Variation of selectivity coefficients: impact on column efficiency

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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. 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
Different formalisms

Gaines-Thomas convention

\[ nH^+ + A^{n+} \rightleftharpoons \overline{A}^{n+} + nH^+ \]

Bonner study\(^1\): Vanselow convention

Resin / solution exchange reaction

\[ \frac{1}{n}A^{n+} + H^+ \rightleftharpoons \frac{1}{n}\overline{A}^{n+} + H^+ \]

Different formalisms

Gaines-Thomas convention

\[ n \text{H}^+ + A^{n+} \rightleftharpoons \overline{A}^{n+} + n \text{H}^+ \]

Bonner study\(^1\): Vanselow convention

\[ \frac{1}{n} A^{n+} + \text{H}^+ \rightleftharpoons \frac{1}{n} \overline{A}^{n+} + \text{H}^+ \]

Thermodynamic equilibrium constant

\[ A_H K_G = \frac{a_{A^{n+}} \times (a_{H^+})^n}{(a_{H^+})^n \times a_{A^{n+}}} \]

\[ A_H K_B = \frac{(a_A)^{1/n} \times a_H}{a_H \times (a_A)^{1/n}} \]

Different formalisms

Gaines-Thomas convention

\[
nH^+ + A^{n+} \rightleftharpoons A^{n+} + nH^+
\]

\[
A_K_{GT} = \frac{a_{A^{n+}} \times (a_{H^+})^n}{(a_{H^+})^n \times a_{A^{n+}}}
\]

\[
a_i = E_i \times \gamma_i \quad E_i = \frac{z_i \cdot C_i}{EC}
\]

Bonner study\(^1\): Vanselow convention

\[
\frac{1}{n} A^{n+} + H^+ \rightleftharpoons \frac{1}{n} A^{n+} + H^+
\]

\[
A_K_B = \frac{(a_A)^{1/n} \times a_H}{a_H \times (a_A)^{1/n}}
\]

\[
a_i = x_i \times \gamma_i \quad x_i = \frac{C_i}{\sum_{j \text{ counter-ions}} C_j}
\]

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Different formalisms

Gaines-Thomas convention

\[ nH^+ + A^{n+} \rightleftharpoons \overline{A^{n+}} + nH^+ \]

Thermodynamic equilibrium constant

\[ A^H K_{GT} = \frac{\overline{a_{A^{n+}}} \times (a_{H^+})^n}{(\overline{a_{H^+}})^n \times a_{A^{n+}}} \]

Activity of sorbed ions

\[ \overline{a_i} = E_i \times \gamma_i \quad \overline{E_i} = \frac{z_i \cdot C_i}{EC} \]

Corrected selectivity coefficient

\[ A^H K_{GT}^a = \frac{\overline{E_{A^{n+}}} \cdot (a_{H^+})^n}{\overline{E_{H^+}} \cdot a_{A^{n+}}} \]

Bonner study\(^1\): Vanselow convention

\[ \frac{1}{n} A^{n+} + H^+ \rightleftharpoons \frac{1}{n} \overline{A^{n+}} + H^+ \]

Thermodynamic equilibrium constant

\[ A^H K_B = \frac{(\overline{a_A})^{1/n} \times a_H}{a_H \times (a_A)^{1/n}} \]

Activity of sorbed ions

\[ \overline{a_i} = x_i \times \gamma_i \quad \overline{x_i} = \frac{\overline{C_i}}{\sum_{j \text{ counter-ions}} \overline{C_j}} \]

Equivalent fraction

\[ \overline{a_i} = E_i \times \gamma_i \quad \overline{E_i} = \frac{z_i \cdot C_i}{EC} \]

Molar fraction

\[ \overline{a_i} = x_i \times \gamma_i \quad \overline{x_i} = \frac{\overline{C_i}}{\sum_{j \text{ counter-ions}} \overline{C_j}} \]

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

Gaines-Thomas convention

\[
\text{Ni}^2+ + \text{H}^+ \rightleftharpoons \text{Ni}^{2+} + \text{H}^+ 
\]

\[
\frac{\text{Ni}}{\text{H}} K^a_{GT} = \frac{E_{Ni} \cdot (a_H)^2}{E^{2} \cdot a_{Ni}}
\]

Bonner study: Vanselow convention

\[
\frac{1}{2} \text{Ni}^{2+} + \text{H}^+ \rightleftharpoons \frac{1}{2} \text{Ni}^{2+} + \text{H}^+ 
\]

\[
\frac{\text{Ni}}{\text{H}} K^a_B = \frac{(x_{Ni})^{1/2} \times (a_H)}{x_H \times (a_{Ni})^{1/2}}
\]

Corrected selectivity coefficient

\[
\frac{\text{Ni}}{\text{H}} K^a_{GT} = \left( \frac{\text{Ni}}{\text{H}} K^a_B \right)^2 \times 2 \left( 1 + \overline{x_{Ni}} \right)
\]

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Relation between selectivity coefficient and thermodynamic constant – H⁺/Ni²⁺ exchange

Gaines-Thomas convention

\[ 2H^+ + Ni^{2+} \rightleftharpoons Ni^{2+} + 2H^+ \]

\[ \frac{Ni}{H} K_{GT}^a = \frac{E_{Ni} \cdot (a_H)^2}{E_H \cdot a_{Ni}} \]

Corrected selectivity coefficient

\[ \frac{Ni}{H} K_{GT}^a = \left( \frac{Ni}{H} K_B^a \right)^2 \times 2 \left( 1 + \frac{x_{Ni}}{x_H} \right) \]

\[ \ln \frac{Ni}{H} K_{GT} = (z_H - z_{Ni}) + \int_0^1 \ln \frac{Ni}{H} K_{GT}^a dE_{Ni} \]

Thermodynamic equilibrium constant calculation\(^1\)

Bonner study: Vanselow convention

\[ \frac{1}{2} Ni^{2+} + H^+ \rightleftharpoons \frac{1}{2} Ni^{2+} + H^+ \]

\[ \frac{Ni}{H} K_B^a = \frac{\left( \frac{x_{Ni}}{x_H} \right)^{1/2} \times (a_H)}{x_H \times (a_{Ni})^{1/2}} \]

\[ \ln \frac{Ni}{H} K_B = \int_0^1 \ln \frac{Ni}{H} K_B^a dE_{Ni} \]

\[ \log \frac{Ni}{H} K_{GT} = 2 \times \log \frac{Ni}{H} K_B \]

Coupling an equilibrium model with a reactive transport code : Three Parameter Model\textsuperscript{1}

- **Numerically easy to introduce in a reactive transport code**
- **The model should be adapted to CHESS\textsuperscript{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

\[
\log\left( A H K_V^a \right) = \bar{x}_A \log\left( A H K_V^a \left( \bar{x}_A \rightarrow 1 \right) \right) + \left( 1 - \bar{x}_A \right) \log\left( A H K_V^a \left( \bar{x}_A \rightarrow 0 \right) \right) + B \bar{x}_A \left( 1 - \bar{x}_A \right)
\]


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

\[ K^a_{GT}^{Ni} = \frac{E_{Ni} \cdot (a_H)^2}{E_H^{-2} \cdot a_{Ni}} \]

\[ E_{i} = \frac{z_i \cdot V \left( \frac{C_{mother}}{dilution} - C_{eq} \right)}{EC} \]

- Large variation of selectivity coefficient
- Saturation < 80% because of acidification
Experimental uncertainties analysis

\[ \frac{Ni}{H} K_{GT} = \frac{E_{Ni} \cdot (a_H)^2}{E_H \cdot a_{Ni}} \]

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

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

**H-Ni exchange on IRN 97H (C_{eq} \pm 2-10 \%)**
Experimental uncertainties analysis

\[ N_i \frac{K^a_{GT}}{H} = \frac{E_{Ni}}{E_H} \cdot \frac{(a_H)^2}{a_{Ni}} \]

\[ z_i \cdot V \cdot \left( \frac{C_{\text{mother}}}{\text{dilution}} - C_{eq} \right) \]

\[ E_i = \frac{E_{Ni}}{EC} \]

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

**H-Ni exchange on IRN 97H (C_{\text{mother}} \pm 3 \%)**

- Experimental uncertainties: strong impact of pH, EC and C_{\text{mother}}
Experimental uncertainties analysis

\[ \frac{\text{Ni}}{\text{H}} K^{a}_{GT} = \frac{E_{Ni} \cdot (a_{H})^{2}}{E_{H}^{-2} \cdot a_{Ni}} \]

\[ E_{i} = \frac{z_{i} \cdot V \cdot (C_{\text{mother}} / \text{dilution} - C_{eq})}{EC} \]

- Large variation of selectivity coefficient
- Saturation < 80% because of acidification
- Experimental uncertainties: strong impact of pH, EC and C_{mother}
Experimental uncertainties analysis

\[ \frac{Ni}{H}K_{GT} = \frac{E_{Ni} \cdot (a_H)^2}{E_H \cdot a_{Ni}} \]

\[ \bar{E_i} = \frac{z_i \cdot V \cdot \left( \frac{C_{mother}}{dilution} - \bar{C_{eq}} \right)}{EC} \]

- **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, $[\text{NiCl}_2] = 70$ to $630$ ppm$_{\text{Ni}}$

IRN97H mass = 0.5 g$_{\text{humid}}$

**H-Ni exchange on IRN 97H (EC ± 6 % / pH ± 0.05)**

\[
\begin{align*}
\log A_K^a (E_A \rightarrow 0) &= 1.52 \\
\log A_K^a (E_A \rightarrow 1) &= 0.92 \\
B &= 0.96 \\
\log A_K^{10.5\% \text{DVB}} &= 0.95 \\
\log A_K^{8\% \text{DVB}} &= 1.19 \\
\log A_K^{16\% \text{DVB}} &= 1.22
\end{align*}
\]
Cesium selectivity coefficient variations

50 mL, [CsCl] = 160 to 2900 ppm\textsubscript{Cs}

IRN97H mass = 0.5 g\textsubscript{humid}

H-Cs Exchange on IRN 97H (EC ± 6 % / pH ± 0.05)

Importance of extrapolation

| \( \log_{10} \frac{A_{K_a}}{GT} \left( E_A \rightarrow 0 \right) \) | 1.06 |
| \( \log_{10} \frac{A_{K_a}}{GT} \left( E_A \rightarrow 1 \right) \) | -0.33 |
| \( B \) | 0.63 |
| \( \log_{10} \frac{A_{K_a}}{GT, 10.5\% \text{ DVB}} \) | 0.47 |
| \( \log_{10} \frac{A_{K_a}}{GT, \text{ Bonner, 8}\% \text{ DVB}} \) | 0.51 |
| \( \log_{10} \frac{A_{K_a}}{GT, \text{ Bonner, 16}\% \text{ DVB}} \) | 0.67 |
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)

\[
\log \left( A K^a_{GT} \right) = E_A \log \left( A K^a_{GT} \left( \overline{E_A} \rightarrow 1 \right) \right) + \left(1 - E_A\right) \log \left( A K^a_{GT} \left( \overline{E_A} \rightarrow 0 \right) \right) + B_{GT} \overline{E_A} \left(1 - \overline{E_A} \right)
\]

- Correction factor \( \gamma' \) to account for non idealities in the resin phase incorporated in the chemical speciation code CHESS

\[
\log \gamma' = \left( \log A K^a_{GT} - a \right) - b \overline{E_A} - c \overline{E_A}^2
\]

\[
a = \log A K^a_{GT} \left( \overline{E_A} \rightarrow 0 \right) ; \quad b = B_{GT} - \log A K^a_{GT} \left( \overline{E_A} \rightarrow 0 \right) + \log A K^a_{GT} \left( \overline{E_A} \rightarrow 1 \right) ; \quad c = -B_{GT}
\]

- Linearization of the mass action law to calculate equivalent fractions

\[
\log \overline{E_A} = \log A K^a_{GT} \gamma' - n \log a_H + n \log \overline{E_H} + \log a_A
\]
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\textsuperscript{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.

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

\(\overline{C_i} = \text{CHESS}(C_i, C_j, \ldots)\)

\(\omega = \text{porosity}\)
\(u = \text{filter velocity (m/s)}\)

Impact of $\log K^a$ variation of cesium on sorption (film)

- **Test case:**
  - Column length = 1 cm
  - $E_{C_{IRN \, 97}} = 2.6$ eq/L
  - $C_{CsCl} = 3.6 \times 10^{-4}$ mol/L
  - Flow rate = 4.5 mL/h
Impact of $\log K^a$ variation of cesium on sorption (breakthrough curve)

- Significant impact on cesium retention
- Compressive front turns dispersive

Column length=1 cm
EC=2.6 eq/L
$C_{CsCl}=3.6 \times 10^{-4}$ mol/L
Flow rate=4.5 mL/h
Impact of log$K^a$ variation of nickel on sorption (breakthrough curve)

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

Column length=1 cm  
EC=2.6 eq/L  
$C_{NiCl_2}=1.8 \times 10^{-4}$ mol/L  
$=3.6 \times 10^{-4}$ eq/L  
Flow rate=4.5 mL/h  
$C_{HCl}=10^{-2}$ mol/L
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)

**Functional groups:**
- Sulfonic acids for a strong acidic cation exchanger

**Gel type**

<table>
<thead>
<tr>
<th></th>
<th>Water retention</th>
<th>Crosslinkage</th>
<th>Ion exchange capacity</th>
<th>Beads diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&amp;H</td>
<td>45 – 49 %</td>
<td>10 %</td>
<td>2.25 eq/L_H</td>
<td>525 ± 25 µm</td>
</tr>
<tr>
<td>Exp</td>
<td>53 %</td>
<td>/</td>
<td>2.16 eq/L_H – 2.6 meq/g</td>
<td>/</td>
</tr>
</tbody>
</table>
Regular solid solutions

Calculation of activity coefficients inside the resin phase

Binary exchange

\[ RT \ln \gamma_1 = W_{12}^G (1 - x_1)^2 \]

Multicomponent exchange

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

- Large knowledge in soil science (mineralogy)
- Model developed for solid solution where exchange are largely homovalent
Calculation of activity coefficients inside the resin phase

\[
\ln \gamma_i = 1 - \ln \left( \sum_{j=1}^{m} x_j \lambda_{ij} \right) - \sum_{k=1}^{m} \frac{x_k \lambda_{ki}}{\sum_{j=1}^{m} x_j \lambda_{kj}}
\]

- Independent of experimental conditions
- Many binary interaction parameters \( \lambda_{ij} \) not widely known
Explicit variation of the selectivity coefficient according to a polynomial which degree is a function of cross-linking

\[ K = cste \]

\[ K = y(0,0)(1-x) + y(0,1)x \]

\[ K = y(2,0)(1-x)^2 + 2y(1,1)(1-x)x + y(0,2)x^2 \]

\[ K = y(3,0)(1-x)^3 + 3y(2,1)(1-x)^2x + 3y(1,2)(1-x)x^2 + y(0,3)x^3 \]

\[ K = y(4,0)(1-x)^4 + 4y(3,1)(1-x)^3x + 6y(2,2)(1-x)^2x^2 + 4y(1,3)(1-x)x^3 + y(0,4)x^4 \]

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

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

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

\[ \gamma = \exp \left( -\frac{\sigma}{RT} \right) = \left( \frac{K_1}{K_2} \right)^{(p_1p_2)^{1/2}} \]

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

- 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⁻

<table>
<thead>
<tr>
<th></th>
<th>Exchange capacity (eq/g)</th>
<th>Exchange capacity (eq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>2.6 ± 0.15 meq/g</td>
<td>2.16 ± 0.1 eq/L</td>
</tr>
<tr>
<td>Supplier, minimum</td>
<td>\</td>
<td>2.00 eq/L</td>
</tr>
<tr>
<td>Supplier, found</td>
<td>\</td>
<td>2.25 eq/L</td>
</tr>
</tbody>
</table>

**Differences originate from**
- Contact time (15 min vs 2 hours)
- Sorption on HCl during regeneration
- Sorption of NaOH during exchange
Nickel chloride exchange: batch procedure

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

\[
\log_{\frac{Ni}{H}} K_{GT}^a = \log \left( \frac{2 \cdot V \cdot C_{\text{mother}}}{\text{dilution}} \right) + \log (EC) + \log (m) + 2pH \\
-2 \log \left( \frac{EC \cdot m - 2 \cdot V \cdot C_{\text{mother}}}{\text{dilution}} \right) - \log(C_{\text{eq}}) \\
- \left( -0.5114 \times 4 \sqrt{\frac{2 \cdot C_{\text{mother}}}{\text{dilution}}} \right) + 0.041 \times 2 \cdot \frac{C_{\text{mother}}}{\text{dilution}}
\]

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