Multiphase reactors modelling & process design for environment friendly production of aluminium

within EU H2020 AlSiCal Project

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This project has received funds from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 820911

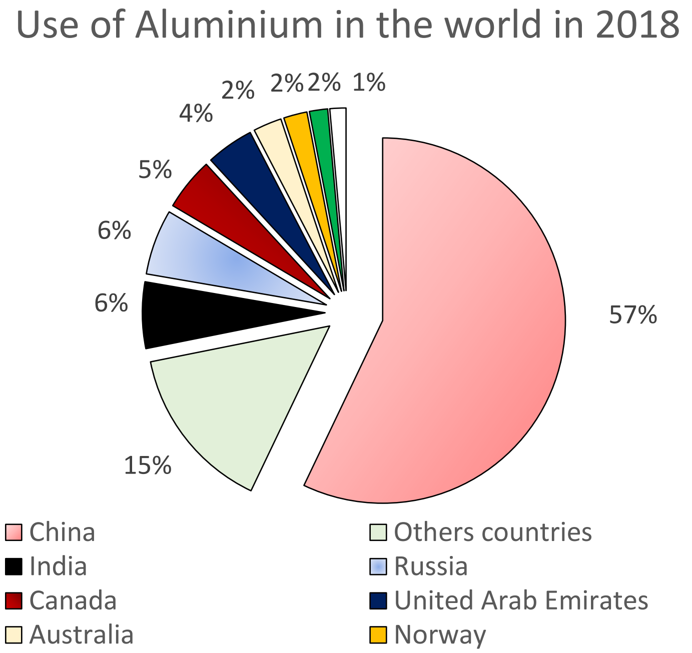
CONTEXT: Aluminium production

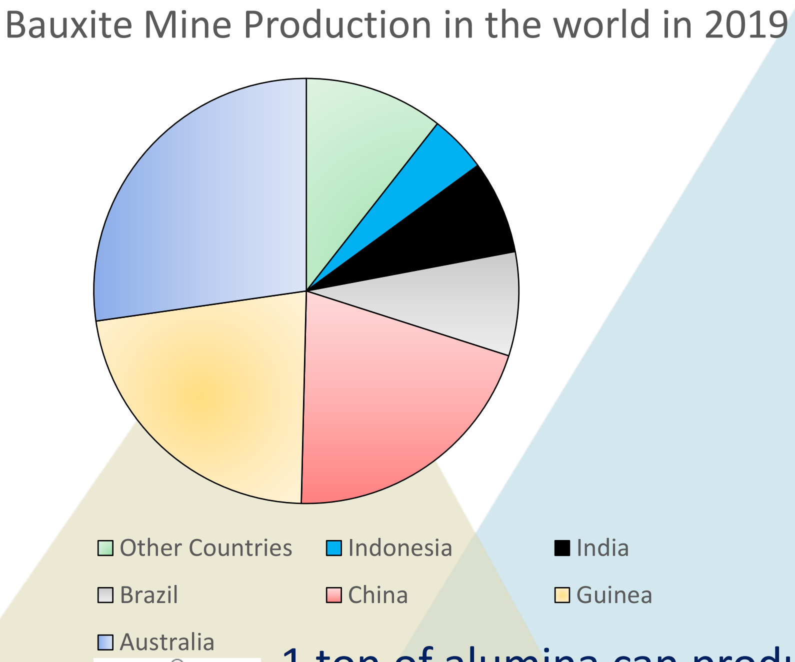
Key figures [1]:

- Worldwide aluminium consumption in 2018: 63 millions tons

- Traditional process: Bayer Patent (1888) using bauxite as raw material

- Consumption of bauxite for 1 ton of alumina varies between 1.9 to 3.6 tons
- 370 millions tons of bauxite mined in 2019





1 ton of alumina can produce 2 tons of **red mud** (140 millions tons per year), an hazardous waste for the environment (high pH, fine particles, heavy metals, etc…)

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[1] USGS

CONTEXT: AlSiCal project

EU concern for <u>sustainable</u> aluminium production

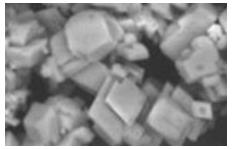
AlSiCal project (lead by IFE, Norway) which aims to produce « green » aluminium

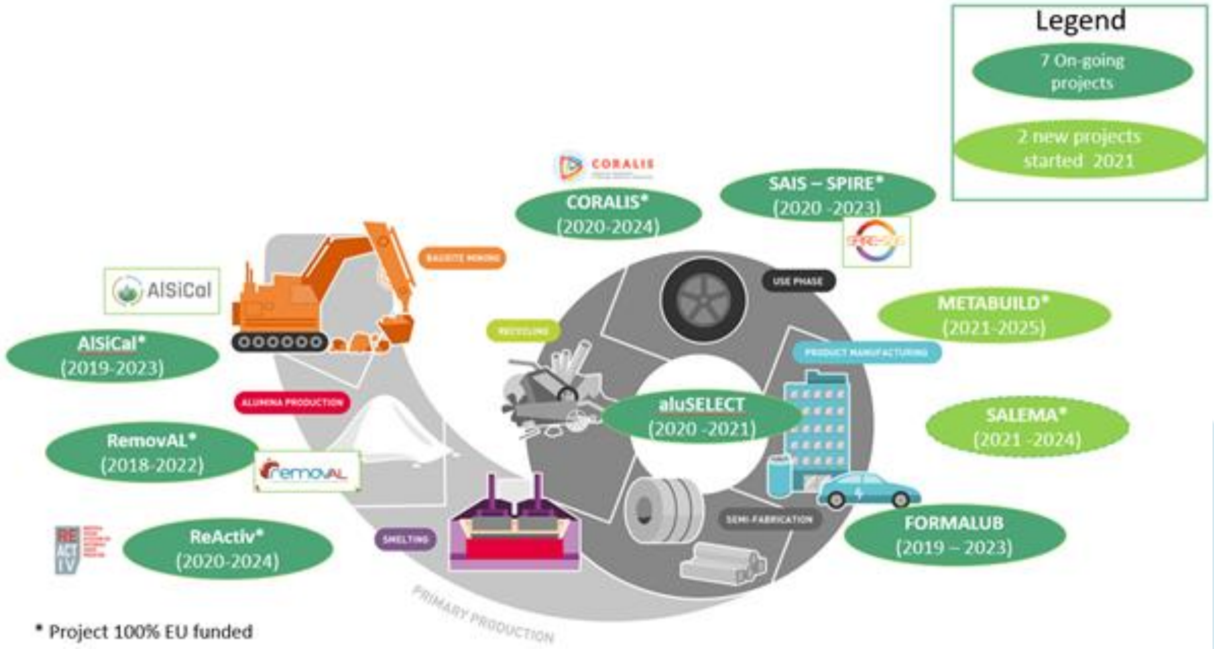
→ **from anorthosite**, an abundant feldspar found for instance in Greenland, Norway & Canada

→ with **integrated CO_2 utilization**

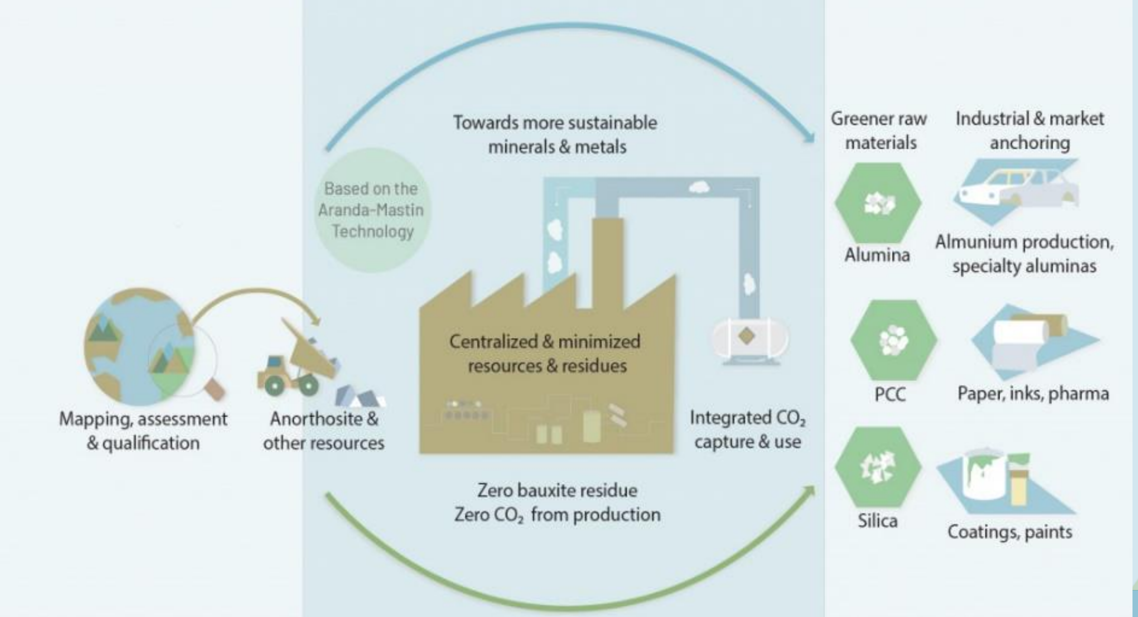
→ with **valorisation of each by-product**

(silica, precipitated calcium carbonate)





* Project 100% EU funded



16 partners, from 9 different countries

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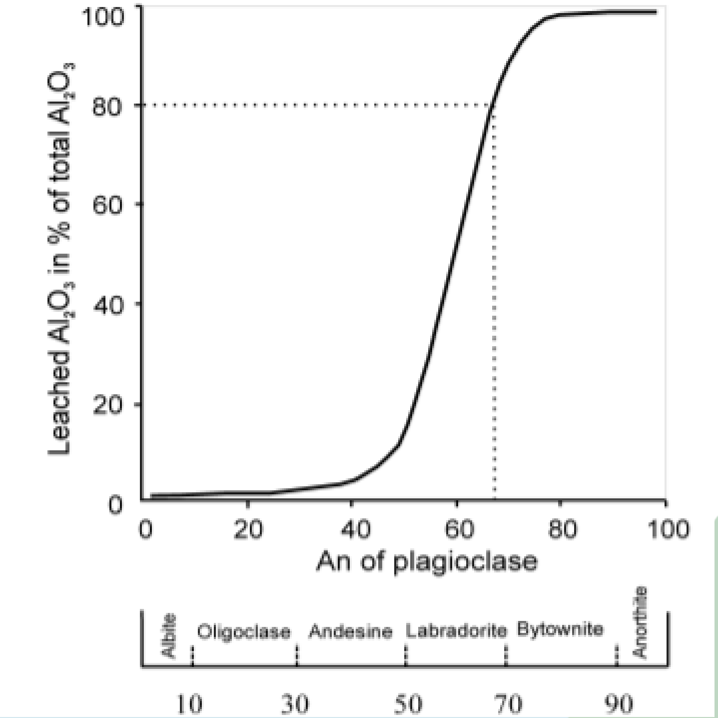
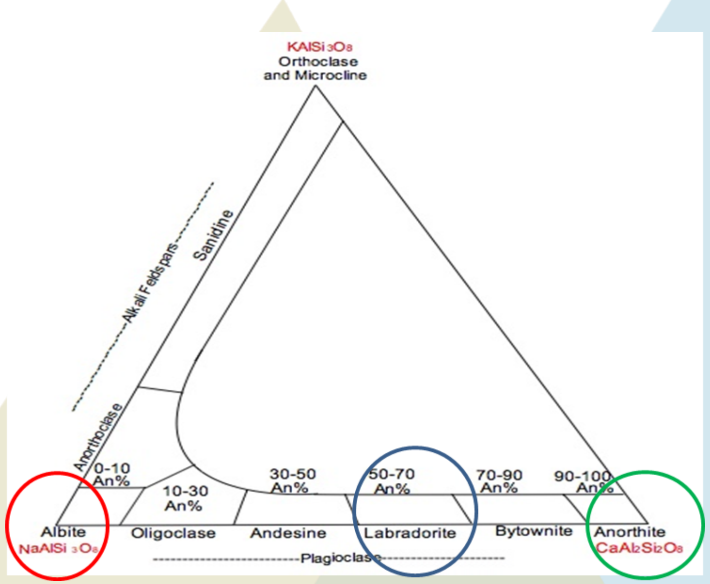
CONTEXT: Aluminium production

Anorthosite

- Plutonic rock
- Composed of plagioclase feldspar (over 90% of the rock is composed of this mineral)
- Plagioclase is a very common mineral group, more than half of the Earth's crust is composed of it
- $(CaAl_2Si_2O_8)_x(NaAlSi_3O_8)_{1-x}$
- The more the % of Anorthite ($CaAl_2Si_2O_8$), the easier is the leaching: x should be > 0. 5





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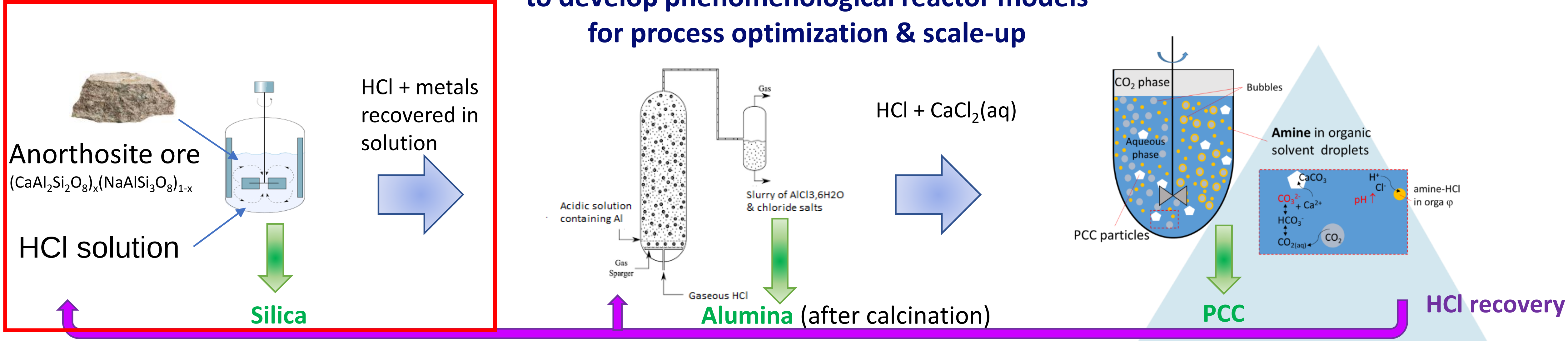
My PhD thesis in AlSiCal project

to develop phenomenological reactor models for process optimization & scale-up



Anorthosite ore

$(CaAl_2Si_2O_8)_x(NaAlSi_3O_8)_{1-x}$

HCl solution

HCl + metals recovered in solution

Silica

Acidic solution containing Al

Gaseous HCl

Slurry of AlCl3,6H2O & chloride salts

HCl + $CaCl_2$(aq)

Alumina (after calcination)

Amine in organic solvent droplets

PCC

HCl recovery

Leaching of the anorthosite

To **provide recommendations** on the operating conditions for the **dissolution of anorthosite** into desired products & to **predict the experimental extraction yields** with respect to process inputs (e.g. particle size distribution)

H^+ activity is a key parameter of ore dissolution rate

Many silicate solids could be formed at too low [HCl]

Sparging & crystallization reactor

To **guide the operating conditions** and the number of operation steps to optimize both **aluminium recovery** and **product purity**

→ includes reactive gas absorption, crystal nucleation & growth

High value of ionic force requiring to use Pitzer model for activity coefficient calculation

L-L extraction & carbonation reactor

To develop a model which takes into account **3 simultaneous phenomena**:

-The **precipitation** of the **calcite**

-The **dissolution** of the gas (**CO_2**), potentially enhanced by the organic phase (amine) and chemical reactions

-The **reactive extraction** of **HCl** by the **amine**, impacting the precipitation of the calcite (by increasing the pH)

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Kinetic modelling
Dissolution model hypotheses, Critical analysis of literature kinetics & optimization of rate parameters, Parametric study, Comparison with available experimental data (patent)

Evaluation of reactor configurations toward a continuous process

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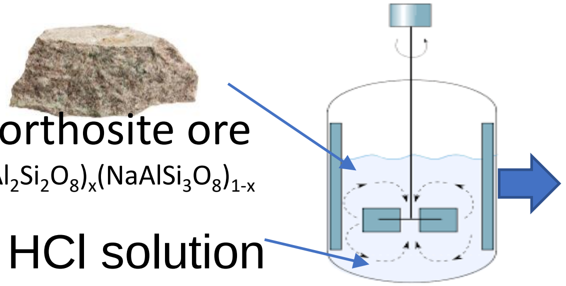
Modelling of leaching reactor: overall strategy



Anorthosite ore

$(CaAl_2Si_2O_8)_x(NaAlSi_3O_8)_{1-x}$

HCl solution

(Proton activity $a_{(H+)}$ is a key parameter of ore dissolution rate)

- HCl solution with dissolved Al, Ca, Na & Si …
- Silica & silicate by-products

(driven by species equilibrium constants, activity coefficients & precipitation kinetics)

Objectives:

- give a first-hand prediction of the product speciation in the aqueous and solid phases
- provide the means to investigate the sensitivity of the process to key operating variables, including HCl & ore concentrations, feed particle size distribution, temperature ...
- predict process performance to select favourable operating conditions
- provide guidance for reactor scale-up

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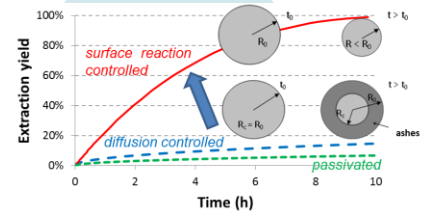
Modelling of leaching reactor: overall strategy

Equilibrium calculations (PhreeqC, OLI Syst. …)
→ to help define the likely operating window for high extraction yield,
→ to anticipate the formation of solid by-products (other aluminosilicates),

Coupling of thermodynamics & dissolution kinetics
→ to predict the time-yield curves with respect to main process inputs

Validity and completeness of thermodynamic databases

Experimentations
- Dissolution tests
- Liquid analysis & solid product characterization



Identification of actual rate-limiting elementary process(es)

Optimization of rate parameters (ex: k_0, E_A …)

Reactor model embedded in a simulation / optimization environment

Challenges:

- electrolyte solutions with ionic strength up to 10 mol/kg → selection of suitable activity coefficients
- no information on possible solid by-products → comparison of predictions from several databases
- dissolution yield depending on the active surface → PSD of the ore to be accounted for
- variability of the reactivity of anorthosite & delay on experimental data due the Covid situation → model assessment & optimization from relevant literature data

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Relevant geochemical tools: PHREEQC vs. OLI

AlSiCal

PHREEQC

Open source geochemical code developed by USGS

Advantages

- Open source code & possibility to modify/extend databases
- PhreePlot software for advanced graphs
- Possibility to implement shrinking core/particle models
- Can be easily coupled with Matlab, Python, Comsol, R languages/softwares … for advanced calculations

Disadvantages

- Limitations of standard B-dot model (low I range), limited Pitzer database

Preferred tool for kinetic modelling

OLI systems, inc.

Commercial thermodynamic software

- Activity coef. models for very high ionic strength (esp. Mixed Solvent Electrolyte model)
- User-friendly interface
- Team of thermodynamic experts available

- Database extension/modification as an option
- Standard kinetic models not suitable
- No available coupling with Matlab

(extra developments needed for using Oli Eng. Dev.)

Used as thermodynamic benchmark

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Relevant geochemical tools: PHREEQC vs. OLI

$Ca_{0.65}Na_{0.35}Al_{1.65}Si_{2.35}O_8$ dissolution with HCl

DATABASES

(Na, Ca, Al, Si, Cl elements)

Thermoddem 2017:

128 solids, 40 aqueous species

Solids found to precipitate:

- *Albite $NaAlSi_3O_8$*
- *Amorphous silica (crystalline SiO_2 deactivated)*
- *Diaspore $AlO(OH)$*
- *Prehnite $Ca_2Al_2Si_3O_{10}(OH)_2$*
- *Kaolinite $Al_2Si_2O_5(OH)_4$*
- *Pyrophyllite $Al_2Si_4O_{10}(OH)_2$*
- *Laumontite $Ca(Al_2Si_4)O_{12}\cdot 4H_2O$*
- ~~*Heulandite(Ca) $Ca_{1.07}Al_{2.14}Si_{6.86}O_{18}\cdot 6.17H_2O$*~~
- ~~*Beidellite(Na) $Na_{0.34}Al_{2.34}Si_{3.66}O_{10}(OH)_2$*~~
- ~~*Gismondine $Ca_2Al_4Si_4O_{16}\cdot 9H_2O$*~~
- ~~*Chabazite $Ca(Al_2Si_4)O_{12}\cdot 6H_2O$*~~
- ~~*Phillipsite(Na) $NaAlSi_3O_8\cdot 3H_2O$*~~

(only in Thermoddem)

Selected for 1st step (H^+, $I < 15$ mol/kg$_w$)

MSE/GEOCHEM (no theoretical limit on I):

79 solids, 16 aqueous species (H_3O^+ instead of H^+ species)

Solids found to precipitate:

- *Albite $NaAlSi_3O_8$*
- *Amorphous silica (crystalline SiO_2 deactivated)*
- *Boehmite $AlO(OH)$*
- *$Al(OH)_3$*
- *Prehnite $Ca_2Al_2Si_3O_{10}(OH)_2$*
- *Kaolinite $Al_2Si_2O_5(OH)_4$*
- *Pyrophyllite $Al_2Si_4O_{10}(OH)_2$*

AQ/GEOCHEM ($I \leq 30$ mol/kg$_w$)

58 solids, 20 aqueous species

Same solids found to precipitate as with MSE/GEOCHEM:

+ Laumontite $Ca(Al_2Si_4)O_{12}\cdot 4H_2O$

+ $AlOHCl_2$ (not found in Thermoddem)

→ **Reduction of Thermoddem database to compare solid phase speciation**

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Thermodynamics: Selection of activity coefficient model

BDOT: $\log_{10}\gamma_i = -\frac{A_{DH} z_i^2 \sqrt{I}}{1+B_{DH}\mathring{a}_i\sqrt{I}} + \dot{b}I$ (I ≤ 1 M)

PITZER: $\ln\gamma_i = \frac{1}{RT}\left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_s,n_j}$

$$\frac{G^E}{RTw_S} = f(I) + \sum_i\sum_j \lambda_{(I)}(i\,;j)\, m_i m_j + \sum_i\sum_j\sum_k \mu(i\,;j\,;k)\, m_i m_j m_k)$$

SIT: $\log_{10}\gamma_i = -\frac{A_{DH} z_i^2 \sqrt{I}}{1+B_{DH}\mathring{a}_i\sqrt{I}} + \sum_k \varepsilon_{(T)}(i\,;k)\, m_k$

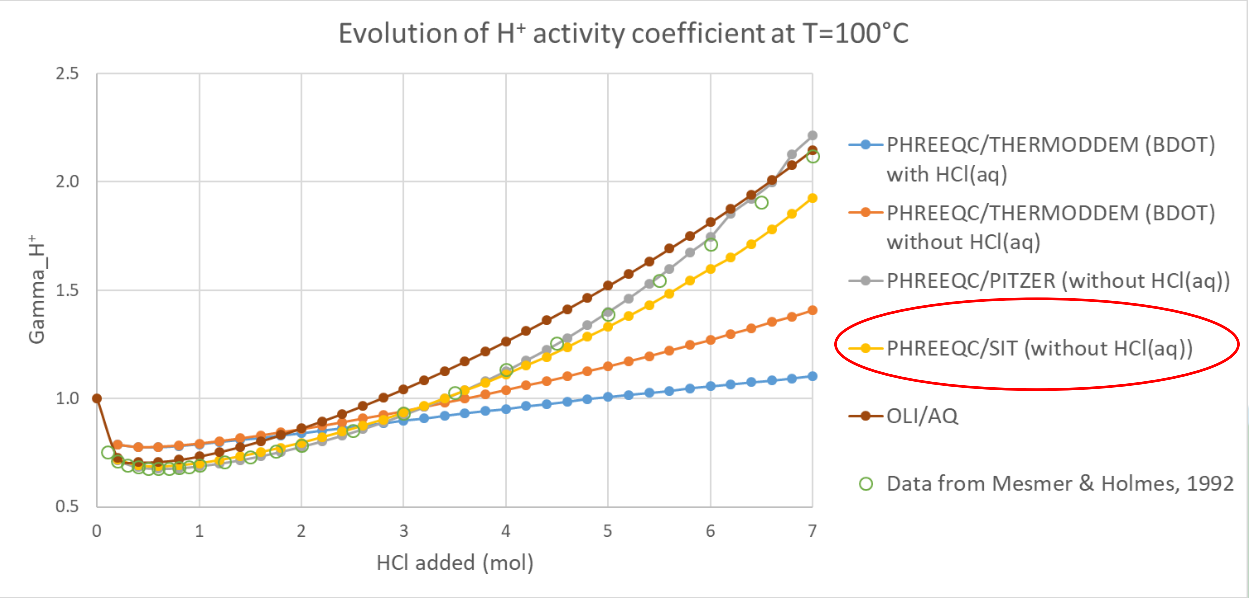
OLI/AQ: $\log_{10}\gamma_\pm = -\frac{A|Z_+Z_-|\sqrt{I}}{1+\sqrt{I}} + \frac{(0.06+0.6B)|Z_+Z_-|\sqrt{I}}{\left(1+\frac{1.5}{|Z_+Z_-|}I\right)^2} + BI + CI^2 + DI^3$

(Bromley-Zemaitis)

→ OLI/AQ predicts almost complete dissociation of HCl: HCl(aq) can be omitted

→ PHREEQC/SIT gives similar γ_{H+} values as PHREEQC/PITZER or OLI/AQ

➢ Predictions for the solvent (HCl)



I up to 8 mol/kg_w

→ SIT to be evaluated for acidic dissolution of anorthosite

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Thermodynamics: Selection of activity coefficient model

➢ Application to acidic anorthosite dissolution

Construction of a new database

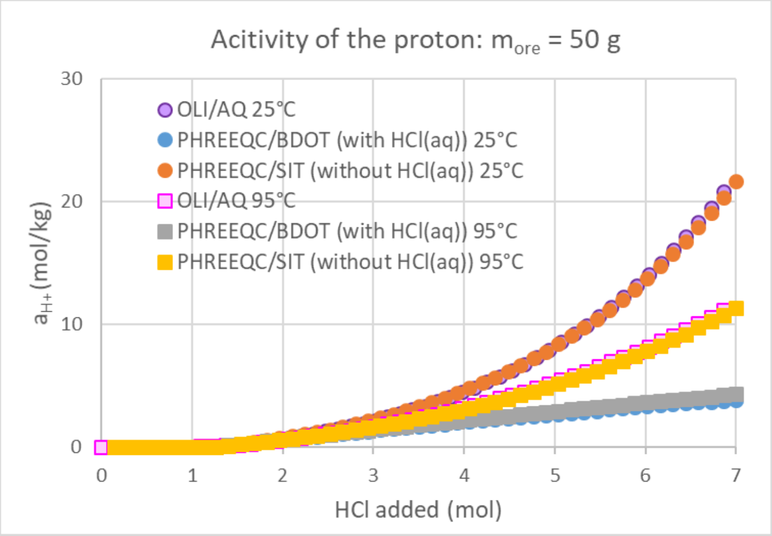
SIT database:

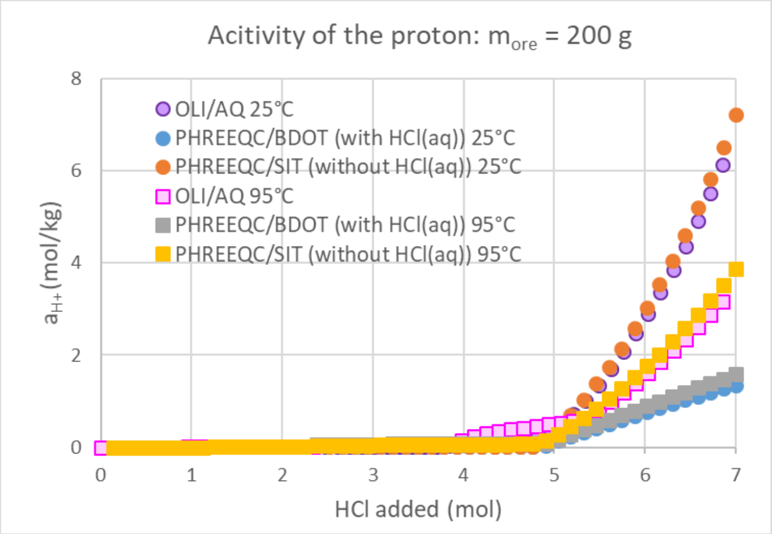
$\varepsilon(H^+; Cl^-)$, $\varepsilon(Ca^{2+}; Cl^-)$, $\varepsilon(Na^+; Cl^-)$, $\varepsilon(Al^{3+}; Cl^-)$
$\varepsilon(Na^+; H_3(SiO_4)^-)$, $\varepsilon(Na^+; H_2(SiO_4)^{2-})$ … at 25°C

+ $\varepsilon(H^+; Cl^-)$, $\varepsilon(Ca^{2+}; Cl^-)$, $\varepsilon(Na^+; Cl^-)$ = f(T) (Xiong, 2006)

+ mineral phases from Thermoddem 2017

→ Higher a_{H+} for SIT vs. B-dot
→ Predictions of SIT in agreement with OLI/AQ





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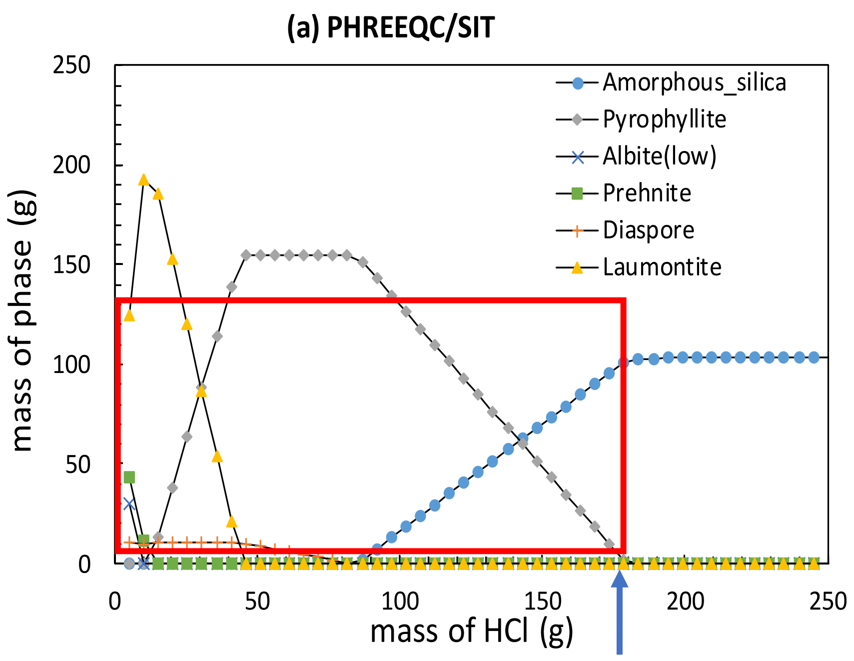
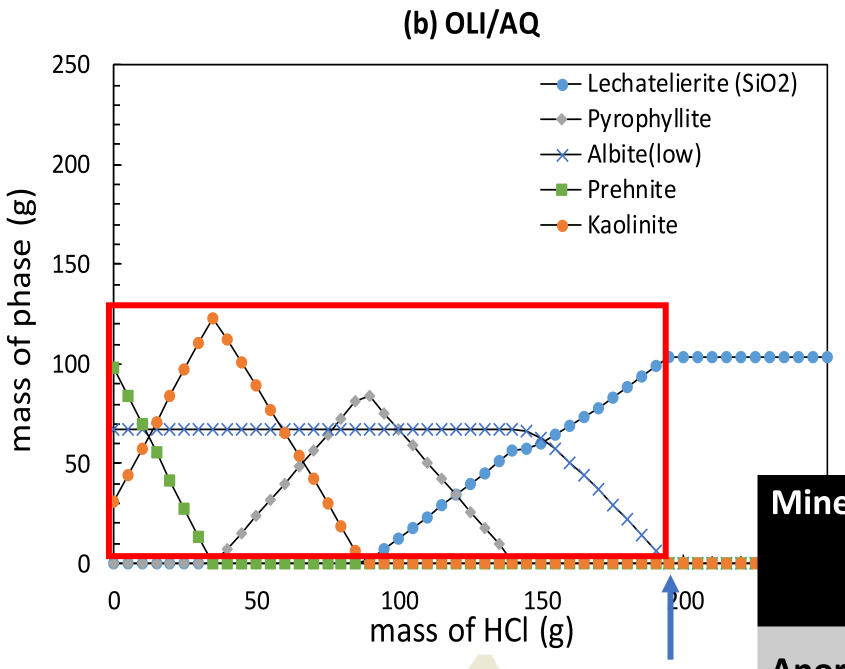
Thermodynamics: Predicted solid phase speciation





200 g of $Ca_{0.65}Na_{0.35}$ anorthosite at 95°C as a function of HCl amount added to 1 kg of water

→ Total amount of HCl required to dissolve all Al-bearing minerals is rather consistent for the 2 databases

→ Discrepancies in solid speciation at lower [HCl] can be explained by slightly different thermodynamic data

Mineral name	Difference in Gibbs energy of formation $\Delta G°_f$ @25°C (kJ/mol) (Thermoddem – OLI/GE)
Anorthite	-15.5
Kaolinite	-4.9
Albite(low)	50.1
Prehnite	-4.7
Pyrophyllite	-11.1
Laumontite	-16.4
Amorphous_silica /Lechatelierite	-1.4
Diaspore	-9.0

(values of $\Delta G°_f$ between -850 & -6700 kJ/mol)

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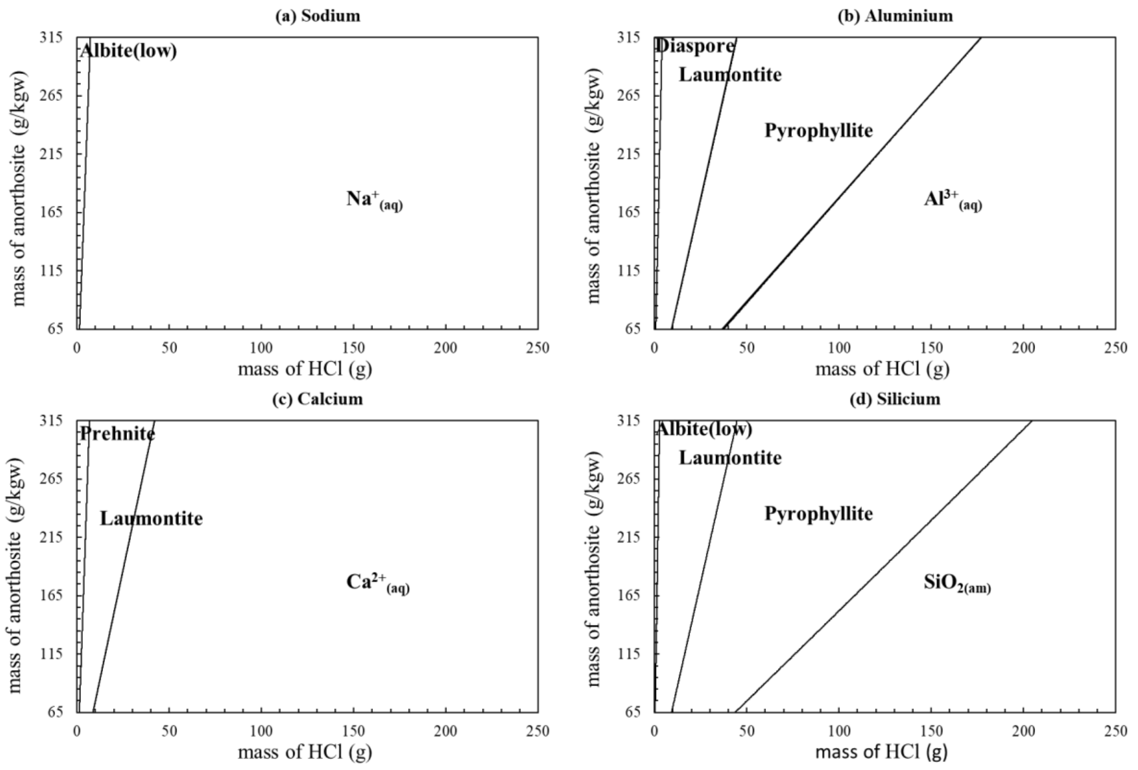
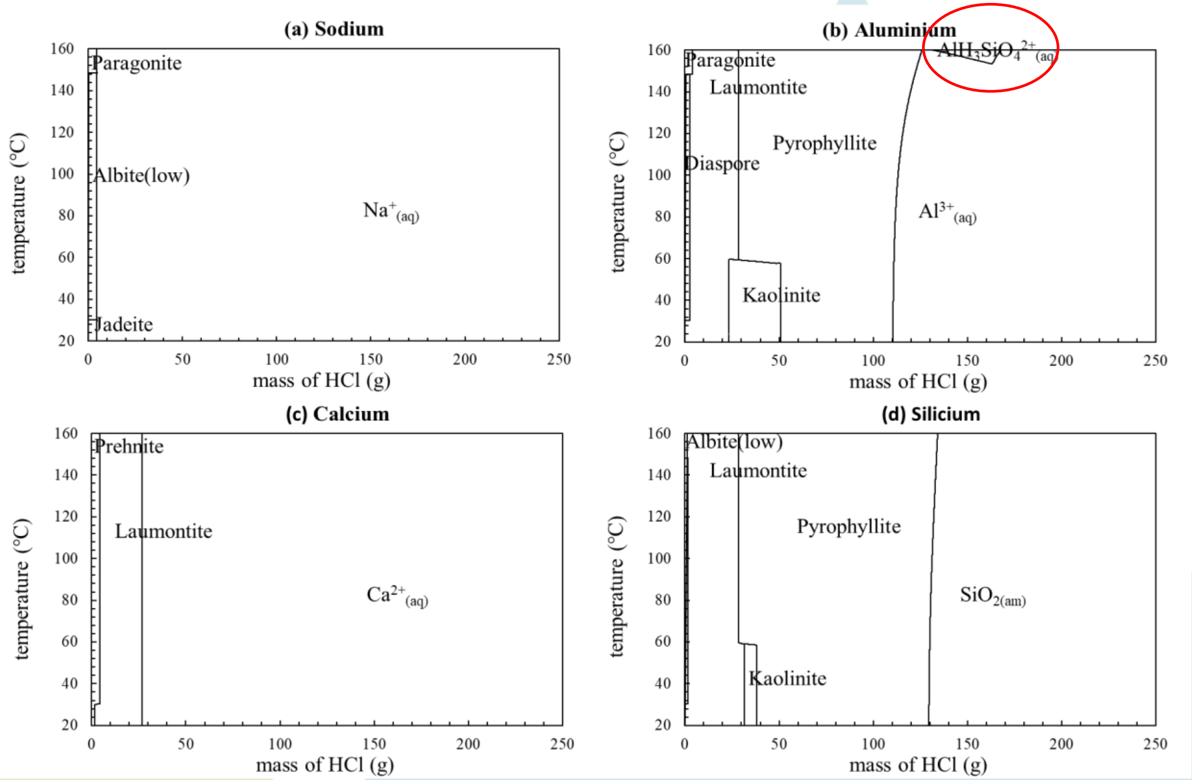
Thermodynamics: Selection of an operating window

➢ Influence of parameters (T, [HCl], S/L, ...)



T=95°C



m_{ore}= 200 g

- The higher is the initial mass of ore, the more HCl is needed
- Rather low effect of T, but complexation of silicon in solution above 150°C ($Al^{3+} \rightarrow AlH_3SiO_4^{2+}$)
- 20 wt.% HCl solution can achieve complete Al, Ca & Na dissolution for S/L as high as 25 wt.%

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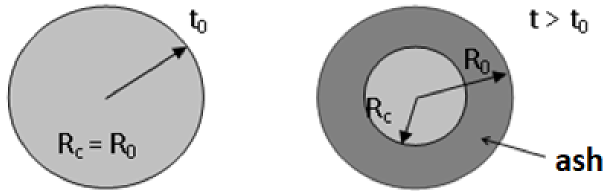
Kinetics: construction of the acidic dissolution model

- Choice of a dissolution model
- Critical analysis of literature kinetic data → Selection of dissolution rate model & relevant experimental data (Gudvangen anorthosite)
- Optimization of rate parameters
- Parametric study to finalize the choice of operating conditions: T, PSD … and comparison with an experimental point

Dissolution kinetics

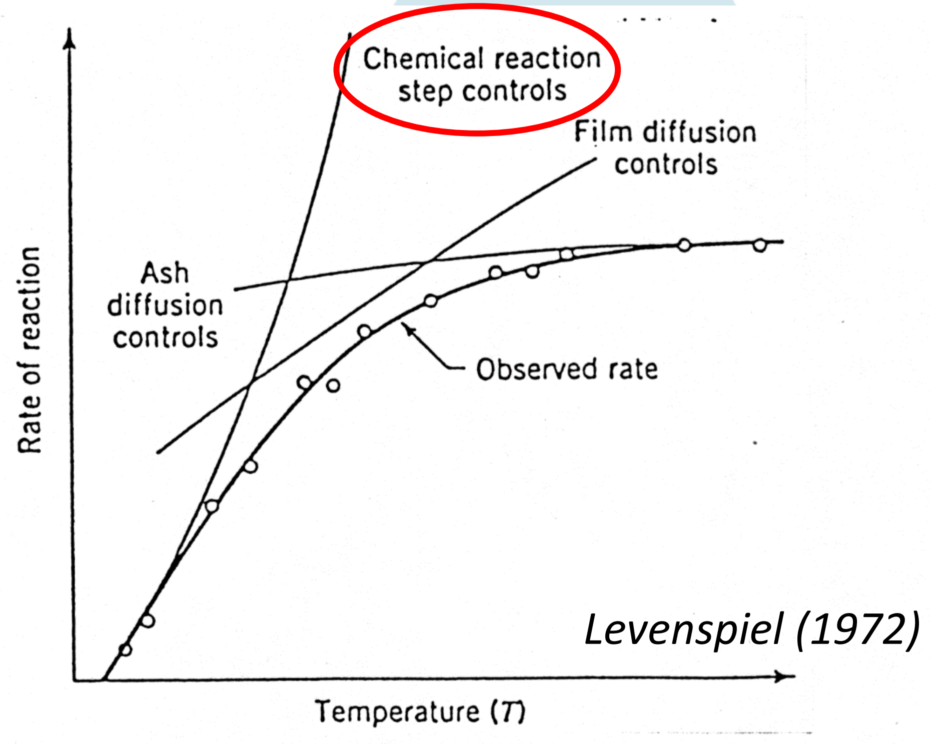
based on shrinking core model with surface reaction control
(no limitation by diffusion in the ash layer)



$$\frac{dn_i}{dt} = -r.SSA_{0i}.w_{0i}.m_0\left(\frac{n_i(t)}{n_{i0}}\right)^{2/3}$$

$$r = k_0.\exp(-E_a/RT).a_{(H+)}{}^{n}.a_{(Al3+)}{}^{m}.(1-10^{SI})$$

SSA_{0i}: specific surface area of class i, m_0: ore mass
w_{0i} / n_{0i}: initial weight fraction / number of moles of class i



Levenspiel (1972)

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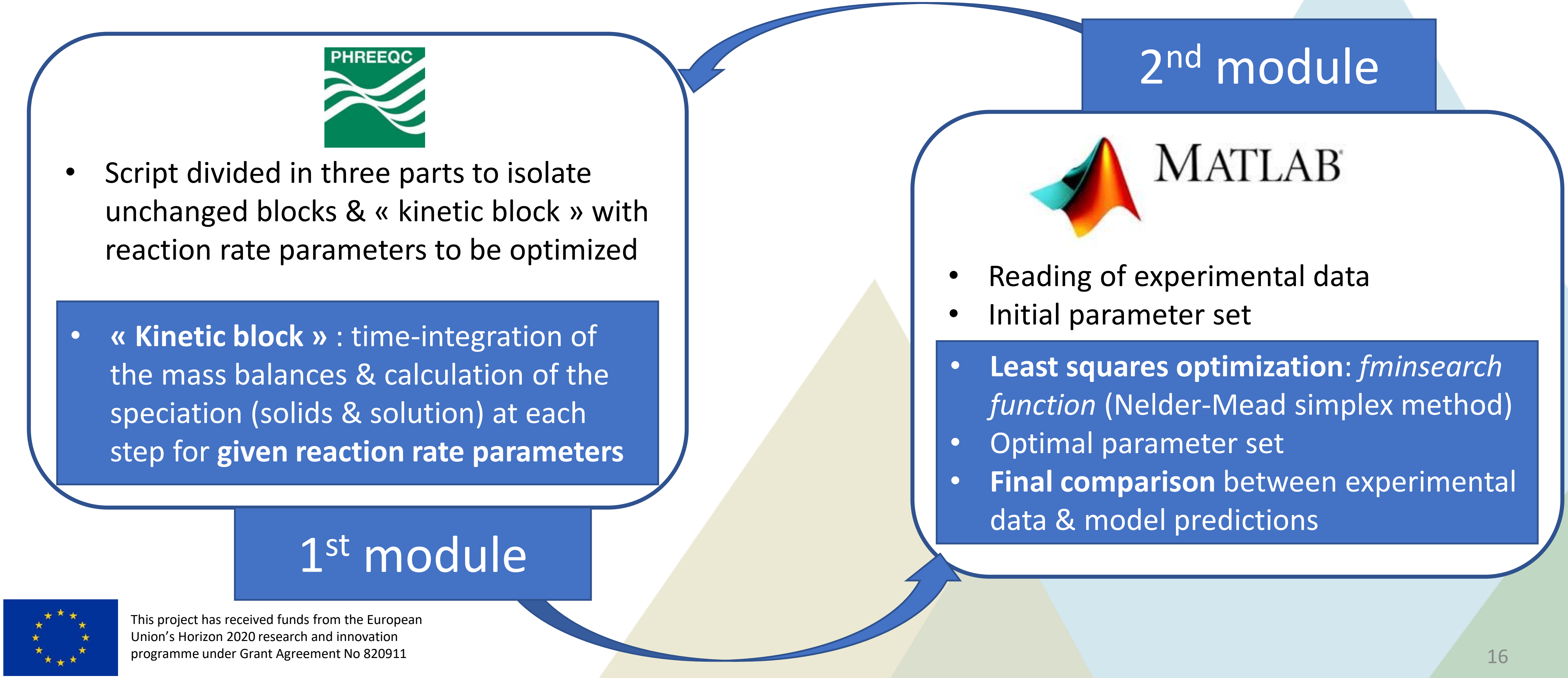
kinetic parameters fitted on literature data

Kinetics: construction of the acidic dissolution model

Matlab code to couple optimization toolbox with the kinetic model embedded in Phreeqc for parameter fitting



- Script divided in three parts to isolate unchanged blocks & « kinetic block » with reaction rate parameters to be optimized
- **« Kinetic block »** : time-integration of the mass balances & calculation of the speciation (solids & solution) at each step for **given reaction rate parameters**

1st module

2nd module

- Reading of experimental data
- Initial parameter set
- **Least squares optimization**: *fminsearch function* (Nelder-Mead simplex method)
- Optimal parameter set
- **Final comparison** between experimental data & model predictions

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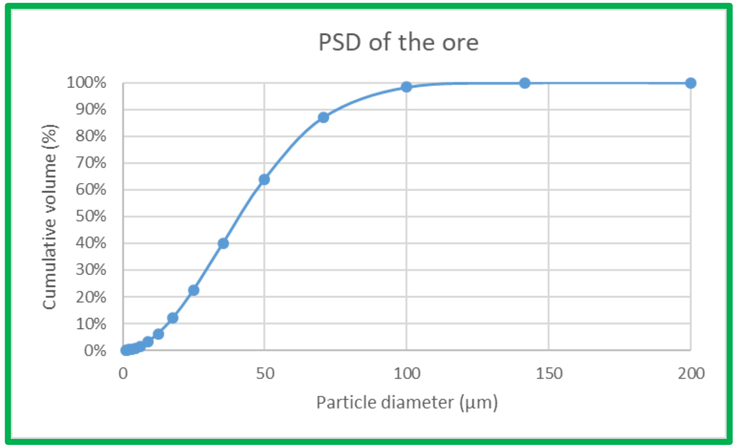
Kinetics: Optimization of rate parameters

- **ANORTAL project data** (Gjelsvik, 1980)

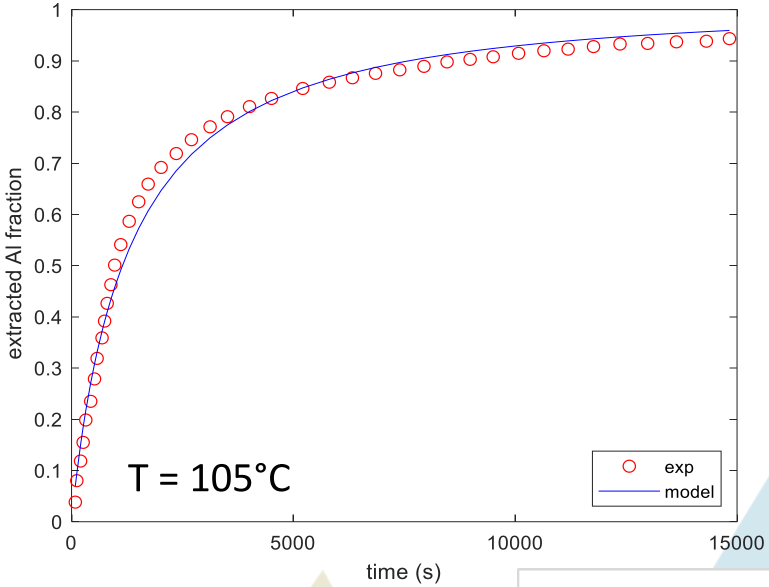
Description of PSD

16 classes (SSA_{0i}, w_{0i})
generated from Rosin Rammler model
(α & d_{90} parameters)

Passing fraction = $1-\exp(-(d_p/d^*)^{\alpha})$

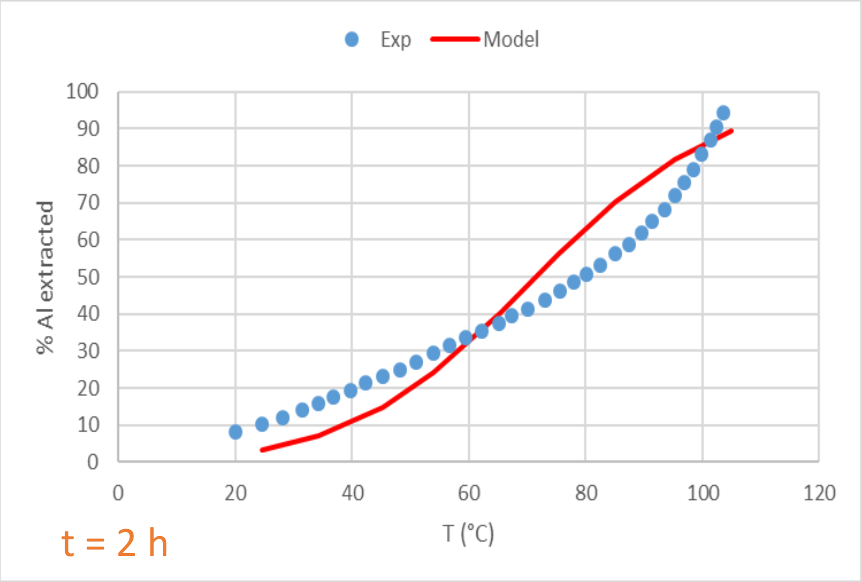


(d_{90} of 75 µm with α = 2)



Optimized values:
E_A = 65.9 kJ/mol,
$k_{105°C} = 1.03 \cdot 10^{-9}$ mol.cm^{-2}.s^{-1}
(n = 0.626, m = 0: set values following Palandri and Kharaka, 2004)

Gudvangen anorthosite
S/L = 23 wt.%, 6N HCl solution



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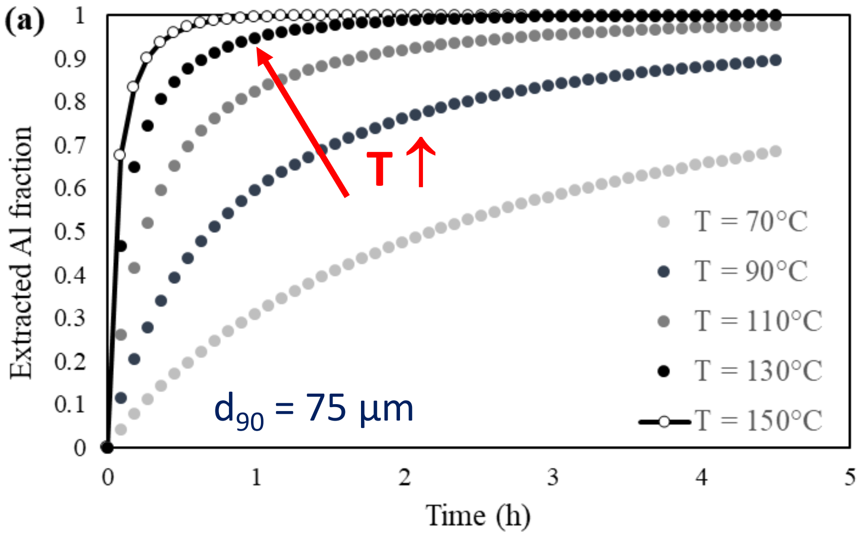
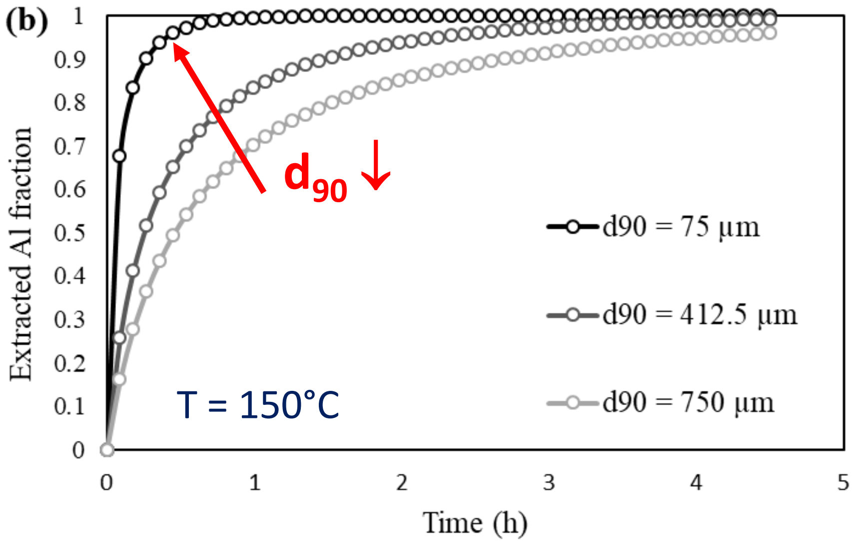
Kinetics: Parametric study



$Ca_{0.65}Na_{0.35}$ anorthosite treated by 6N HCl (S/L = 23 wt.%)



As expected :

- the higher the temperature, the faster the leaching
- the smaller the particles, the faster the leaching.

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Kinetics: Comparison to Aranda-Mastin patent data

Aranda & Mastin patent (2015)

100 Liters reactor

10.05 kg of anorthosite

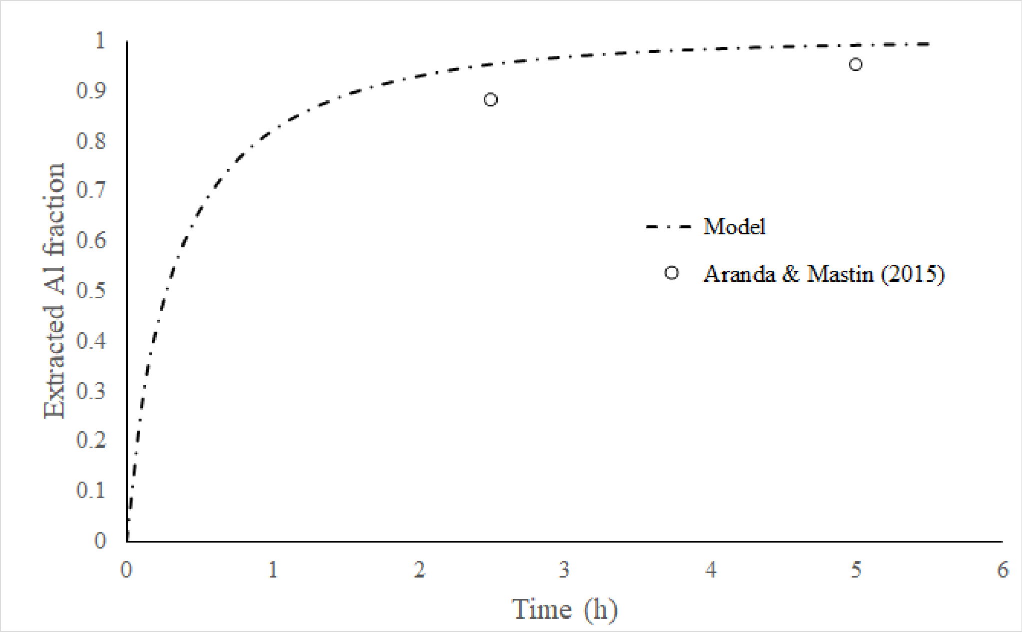
46.75 kg of HCl solution (19.7 wt.% HCl)

T=140°C

Particle size is ~ 300 µm

Extracted Al fraction is :

- 88% at 2.5 h
- 95% at 5 h



Simulation with polydisperse ore (d_{90} of 300 µm with $\alpha = 2$)

→ Validation of the dissolution model at higher temperatures

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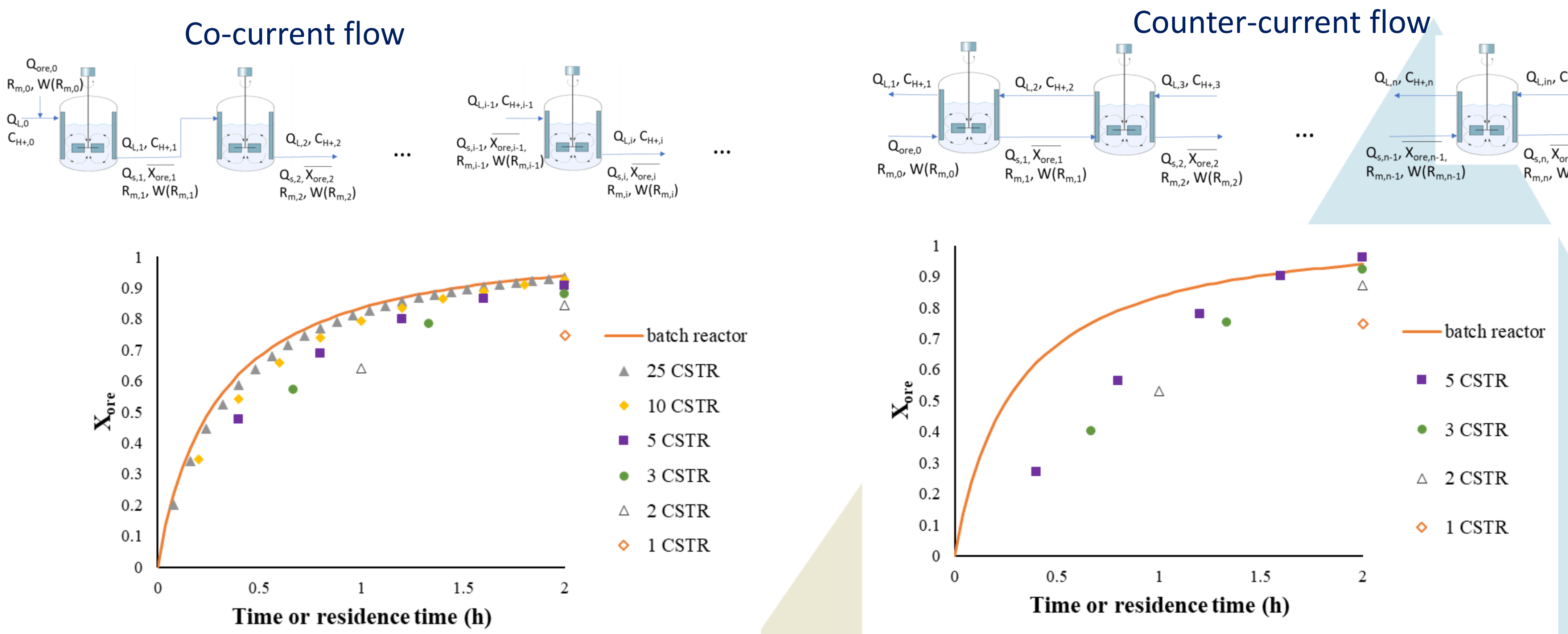
Evaluation of reactor configurations toward a continuous process

AlSiCal


Co-current flow

Counter-current flow

Evolution of the conversion extent of anorthosite as a function of the reaction time (batch reactor) or mean residence time (continuous process) for a series a CSTR operating (a) with co-current flow of solid and liquid and (b) with counter-current flow (T = 150°C, feed acid concentration = 20 wt.% HCl, S/L = 23 wt.%, total residence time = 2 hours, polydisperse ore with d_{90} = 412.5 µm).

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Conclusions & perspectives

AlSiCal

Modelling of leaching reactor:

- A model of batch/continuous stirred reactor (series) is available for Ca-rich anorthosite dissolution
- Model hypotheses (shrinking core under chemical reaction control), thermodynamic environment (selected activity coefficient model & geochemical database) and optimized parameters seem relevant with respect to the Aranda-Mastin patent data
- This model has been further assessed against extraction yields measured by IFE partner in confidential conditions and is able to conveniently predict the observed trends
- An article has been submitted on the theoretical aspects and construction of the leaching model to Minerals Engineering and is currently under review

Perspectives:

Modelling of the two other steps (sparging/crystallization reactor & extraction/carbonation reactor) is under progress

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