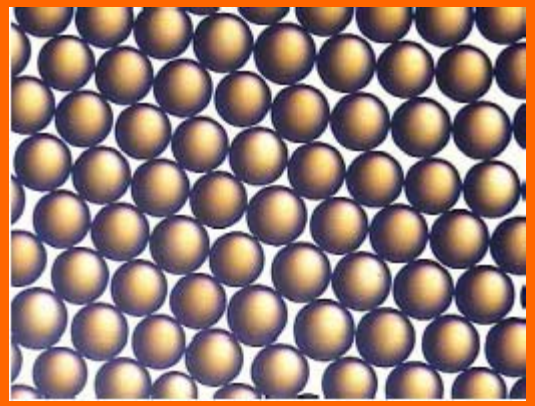

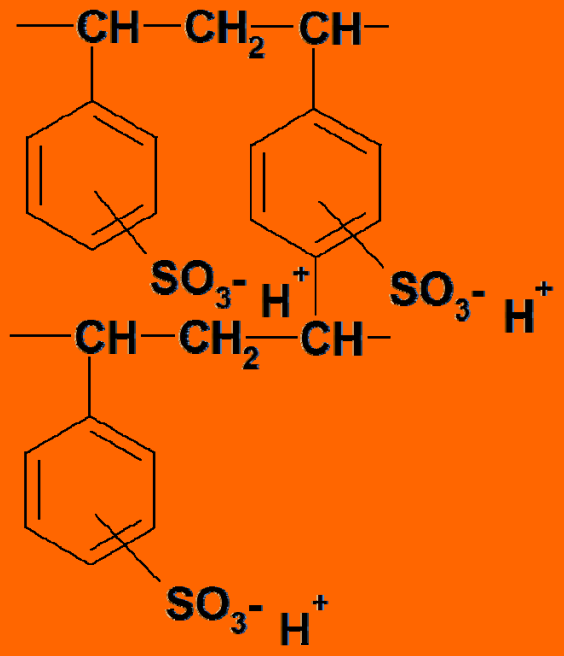

Variation of selectivity coefficients: impact on column efficiency

Frédéric GRESSIER

Jan van der LEE, Hélène SCHNEIDER, Martin BACHET

Context of the study

- **Selectivity variations have been described experimentally:**

  => Bonner, Argersinger, Helfferich, Soldatov, Högfeldt, Shallcross, Höll…

- **Some models have been proposed to take into account this phenomenon:**

  => Three Parameter Model, Soldatov model, Wilson, Regular solid solution, Surface complexation, multisite sorption

- **Few attempts have been made to include selectivity variation in a reactive transport code**

- **Objective : to model a deep bed column of Ion Exchange Resin at equilibrium taking into account selectivity variation**

1

1. Theoretical background

- Different formalisms
- Selectivity coefficient and thermodynamic constant
- Three Parameter Model

2. Equilibrium study : Ni and Cs selectivity

3. Modelling variable selectivity coefficient : impact on the ion retention

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Different formalisms

Gaines-Thomas convention

$$n\overline{H^+} + A^{n+} \rightleftharpoons \overline{A^{n+}} + n\,H^+$$

Resin / solution exchange reaction

Bonner study[1]: Vanselow convention

$$1/\mathrm{n}\,A^{n+} + \overline{H^+} \rightleftharpoons 1/\mathrm{n}\,\overline{A^{n+}} + H^+$$

[1] Bonner O.D., Smith L.L., 1957: "A selectivity scale for some divalent cations on Dowex 50", *The Journal of Physical Chemistry*, **61**, pp.326-329.

Different formalisms

Gaines-Thomas convention

$$n\overline{H^+} + A^{n+} \rightleftharpoons \overline{A^{n+}} + n\,H^+$$

$${}^{A}_{H}K_{GT} = \frac{\overline{a_{A^{n+}}} \times \left(a_{H^+}\right)^n}{\left(\overline{a_{H^+}}\right)^n \times a_{A^{n+}}}$$

Resin / solution exchange reaction

Thermodynamic equilibrium constant

Bonner study[1]: Vanselow convention

$$1/\mathrm{n}\,A^{n+} + \overline{H^+} \rightleftharpoons 1/\mathrm{n}\,\overline{A^{n+}} + H^+$$

$${}^{A}_{H}K_{B} = \frac{\left(\overline{a_A}\right)^{1/n} \times a_H}{\overline{a_H} \times \left(a_A\right)^{1/n}}$$

[1] Bonner O.D., Smith L.L., 1957: "A selectivity scale for some divalent cations on Dowex 50", *The Journal of Physical Chemistry*, **61**, pp.326-329.

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Resin / solution exchange reaction

Thermodynamic equilibrium constant

Activity of sorbed ions

$$\overline{a_i} = \overline{E_i} \times \overline{\gamma_i} \qquad \overline{E_i} = \frac{z_i \cdot \overline{C_i}}{EC}$$

Equivalent fraction

$$\overline{a_i} = \overline{x_i} \times \overline{\gamma_i} \qquad \overline{x_i} = \frac{\overline{C_i}}{\sum_{j\ counter-ions} \overline{C_j}}$$

Molar fraction

[1] Bonner O.D., Smith L.L., 1957: "A selectivity scale for some divalent cations on Dowex 50", *The Journal of Physical Chemistry*, **61**, pp.326-329.

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$$\overline{a_i} = \overline{E_i} \times \overline{\gamma_i} \qquad \overline{E_i} = \frac{z_i \cdot \overline{C_i}}{EC}$$

Equivalent fraction

$${}^{A}_{H}K^{a}_{GT} = \frac{\overline{E_{A^{n+}}} \cdot \left(a_{H^+}\right)^n}{\overline{E_{H^+}}^{\,n} \cdot a_{A^{n+}}}$$

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$$\overline{a_i} = \overline{x_i} \times \overline{\gamma_i} \qquad \overline{x_i} = \frac{\overline{C_i}}{\sum_{j\ counter-ions} \overline{C_j}}$$

Molar fraction

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Resin / solution exchange reaction

Thermodynamic equilibrium constant

Activity of sorbed ions

Corrected selectivity coefficient

[1] Bonner O.D., Smith L.L., 1957: "A selectivity scale for some divalent cations on Dowex 50", *The Journal of Physical Chemistry*, **61**, pp.326-329.

Relation between selectivity coefficient and thermodynamic constant – H^+/Ni^{2+} exchange

Gaines-Thomas convention

$$2\overline{H^+} + Ni^{2+} \rightleftharpoons \overline{Ni^{2+}} + 2H^+$$

$${}^{Ni}_{H}K^{a}_{GT} = \frac{\overline{E_{Ni}} \cdot \left(a_H\right)^2}{\overline{E_H}^2 \cdot a_{Ni}}$$

Bonner study: Vanselow convention

$$1/2\, Ni^{2+} + \overline{H^+} \rightleftharpoons 1/2\, \overline{Ni^{2+}} + H^+$$

$${}^{Ni}_{H}K^{a}_{B} = \frac{\left(\overline{x_{Ni}}\right)^{1/2} \times \left(a_H\right)}{\overline{x_H} \times \left(a_{Ni}\right)^{1/2}}$$

Corrected selectivity coefficient

$${}^{Ni}_{H}K^{a}_{GT} = \left({}^{Ni}_{H}K^{a}_{B}\right)^2 \times 2\left(1 + \overline{x_{Ni}}\right)$$

[1] Argersinger Jr. W.J., Bonner O.D., 1950: "Thermodynamics and Ion Exchange Phenomena", *Transactions of the Kansas Academy of Science* **53** (3): p. 404-410.

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$${}^{Ni}_{H}K^{a}_{B} = \frac{\left(\overline{x_{Ni}}\right)^{1/2} \times (a_H)}{\overline{x_H} \times (a_{Ni})^{1/2}}$$

Corrected selectivity coefficient

$${}^{Ni}_{H}K^{a}_{GT} = \left({}^{Ni}_{H}K^{a}_{B}\right)^2 \times 2\left(1 + \overline{x_{Ni}}\right)$$

Thermodynamic equilibrium constant calculation[1]

$$\ln {}^{Ni}_{H}K_{GT} = (z_H - z_{Ni}) + \int_0^1 \ln {}^{Ni}_{H}K^{a}_{GT}\, d\overline{E_{Ni}}$$

$$\ln {}^{Ni}_{H}K_{B} = \int_0^1 \ln {}^{Ni}_{H}K^{a}_{B}\, d\overline{E_{Ni}}$$

$$\log {}^{Ni}_{H}K_{GT} = 2 \times \log {}^{Ni}_{H}K_{B}$$

[1] Argersinger Jr. W.J., Bonner O.D., 1950: "Thermodynamics and Ion Exchange Phenomena", *Transactions of the Kansas Academy of Science* **53** (3): p. 404-410.

Coupling an equilibrium model with a reactive transport code : Three Parameter Model[1]

- **Numerically easy to introduce in a reactive transport code**
- **The model should be adapted to CHESS[2] formalism**
- **Easy to linearize for numerical calculation techniques to be used**
- **Model that describes well the experimental data**
  - Multisite approach: no good fit for a monovalent / divalent exchange
  - The Three Parameter Model (TPM) provides an easy-to-fit and an easy-to-use model : sorbed ion activities are incorporated in a lumped parameter

$$\log\left({}^{A}_{H}K^{a}_{V}\right) = \overline{x_A}\log\left({}^{A}_{H}K^{a}_{V}\left(\overline{x_A}\to 1\right)\right) + \left(1-\overline{x_A}\right)\log\left({}^{A}_{H}K^{a}_{V}\left(\overline{x_A}\to 0\right)\right) + B\overline{x_A}\left(1-\overline{x_A}\right)$$

[1] Högfeldt E., Soldatov V.S., 1979: "On the properties of solid and liquid ion exchangers – VII", *Journal of Inorganic and Nuclear Chemistry*, **41**, pp.575-577.

[2] Van der Lee J., 1998 : *Thermodynamic and mathematical concepts of CHESS*, Technical report LHM/RD/98/39, Ecole Nationale Supérieure des Mines de Paris, Centre de Géosciences, France.

2

1. Theoretical background

1. Equilibrium study : Ni and Cs selectivity

- Experimental protocol
- Imprecision analysis
- Selectivity variation plots

3. Modelling variable selectivity coefficient : impact on the ion retention

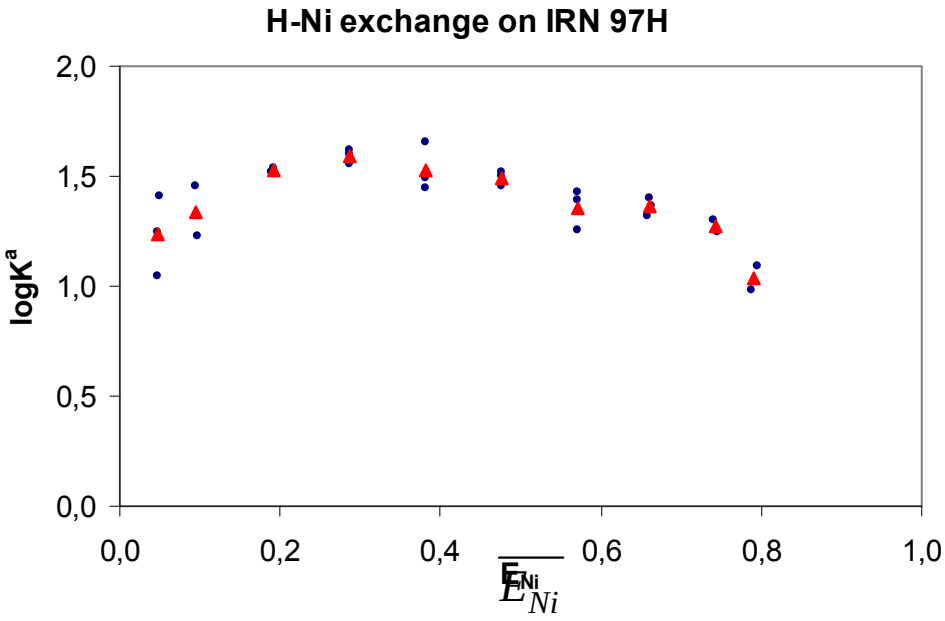
Nickel chloride exchange: batch procedure

- **n mL of a mother solution at C_{mother} = 1400 ppm_{Ni} ± 3%** are mixed with UP water in a V = 50 mL gauged vial : C_0 = 70 to 630 ppm_{Ni}
- **m = 0.5 g_{humid} ± 0.05g of IRN 97H** (Rohm&Haas) are poured in the beaker
- Stirring for 3 hours with a magnetic stirrer
- **pH (± 0.05) is measured** at 25 °C
- **C_{eq} = Ni^{2+} equilibrium concentration** measured by ICP-AES/MS **(± 2- 10%)**
- **EC = Exchange capacity** = 2.5 ± 0.15 meq/g_{humid}

Experimental uncertainties analysis

$$ {}^{Ni}_{H}K^{a}_{GT} = \frac{\overline{E_{Ni}} \cdot \left(a_H\right)^2}{\overline{E_H}^2 \cdot a_{Ni}} $$

$$ \overline{E_i} = \frac{z_i \cdot V \cdot \left(\overline{C_{mother}} / dilution - \overline{C_{eq}} \right)}{EC} $$



- **Large variation of selectivity coefficient**
- **Saturation < 80% because of acidification**

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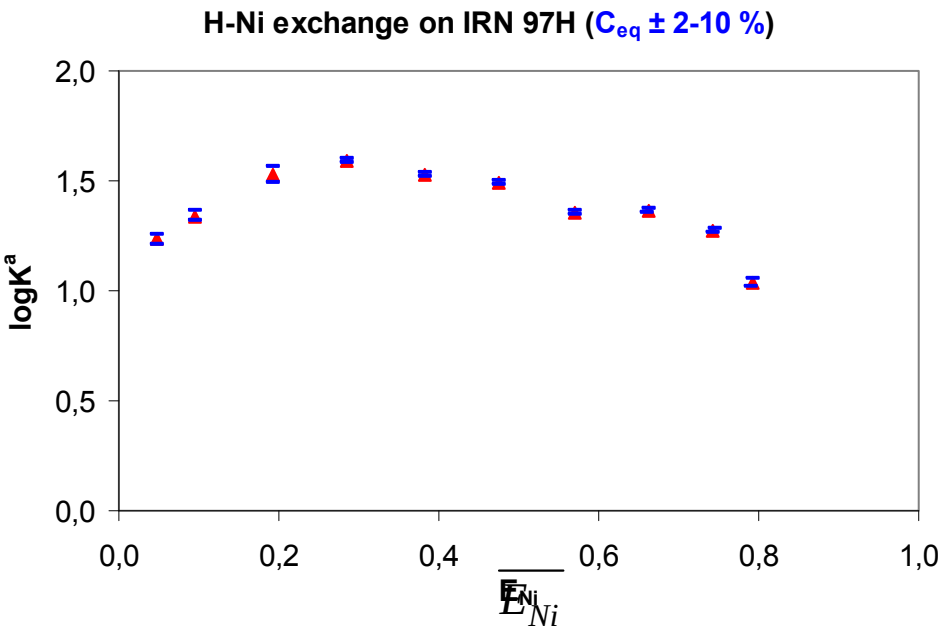

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- **Experimental uncertainties: strong impact of pH, EC and C_{mother}**

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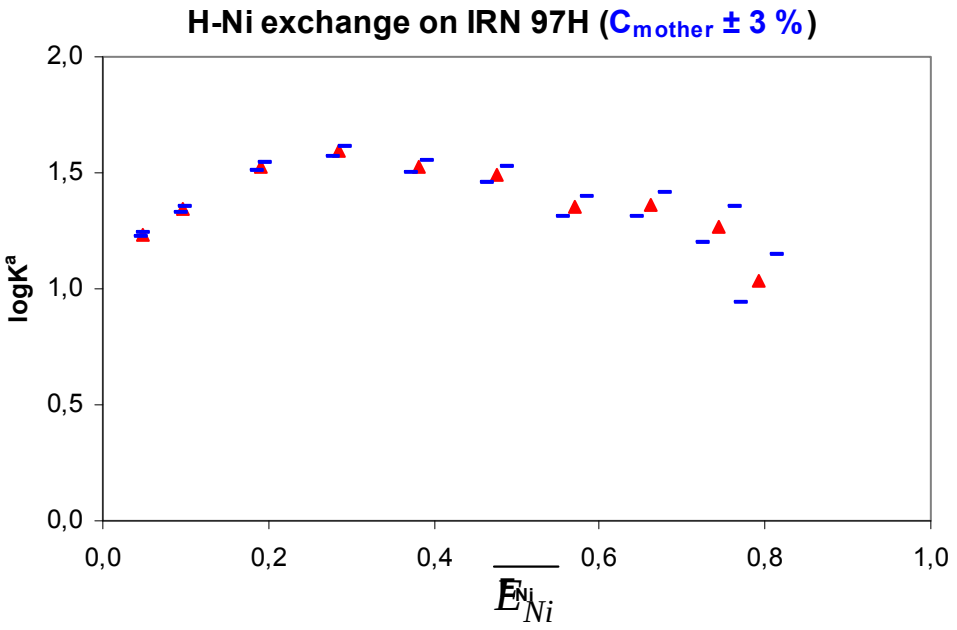

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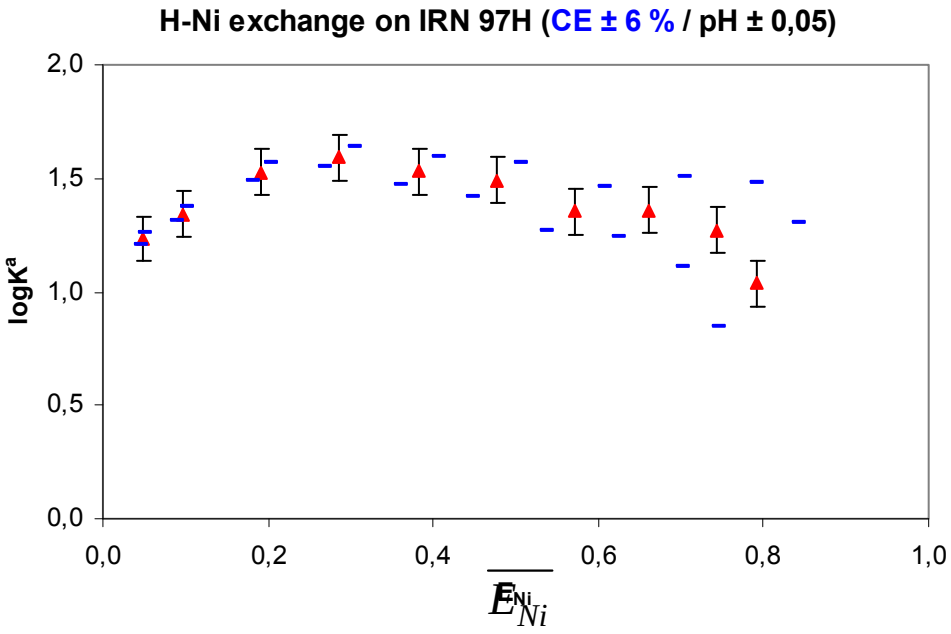

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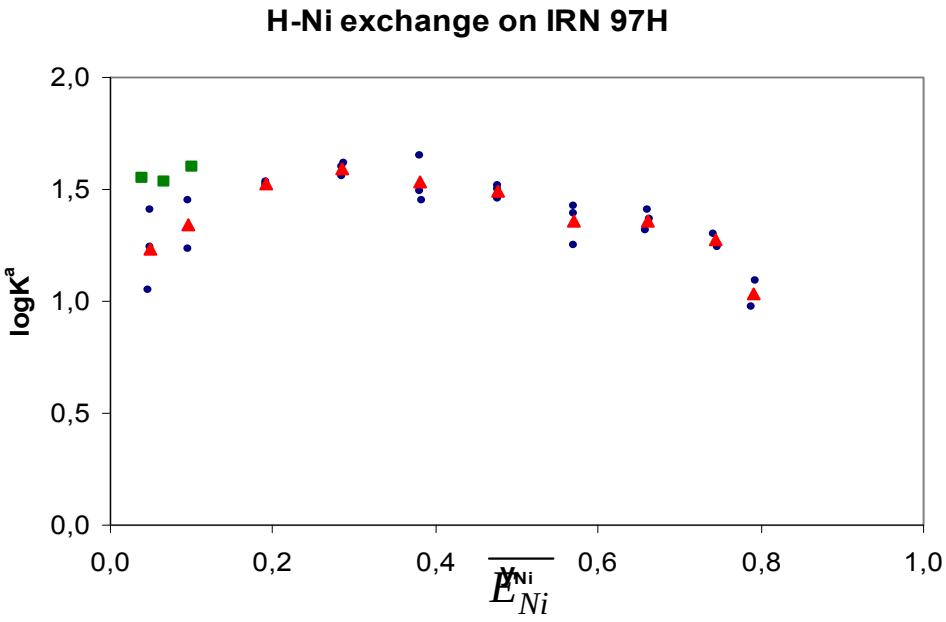


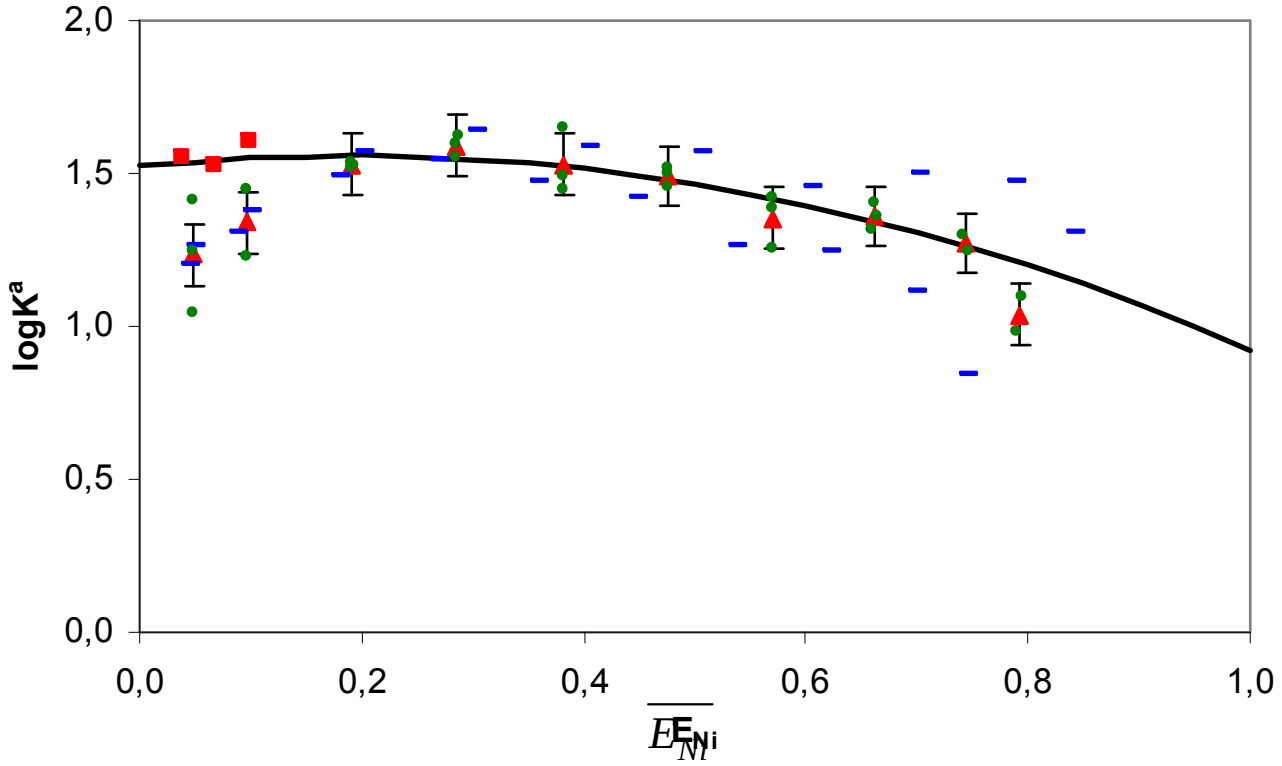
- **Large variation of selectivity coefficient**
- **Saturation < 80% because of acidification**
- **Pollution problems for the 2 first points (fixed by acidification)**
- **Experimental uncertainties: strong impact of pH, EC and C_{mother}**

Nickel selectivity coefficient variations

50 mL, $[NiCl_2]$ = 70 to 630 ppm_{Ni}

IRN97H mass = 0.5 g_{humid}

H-Ni exchange on IRN 97H (EC ± 6 % / pH ± 0,05)



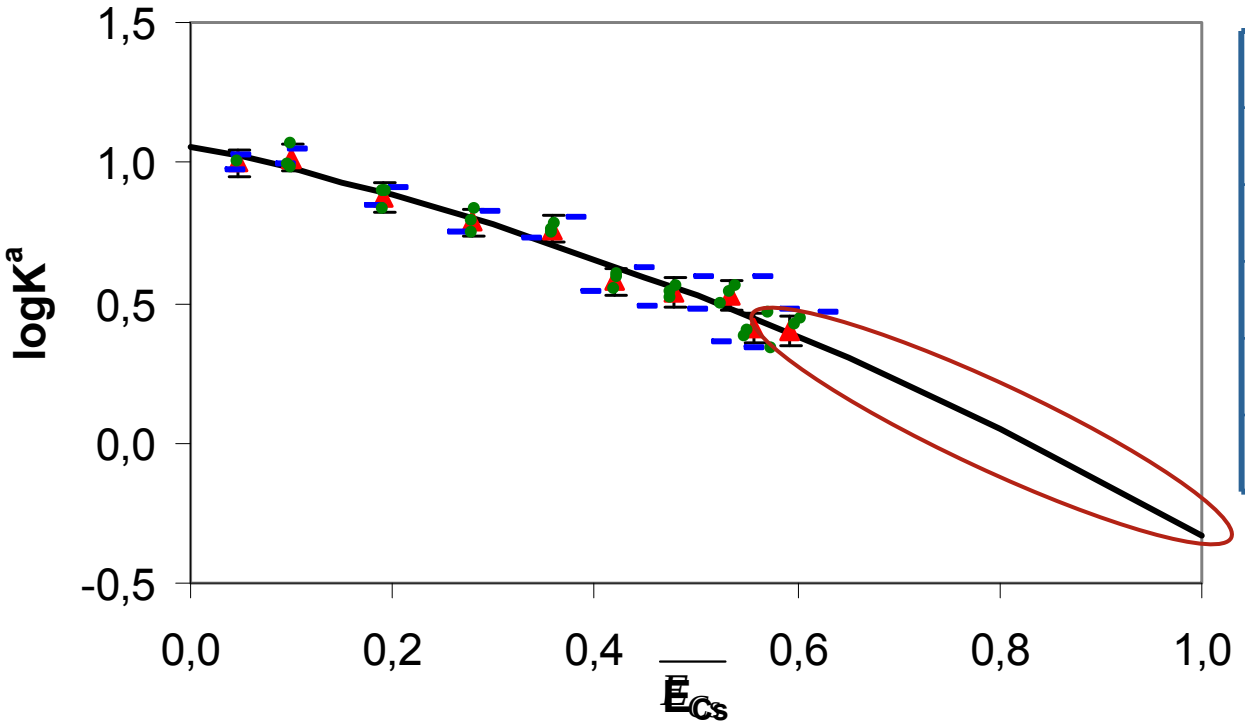
$\log {}_H^A K_{GT}^a \left(\overline{E_A} \to 0\right)$	1.52
$\log {}_H^A K_{GT}^a \left(\overline{E_A} \to 1\right)$	0.92
B	0.96
$\log {}_H^A K_{GT}$ 10,5% DVB	0.95
$\log {}_H^A K_{GT,Bonner}$ 8% DVB	1.19
$\log {}_H^A K_{GT,Bonner}$ 16% DVB	1.22

Cesium selectivity coefficient variations

50 mL, [CsCl] = 160 to 2900 ppm_{Cs}

IRN97H mass = 0.5 g_{humid}

H-Cs Exchange on IRN 97H (EC ± 6 % / pH ± 0,05)



$\log {}_H^A K_{GT}^a \left(\overline{E_A} \to 0\right)$	1.06
$\log {}_H^A K_{GT}^a \left(\overline{E_A} \to 1\right)$	-0.33
B	0.63
$\log {}_H^A K_{GT}$ 10,5% DVB	0.47
$\log {}_H^A K_{GT,Bonner}$ 8% DVB	0.51
$\log {}_H^A K_{GT,Bonner}$ 16% DVB	0.67

Importance of extrapolation

3

1. Theoretical background
2. Equilibrium study : Ni and Cs selectivity

1. Modelling variable selectivity coefficient : impact on the ion retention

- Model developments
- Impact of selectivity variations on the retention in a deep bed experiment

Model developments

- **Based on modified TPM (Gaines-Thomas formalism)**

$$\log\left({}^{A}_{H}K^{a}_{GT}\right)=\overline{E_A}\log\left({}^{A}_{H}K^{a}_{GT}\left(\overline{E_A}\to 1\right)\right)+\left(1-\overline{E_A}\right)\log\left({}^{A}_{H}K^{a}_{GT}\left(\overline{E_A}\to 0\right)\right)+B_{GT}\,\overline{E_A}\left(1-\overline{E_A}\right)$$

- **Correction factor $\overline{\gamma'}$ to account for non idealities in the resin phase incorporated in the chemical speciation code CHESS**

$$\log\overline{\gamma'}=\left(\log {}^{A}_{H}K_{GT}-a\right)-b\overline{E_A}-c\overline{E_A}^{2}$$

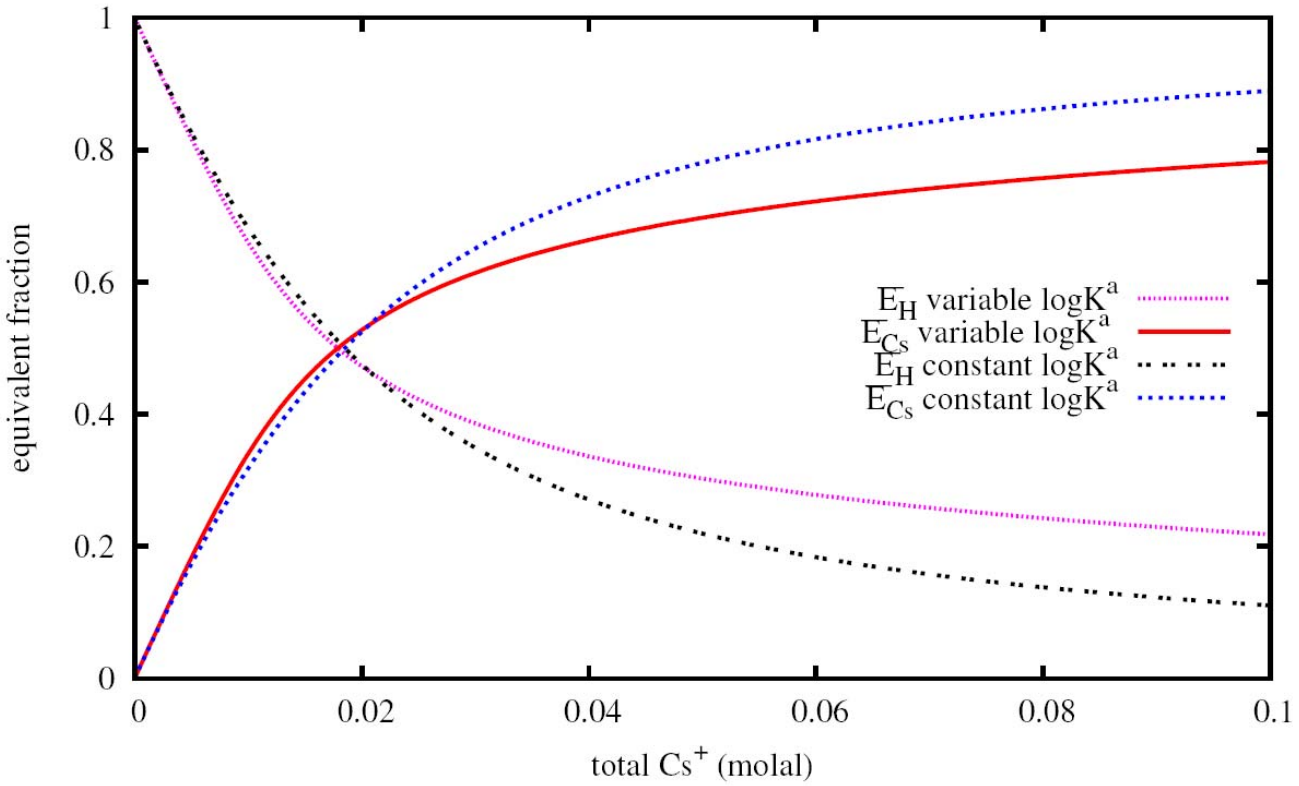
$$a=\log {}^{A}_{H}K^{a}_{GT}\left(\overline{E_A}\to 0\right)\;;\; b=B_{GT}-\log {}^{A}_{H}K^{a}_{GT}\left(\overline{E_A}\to 0\right)+\log {}^{A}_{H}K^{a}_{GT}\left(\overline{E_A}\to 1\right)\;;\; c=-B_{GT}$$

- **Linearization of the mass action law to calculate equivalent fractions**

$$\log\overline{E_A}=\log {}^{A}_{H}K_{GT}-\log\overline{\gamma'}-n\log a_H+n\log\overline{E_H}+\log a_A$$

Impact of logK^a variation on batch sorption

- **Simulations of a batch saturation experiment :**
  - 0.5 g_{humid} in 50 mL
  - Initial concentration of Cs^+ ranging from 0 to 0.1 mol/L



➢ **Significant impact of selectivity variations on site occupancy**

Reactive transport coupling code at equilibrium

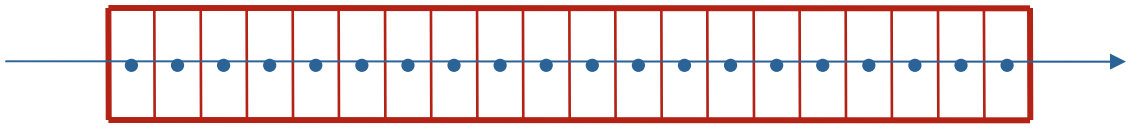
- **Including the model to the reactive transport code HYTEC[1]**
- **This allows to simulate a column experiment.**
- **HYTEC solves the transport equation while calculating equilibrium chemistry in each node for each step, by finite volumes.**
- **Assumption of an homogeneous flow through the deep bed (1D calculation).**
- **Equilibrium model: we have not considered any kinetics in the system.**

$$\omega \frac{\partial C_i}{\partial t} + \omega \frac{\partial \overline{C_i}}{\partial t} = -u \frac{\partial C_i}{\partial x}$$

$$\overline{C_i} = CHESS\left(C_i, C_j \ldots\right)$$

ω = porosity

u = filter velocity (m/s)



[1] Van der Lee J. *et al*, 2003 : "Module-oriented modeling of reactive transport with HYTEC", *Computers & Geosciences*, **29**(3) pp. 265-275.

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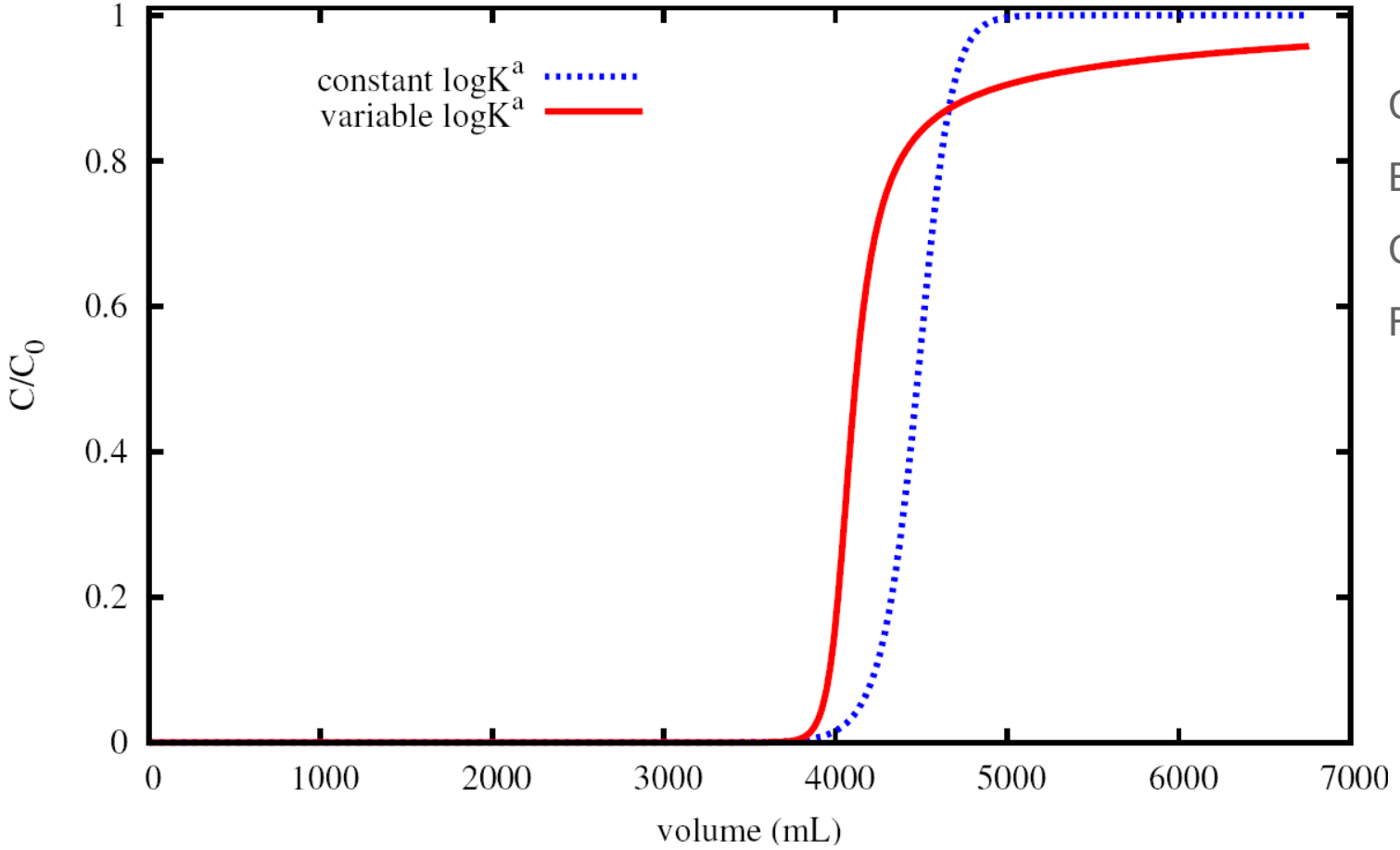
Impact of logK^a variation of cesium on sorption (film)

- **Test case:**
  - Column length = 1 cm
  - $EC_{IRN\ 97H}$ = 2.6 eq/L
  - C_{CsCl} = 3.6 10^{-4} mol/L
  - Flow rate = 4.5 mL/h

Impact of logK^a variation of cesium on sorption (breakthrough curve)



Column length=1 cm

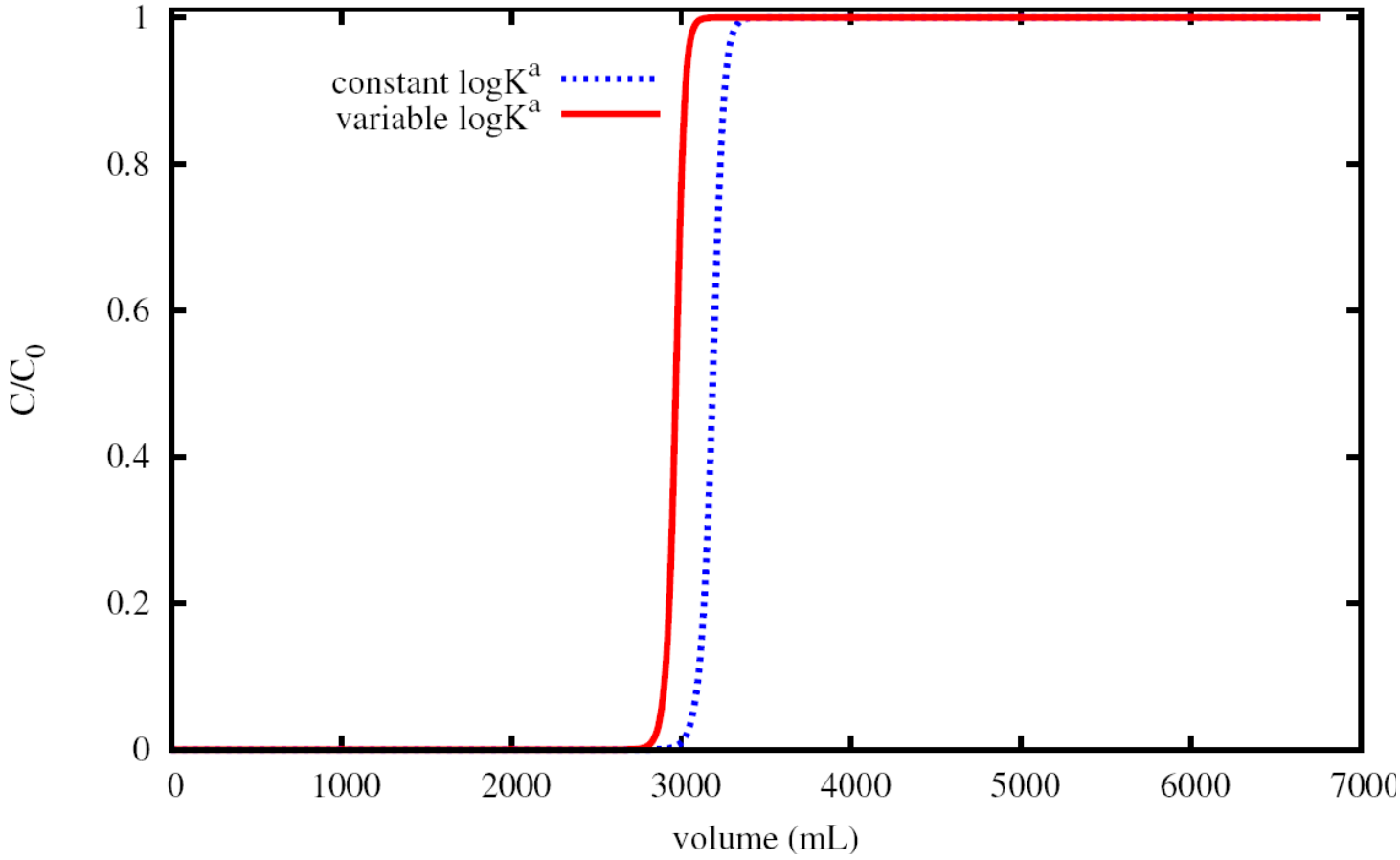
EC=2.6 eq/L

C_{CsCl}=3.6 10^{-4} mol/L

Flow rate=4.5 mL/h

- **Significant impact on cesium retention**
- **Compressive front turns dispersive**

Impact of logK^a variation of nickel on sorption (breakthrough curve)



Column length=1 cm

EC=2.6 eq/L

C_{NiCl2}=1.8 10^{-4} mol/L

=3.6 10^{-4} eq/L

Flow rate=4.5 mL/h

C_{HCl}=10^{-2} mol/L

- **Nickel leaches earlier when K^a varies**
- **Electroselectivity: nickel is well retained**
- **Potential impact on nickel retention**

Conclusions

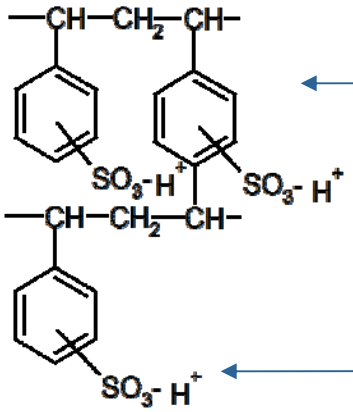
- Selectivity coefficients can vary of 1 order of magnitude.
- We propose a model for divalent/monovalent exchange with non-ideality correction.
- We applied a reactive transport code to simulate ion retention in deep bed columns at equilibrium.

➡ We showed that selectivity variations should be accounted for when modelling ion exchange resins.

WHAT'S NEXT ?

- To compare model with experimental results
- We should refine the non-ideality model: regular solid solutions are considered.
- This model will be better suited to deal with multicomponent exchange.
- We will incorporate kinetics and impact of flow rate in HYTEC.

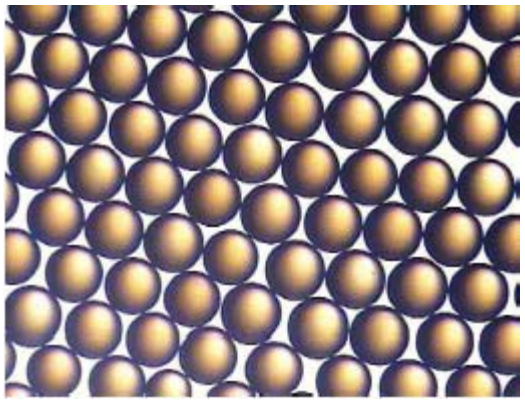
Structure of the resin studied : IRN 97H (Rohm&Haas)



polystyrene skeleton cross-linked with DiVinylBenzene

Functional groups:

Sulfonic acids for a strong acidic cation exchanger



Gel type

	Water retention	Crosslinkage	Ion exchange capacity	Beads diameter
R&H	45 – 49 %	10 %	2.25 eq/L_H	525 ± 25 µm
Exp	53 %	/	2.16 eq/L_H – 2.6 meq/g	/

Regular solid solutions

Calculation of activity coefficients inside the resin phase

Binary exchange

$$RT \ln \overline{\gamma_1} = W_{12}^G \left(1 - \overline{x_1}\right)^2$$

Multicomponent exchange

$$RT \ln \overline{\gamma_1} = \sum_{j>1}^{n} W_{1j}^G \overline{x_j}\left(1 - \overline{x_1}\right) - \sum_{i>1}^{n}\sum_{j>i}^{n} W_{ij}^G \overline{x_i x_j} + \sum_{i>1}^{n}\sum_{j>i}^{n} W_{1ij}^G \overline{x_i x_j}\left(1 - 2 \cdot \overline{x_1}\right) - \sum_{i>1}^{n}\sum_{j>i}^{n}\sum_{k>j}^{n} W_{ijk}^G \overline{x_i x_j x_k}$$

- **Large knowledge in soil science (mineralogy)**
- **Model developped for solid solution where exchange are largely homovalent**

WILSON model

✓ **Calculation of activity coefficients inside the resin phase**

$$\ln \overline{\gamma_i} = 1 - \ln\left(\sum_{j=1}^{m} \overline{x}_j \lambda_{ij}\right) - \sum_{k=1}^{m} \frac{\overline{x_k} \lambda_{ki}}{\sum_{j=1}^{m} \overline{x}_j \lambda_{kj}}$$

- **Independent of experimental conditions**
- **Many binary interaction parameters λ_{ij} not widely known**

SOLDATOV model

- ✓ **Explicit variation of the selectivity coefficient according to a polynomial which degree is a function of cross-linking**

$$K = cste$$

$$K = y(0,0)\left(1-\bar{x}\right) + y(0,1)\bar{x}$$

$$K = y(2,0)\left(1-\bar{x}\right)^2 + 2y(1,1)\left(1-\bar{x}\right)\bar{x} + y(0,2)\bar{x}^2$$

$$K = y(3,0)\left(1-\bar{x}\right)^3 + 3y(2,1)\left(1-\bar{x}\right)^2\bar{x} + 3y(1,2)\left(1-\bar{x}\right)\bar{x}^2 + y(0,3)\bar{x}^3$$

$$K = y(4,0)\left(1-\bar{x}\right)^4 + 4y(3,1)\left(1-\bar{x}\right)^3\bar{x} + 6y(2,2)\left(1-\bar{x}\right)^2\bar{x}^2 + 4y(1,3)\left(1-\bar{x}\right)\bar{x}^3 + y(0,4)\bar{x}^4$$

- **Parameters are determined from the resin geometry, not function of experimental conditions**
- **Not developed for 2:1 exchange**
- **Extrapolation to multicomponent exchange**

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MELIS model

- ✓ **Surface complexation model (Nernst) + distribution of exchange sites (each site has its own sorption constant)**

$$K = \left(K_1\right)^{p_1}\left(K_2\right)^{p_2}$$

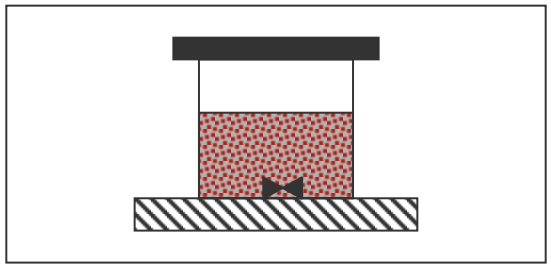
$$\gamma = \exp\left(-\frac{\sigma}{RT}\right) = \left(\frac{K_1}{K_2}\right)^{\left(p_1 p_2\right)^{1/2}}$$

$$K_j = \frac{\overline{y_{A^{n+},j}} \times \left(x_{H^+}\right)^n}{\left(\overline{y_{H^+,j}}\right)^n \times x_{A^{n+}}} \left(\frac{q_{0j}}{N}\right)^{1-n}$$

  - **Surface complexation model can always be applied (even if it is far away from reality)**
  - **Not adapted to 2:1 exchange**
  - **Extrapolation to multicomponent exchange**

Ion exchange capacity determination (EC)

- ✓ 0.5 g of regenerated resin
- ✓ 100 mL of 0.025M NaOH
- ✓ 2 hours stirring
- ✓ 50 mL are titrated for remaining OH^-



$$\overline{H^+} + Na^+ \rightleftharpoons \overline{Na^+} + H^+$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

	Exchange capacity (eq/g)	Exchange capacity (eq/L)
Experimental	2.6 ± 0.15 meq/g	2.16 ± 0.1 eq/L
Supplier, minimum	\	2.00 eq/L
Supplier, found	\	2.25 eq/L

- ✓ **Differences originate from**
  - ✓ Contact time (15 min vs 2 hours)
  - ✓ Sorption on HCl during regeneration
  - ✓ Sorption of NaOH during exchange

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Nickel chloride exchange: batch procedure

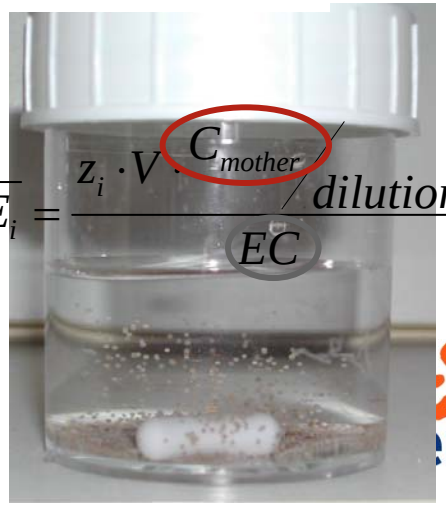
- **n mL of a mother solution at C_{mother} = 1400 ppm_{Ni} ± 3%** are mixed with UP water in a V = 50 mL gauged vial : C_0 = 70 to 630 ppm_{Ni}
- **m = 0.5 g_{humid} ± 0.05g of IRN 97H** (Rohm&Haas) are poured in the beaker
- Stirring for 3 hours with a magnetic stirrer
- **pH (± 0.05) is measured** at 25 °C
- **C_{eq} = Ni^{2+} equilibrium concentration** measured by ICP-AES/MS **(± 2- 10%)**
- EC = Exchange capacity = 2.5 ± 0.15 meq/g_{humid}
- **Hypothesis :** Equilibrium concentration (C_{eq}) << initial concentration (C_0)

$$\log {}^{Ni}_{H}K^{a}_{GT} = \log\left(2.V.C_{mother}/dilution\right) + \log(EC) + \log(m) - 2\,pH$$

$$-2\log\left(EC.m - 2.V.C_{mother}/dilution\right) - \log(C_{eq})$$

$$-\left(\frac{-0.5114\times 4\sqrt{2.C_{mother}/dilution}}{1+0.3288\times 3\sqrt{2.C_{mother}/dilution}} + 0.041\times 2.C_{mother}/dilution\right)$$

$$\overline{E_i} = \frac{z_i \cdot V.C_{mother}/dilution}{EC}$$



NB : For the ionic strength calculation, pH = H^+ concentration