

Blue line, same diffusion rates in x and y direction (Andersson kinetic model)

Content of lignin on wood as a function of reaction time



Lignin concentration (w-%) in wood chip as a function of reaction time (min) with Andersson kinetic model (left) and Purdue kinetic model (right).

Simulation software

- 2-D model for a wood chip in a batch reactor
- Different kinetic and diffusion models available
- Structural change model included (porosity)
- Dynamic model
  - all results can be presented as a function of reaction time
- Temperature and alkali concentrationprofiles can be programmed as a function of reaction time

Conclusions

- A general dynamic model and software for the description of wood delignification
- Solved numerically for example cases, which concerned delignification of wood chips in perfectly backmixed batch reactors.
- Structural changes and anisotropies of wood chips are included in the model.
- The software utilizes standard stiff ODE solvers combined with a discretization algorithm for parabolic partial differential equations.
- Example simulations indicated that the selected approach is fruitful, and the software can be extended to continuous delignification processes with more complicated flow patterns.

Thank you!