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### Chelating adsorption with variable stoichiometry: Separation of nickel and zinc in concentrated sulfate solution



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#### HIGHLIGHTS

- A step-wise chelation model is proposed for metal uptake in chelating adsorbents.
- The model is tested for nickel adsorption from concentrated zinc sulfate solutions.
- The proposed model explains well the experimental batch and break-through data.
- Strong competition by zinc is explained by the variable nickel/ligand ratio.

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#### ABSTRACT

A new approach is proposed for modeling of metal uptake data in chelating ion exchangers and adsorbents. In contrast to conventional equilibrium models assuming a constant stoichiometry for the surface complex, a step-wise reaction scheme is used in analogy with complex formation in bulk solution. The model is tested against equilibrium and dynamic uptake data, and the results are compared with those obtained using a conventional isotherm model. Nickel removal from  $ZNSO_4$  solutions using a commercial chelating adsorbent is used as test case. According to the results, the observed decrease in nickel uptake with increasing zinc concentration can be explained much better using the proposed model than with conventional isotherm models. Model parameters estimated from single-metal equilibrium data predict the behavior of batch and fixed-bed systems up to zinc concentrations of 2.2 mol/L with Zn/Ni mole ratio of about 10<sup>4</sup>.

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#### 1. Introduction

Solid materials containing chelate-forming functional groups are important in solid phase extraction (SPE) [1–3] as well as in industrial-scale separation of metals from aqueous process solutions [4–7]. Depending on the type of the functional group, metal uptake can be described as competitive ion exchange of the metal cations or adsorption of the metal salts. Irrespective of the mechanism, equilibrium uptake is treated in vast majority of studies with simple models like Langmuir and Freundlich isotherms. Moreover, only single-metal parameters are in many cases determined without adequate testing in multi-component systems. Although these isotherms can be extended also to multi-component and competitive systems, more advanced models are needed in cases involving strongly competing metal species. Non-ideal competitive adsorption (NICA) model [8] has been developed for geochemical purposes but it has been also applied to metal sorption from concentrated metal processing streams [9,10]. Another approach widely used in geoscience is based on the concept of surface complexation (SC) [11]. Large number of different SC models exists and a variant for engineering purposes was developed by Höll and co-workers [12].

Understanding of the phenomena involved in industrially relevant metals separation processes is important for modeling and development of tools for process design. A major challenge in modeling of real process solutions is that the concentrations of the competing species usually vary in wide limits [13–15]. In our previous studies we have investigated removal of copper and nickel from concentrated ZnSO<sub>4</sub> solutions using a commercial chelating adsorbent functionalized with 2-(aminomethyl)pyridine (amp) [10,16–17]. In that system, feed concentrations of nickel and zinc are  $2.2 \cdot 10^{-4}$  and 2.2 mol/L, which means that the ZnSO<sub>4</sub> matrix can be correlated well using conventional isotherm models but nickel behaved differently. Nickel uptake from the ZnSO<sub>4</sub>





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#### Nomenclature

С	concentration (mol/L)
$d_s$	average particle diameter (m)
$D_{ax}$	axial dispersion coefficient (m <sup>2</sup> /s)
$D_p$	pore diffusion coefficient $(m^2/s)$
h	NICA parameter (–)
Ι	ionic strength (mol/L)
Κ	step-wise stability constant (L/mol)
т	CHEL parameter (–)
п	number of steps (–)
Namp	average number of amp ligands coordinated to the me-
•	tal cation (–)
$N_{dp}$	number of data points (-)
p	NICA parameter (–)
q	adsorbed amount (mol/kg)
$\bar{\bar{q}}$	volume-averaged value of $q$ (mol/kg)
$q_{tot}$	amount of functional groups (mol/kg)
T	temperature (°C)
t	time (s)
V	volume (m <sup>3</sup> )

matrix was much less than predicted on the basis of independent sorption data, and both kinetic and equilibrium factors were considered as reasons for this discrepancy. For example, tests with the original solution and a copper-free solution indicated that the presence of strongly adsorbing copper does not explain the behavior of nickel [10]. It is also possible that the high zinc concentration disturbs complex formation between nickel and the amp ligand. This possibility was, however, ruled out in a spectroscopic study, where the stability constants of Ni-amp complexes in aqueous solutions were determined at different zinc concentrations [18]. It was further shown that the high zinc concentration effectively suppresses formation of  $[Ni(amp)_2]^{2+}$  and  $[Ni(amp)_3]^{2+}$  and the only complex present at such conditions is  $[Ni(amp)]^{2+}$ .

Step-wise reaction mechanism is the standard approach for metal complexes in bulk solutions [19]. The Bjerrum method is typically used to determine the stability constants and it has been also applied to soluble polymeric ligands [20] and ligands anchored on solid support [21]. There are, however, factors which make these cases different from the reactions taking place with monomeric ligands in bulk solution. First, the local ligand concentration is much higher than the average value. Secondly, the mobility of the ligands is restricted and interactions between the neighboring groups must be included [20]. Charging of the functional groups upon neutralization or protonation gives rise to a Donnan potential, which hinders approach of the co-ions to the ligand groups. When these factors are adequately accounted for, a more realistic model for metal uptake in chelating materials can be obtained. In particular, validity of the parameters in much wider concentration range is expected.

The aim of this study is to demonstrate that both equilibrium and dynamic adsorption behavior of nickel in the absence or presence of the concentrated ZnSO<sub>4</sub> matrix can be described assuming variable metal/ligand stoichiometry. For that purpose, previously reported data as well as results from new measurements are correlated using a chelating model (CHEL) constructed to allow stepwise formation of surface complexes with different metal/ligand ratios. The data are also re-calculated using the non-ideal competitive adsorption (NICA) model in order to make detailed comparison between the two approaches. In both cases, intra-particle mass transport is described using a diffusion model based on the linear driving force approximation. The novelty of this study is thus a mechanistically reasonable adsorption model for highly

$\begin{array}{c} x\\ z\\ \beta\\ \varepsilon_b\\ \varepsilon_p\\ \kappa\\ \vdots\end{array}$	axial coordinate (m) lumped concentration variable (mol/kg) cumulative stability constant bed porosity (–) particle porosity (–) affinity constant (L/mol)
V Q	fractional coverage (
$\rho_s$	adsorbent density (kg/L)
Supersc	ripts and subscripts
0	initial value
ads	adsorbent
b	bed
feed	feed solution
liq	liquid phase
M	divalent metal cation
р	pore

asymmetric systems involving strong coordinative interactions. Such systems typically approach chemisorption, where validity of conventional isotherm models is less obvious.

#### 2. Experimental

#### 2.1. Materials

Chelating adsorbent CuWRAM (now marketed as CuSelect) was obtained from Purity Systems Inc. CuWRAM is mesoporous silica with an anchored polyamine layer that is further functionalized with 2-(aminomethyl)pyridyl groups [22]. Due to the amine functionality, CuWRAM is weak anion exchanger but because binding of acids and metal cations proceeds via the lone electron pairs of the nitrogen atoms, they are considered here as chelating adsorbents. Electro-neutrality thus requires that equivalent amount of cations and anions are adsorbed simultaneously.

Before use, CuWRAM was extracted over-night with methanol. The washed adsorbent was then treated with 2 M H<sub>2</sub>SO<sub>4</sub>, water, and 4 M NH<sub>4</sub>OH and finally rinsed with water to about pH 3. This cycle was repeated three times and then the base-form adsorbent was dried in vacuum. The average particle size  $d_s = 0.23 \pm 0.05$  mm, the intra-particle porosity  $\varepsilon_p = 0.40$  and the total amount of amine groups  $q_{tot} = 4.5$  mol/kg were determined earlier [10].

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Та

Composition of the copper-free process solution.

Metal	<i>c</i> (mol/L)
Zn	2.2
Mg	0.40
Mn	0.10
Cu	n.d.
Ca	$6.5 \cdot 10^{-3}$
Cl	$4.0 \cdot 10^{-3}$
Cd	$2.2 \cdot 10^{-3}$
Al	$1.1 \cdot 10^{-4}$
Со	$3.6 \cdot 10^{-4}$
Ni	$2.2 \cdot 10^{-4}$
Pb	$7.5 \cdot 10^{-5}$
Fe	n.d.
As	n.d.
рН	1.8

n.d.: not detected.

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