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# 1 Recovery of nickel from strongly acidic bio-ore leachate using a bispicolylamine- 2 based chelating resin

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5

## 6 **ABSTRACT**

7 Given the increasing demand for nickel (Ni) in the Li-ion battery industry, the agromining chain of processes, based  
8 on phytomining of Ni combined with hydrometallurgy, has the potential to form an important source of Ni. Currently,  
9 plants grown on Ni-rich soils (in this case *Odontarrhena chalcidica*), having hyperaccumulated Ni, are ashed, and the  
10 Ni is transferred from ash to solution by sulfuric acid leaching. This work focuses on the recovery of Ni-sulfate from  
11 this strongly acidic leachate that contains many cations. For this purpose, a bispicolylamine-based chelating resin  
12 (Dowex M4195) was tested to better understand the functioning of this resin under these conditions.

13 Column experiments were performed with model synthetic solutions containing Ni and Na-sulfate at pH 2. A set  
14 of reactions has been formulated to describe the interactions involved and used in a model combining transport in  
15 porous media and chemical reactions at equilibrium. Excellent agreement between the experimental and the  
16 calculated breakthrough curves were obtained by adjusting only two parameters. The set of reactions and parameters  
17 allowed to fit with sufficient accuracy the breakthrough curves obtained from an ash leachate of the  
18 hyperaccumulator plant *O. chalcidica*.

19 A better understanding of the use of the Dowex M4195 resin for the extraction of Ni from a strong acid  
20 multicomponent solution has been achieved, and this separation has been shown to be promising for the recovery of  
21 Ni extracted from hyperaccumulator plant bio-ores as part of the agromining process.

22

23

24 **Keywords**

25 Chelating resin; hydrometallurgy; nickel recovery; column experiments; phytomining; agromining

26 **Highlights**

- 27 • Nickel can be separated from a strong acid solution by a chelate resin.
- 28 • Nickel separation was tested by column experiments and modeling.
- 29 • A reaction scheme and equilibrium constants model the functioning of Dowex M4195 resin.
- 30 • NiSO<sub>4</sub> purities of two plant ash leachates were upgraded to 97% and 99%.
- 31 • Nickel separation by Dowex M4195 resin is promising for use in the agromining chain.

32

## 33 1. Introduction

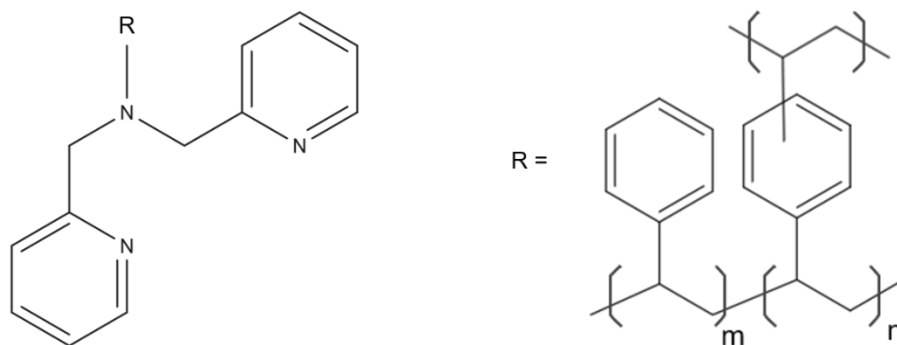
34 The demand for metals is booming, especially because of the decarbonization and the development of electric  
35 vehicles using Ni-containing Li-ion batteries. This is reflected in an increase in the price of Ni, which has doubled since  
36 2017 [1]. For this reason, and as mining becomes increasingly challenging with declining ore grades, processes are  
37 being developed to exploit secondary resources of Ni which contribute to implementing the circular economy. Among  
38 the processes for secondary resources, agromining (also called “phytomining”) is attracting substantial interest. The  
39 agromining process consists of extracting metals from low concentrations in soils using hyperaccumulator plants by  
40 means of phytoextraction [2]. The metals are then recovered by hydrometallurgical processes from the harvested  
41 bio-ore. This chain has been developed for Ni due to the interest in this metal and because nearly 3% of the Earth’s  
42 surface is covered by ultramafic (Ni-rich) soils and more than 500 species of Ni hyperaccumulator plant species have  
43 been discovered to date. Recent field studies have evaluated the production of phytomined Ni in several regions of  
44 the world (Malaysia, Mexico, Austria) with surfaces from 500 m<sup>2</sup> to 1 ha [3–5]. Nickel agromining is now a staple  
45 Nature-Based Solution and using *Odontarrhena chalcidica* annual yields up to 150 kg<sub>Ni</sub>/ha have been obtained with  
46 optimized agronomic practices [6,7].

47 To recover the Ni present in the plant tissues, several processing routes have been explored. The most advanced  
48 and promising processes stem from the recovery of Ni from plant ash, which can contain up to 20% by weight of Ni  
49 [8]. Leaching the ash with sulfuric acid at mild temperatures (*ca.* 90 °C) yields a Ni-rich solution containing up to  
50 30 g<sub>Ni</sub>/L [9], but also unwanted elements, including calcium (Ca), magnesium (Mg), iron (Fe), and potassium (K). Nickel  
51 can be separated by solvent extraction [10] or preferential precipitation to obtain Ni-salts or oxides of high purity  
52 [8,9,11]. It is essential to implement efficient separation in the hydrometallurgical processing of Ni bio-ores.

53 To reduce the consumption of reagents, an alternative process can involve ion exchange (IX) and/or selective  
54 adsorption using a selective resin composed of polymers beads with functional groups that bind the target metal. The  
55 performance and robustness of these resins have been proven by the metallurgical industry in the high-pressure acid  
56 leaching process of Ni laterites [12], or for the removal of Ni from cobalt (Co) electrolytic solutions [13]. To exhaust  
57 complex multi-metallic solutions from Ni, high selectivity is crucial. To meet this objective, resins with highly selective

58 functional groups have been developed, and these are called chelating resins. Their functional groups form strong  
59 and selective bonds with the target metals. Because they are weak bases or acids, the sorption is reversible, and  
60 elution can be conducted by displacing the bound metal with the proton ( $H^+$ ). Conversely, their main drawback is their  
61 limited capacity to treat acidic feeds where  $H^+$  competes with the metal cation. Recently, IX separation processes  
62 using chelating resin have gained increasing attention, to concentrate and purify feeds prior to solvent extraction  
63 [14], or to treat concentrated Ni feeds originating from lithium ion battery recycling [15], or multimetallic industrial  
64 effluent [16].

65 Bis-2-picolylamine (*bpa*) grafted resin (Fig. 1), marketed as Dowex M4195 (Dow) or Lewatit 220 (Lanxess), is  
66 renowned for its high affinity for copper (Cu) and, to a lesser extent, for Ni. Sirola described an analogous silicon  
67 polymer grafted with *bpa* (CuWRAM<sup>®</sup>) for the removal of Ni and Cu from a concentrated solution of zinc sulfate  
68 ( $ZnSO_4$ ) [17].



69  
70 Fig. 1. Structural representation of the *bpa* group grafted on the polymeric matrix (R): polystyrene cross-linked  
71 with divinyl-benzene (PS-DVB)

72  
73 The three nitrogen (N) atoms of the *bpa* group are electron donors and form strong bonds with the transition  
74 metals [18]. Thus, the order of selectivity in sulfate media is:  $Cu(II) \gg UO_2(IV) > Ni(II) > Fe(III) > Zn(II) > Co(II) > Cd(II) >$   
75  $Fe(II)$  [19,20]. In this list, only the retention of uranate anion ( $UO_2$ ) results from an anion exchange mechanism rather  
76 than chelation [21]. The electronic doublets of the N atoms are stabilized by a large  $\pi$ -system, allowing chelation even  
77 in acidic media, outperforming conventional weak base groups. The three N atoms can be protonated, but it is difficult

78 to distinguish their behavior and the experimental determination of their dissociation constants  $K_{a_i}$  ( $1 \leq i \leq 3$ ) is  
79 complicated. The first two acidities are far from neutrality [20,22], the inflection points of the titration curves are  
80 hardly discernible, and there is no consensus on the  $pK_{a_i}$  values, which also appears to depend on the acid used.  
81 Regarding the third acidity, Grinstead initially suggested that the  $pK_{a_3}$  value (corresponding to tertiary amine  
82 protonation) was 3.5 in sulfate media [20]. Further proton uptake did not yield any inflexion points in the titration  
83 curve. Diniz and coworkers reinterpreted the data of Grinstead in sulfate media and proposed 1.5 and 2.7 for the  
84 values of the first two  $pK_a$ , respectively [23]. Recently, Ogden and coworkers found  $pK_{a_2}$  and  $pK_{a_3}$  values of 2.1 and  
85 4.1 respectively in chloride media, while the  $pK_{a_1}$  value could not be calculated [19].

86 Although these data are helpful for estimating the relative protonation of the resin and assessing the competition  
87 between  $H^+$  and  $Ni^{2+}$ , the counter-ion (here sulfate) also plays an important role. Not only must the pH buffering effect  
88 near  $pH = pK_{a_{H_2SO_4/SO_4}}$  ( $=1.9$ ) be significant, but the complexation effect must also be considered. In concentrated  
89 solution, it forms complexes with  $Na^+$  ( $NaSO_4^-$ ), and with  $Ni^{2+}$ . Understanding the role of sulfate is therefore essential  
90 for quantitative prediction of retention. In addition, its effects on sorption could be modified in the presence of other  
91 metal cations known to react with it (*e.g.*,  $Ca^{2+}$ ,  $Mg^{2+}$ ).

92 Finally, whether protonated ( $Hbpa^+$  or  $H_2bpa^{2+}$ ), or chelating a  $Ni^{2+}$  cation ( $Nibpa^{2+}$ ), resin groups carry a net  
93 positive charge and are therefore anion exchangers. In sulfate media, the complexity is supplemented by the fact that  
94 a “site-sharing” reaction occurs: a sulfate anion can be replaced by two bisulfate anions, resulting in the overall  
95 adsorption of one molecule of sulfuric acid [24].

96 The objective of this work is to better understand the usefulness of Dowex M4195 resin in an acid solution derived  
97 from dissolution of bio-ore ash to recover Ni. As this is a multicomponent solution, we focused on the sorption and  
98 desorption steps with simpler model solutions. The main characteristics were kept, namely the presence of  $Na_2SO_4$   
99 at relatively high concentrations, the acid pH value (2) and the relevant Ni concentration,  $c_{Ni} \approx 0.3$  mol/L. The influence  
100 of  $Na_2SO_4$  concentration was also investigated with the objective of better understanding its effect on pH and on the  
101 retention of Ni and  $SO_4$  by the resin.

102 The experimental results are interpreted using a model to describe the in-column transport coupled with reactions  
103 at thermodynamic equilibrium. This model will test the following hypotheses: retention is governed by the pH-  
104 dependent chelation of Ni by *bpa* groups and by the "site sharing" reaction that is suspected to play a key role in pH  
105 regulation. The model will allow us to calculate breakthrough curves during the adsorption and elution steps, and to  
106 fit constants by comparison with experimental curves. Finally, we will investigate whether the results obtained with  
107 the simplified solutions applies satisfactory to ash leachate solutions.

## 108 2. Materials and methods

### 109 2.1 Resin and solutions

110 Dowex M4195 resin (Sigma Aldrich, free form) is composed of a macroporous styrene-divinyl benzene matrix onto  
111 which bis-picolyamine functional groups (*bpa*) are grafted. It is available in the form of brown beads with a size of  
112 0.3 to 0.8 mm, a moisture content of 40–60%, and a Cu capacity of 1.1 eq/L. Resin granulometry was verified by laser  
113 diffractometry using a Mastersizer 3000 (Malvern Panalytical). The measured median diameter ( $D_{50}$ ) was 400  $\mu\text{m}$  with  
114 a uniformity coefficient of 0.068.

115 Solutions were prepared using nickel sulfate hexahydrate (purity >99.5%, Sigma Aldrich), ACS reagent grade  
116 sulfuric acid (Sigma Aldrich), and sodium hydroxide pellets (purity >98.5%, Sigma Aldrich). Deionized water (Elga,  
117 Purelab Chorus) was used in all the experiments.

118 To prepare the pre-equilibration and loading solutions, sulfuric acid was diluted to the desired concentration, and  
119 the pH was then adjusted by additions of concentrated sodium hydroxide. Nickel sulfate was dissolved in the sodium  
120 sulfate solution and the pH was adjusted if needed. The final concentrations used for data treatment were the ones  
121 measured by ICP.

122 Nickel-rich leachates were obtained from hyperaccumulator plant ash (*Odontarrhena chalcidica*) as described in  
123 [9]. Aerial parts of *O. chalcidica* collected in Albania were ashed at 900 °C in a continuous biomass furnace (KWB  
124 Multifire MF2) with an average residence time of 20 min. Ash was sieved to 200  $\mu\text{m}$  to remove unburnt particles. The  
125 ash was then washed twice using water to remove potassium (K), and then leached with sulfuric acid (2 mol/L) at

126 reflux for 2 h. After cooling and filtering, a Ni-rich solution was produced. The pH of the solution was increased to 2  
 127 using concentrated sodium hydroxide (Leachate 1) to permit Ni adsorption onto the resin. The same method was  
 128 applied to a different batch of plant ash. This time, the solution produced was less acidic and H<sub>2</sub>SO<sub>4</sub> was used to  
 129 decrease its pH to 2 (Leachate 2) for comparison. The composition of the leachates is displayed in Table 1.

130

131 **Table 1**

132 Composition of the ash leachates adjusted to pH 2 with either NaOH or H<sub>2</sub>SO<sub>4</sub>.

	Leachate 1			Leachate 2		
	c (mol/L)					
Na	2.00	±	0.10	< 0.001		
S	1.68	±	0.08	1.09	±	0.05
Ni	0.24	±	0.01	0.37	±	0.02
Mg	0.28	±	0.01	0.48	±	0.02
K	0.18	±	0.01	0.26	±	0.01
P	0.030	±	0.002	0.167	±	0.008
Al	0.014	±	0.001	0.001	±	0.0001
Ca	0.008	±	0.001	0.016	±	0.001
Fe	0.003	±	0.0001	0.024	±	0.001
Mn	0.002	±	0.0001	0.001	±	0.0001
Zn	< 0.001			< 0.001		

133

134 The ash leachates are characterized by their high Ni content (up to 22 g<sub>Ni</sub>/L) but contain large amounts of unwanted  
 135 elements (mainly Mg, Fe, K).

136

137 *2.2 Experimental set-up*

138 The experimental set-up consisted of a volumetric pump (KNF), a borosilicate glass column (GE Healthcare, internal  
 139 diameter 16 mm), an on-line conductivity detector, an on-line pH cell (Meterlab PH210) with a glass electrode



140 (Mettler Toledo), and a programmable fraction collector (Gilson). Conductivity and pH data were recorded with  
141 increments of 10 s. To pre-fill all the tubing, a by-pass circuit was arranged around the column.

142 The column was filled with resin beads suspended in deionized water and the height of the bed was adjusted by  
143 means of a piston, thus measuring 18 cm. The total bed volume was  $BV = 37$  mL. The column was connected to the  
144 circuit and then the solutions were injected from the bottom upwards. For all experiments (except rinsing), the flow  
145 rate was set at 1 mL/min. The column itself was not thermo-regulated but experiments were conducted in a  
146 temperature-controlled room, with the temperature set to 20 °C.

### 147 *2.3 Analyses*

148 Elemental concentrations were determined by Inductively-coupled plasma emission spectroscopy (ICP-OES,  
149 Thermo ICAP 6000). External calibration was conducted using a certified solution (SCP-Sciences) in  $\text{HNO}_3$  3 wt%. The  
150 calibration standards contained either Na, Ni, and S as analytes or a multi-element mix (Na, Ni, S, K, Ca, Mg, Fe, Mn,  
151 Zn, P, Cu, Co, Al, and Pb) depending on the sample composition. Prior to analysis, the experimental samples were  
152 diluted in the same matrix as the calibration standards ( $\text{HNO}_3$  3 wt%). Solutions were analyzed in triplicate and the  
153 averaged values were retained. Concentration values with relative standard errors greater than 5% were rejected.  
154 Quality control checks using an independently prepared standard solution were performed every 12 samples to  
155 monitor drift and instrument accuracy.

### 156 *2.4 Tracing experiments*

157 The residence time distribution (RTD) of the fluid in the packed bed was measured by performing stepwise  
158 injections of tracing solutions at different concentrations. The column was pre-equilibrated with 0.15 mol/L  $\text{Na}_2\text{SO}_4$   
159 solution and fed with 1.02 mol/L  $\text{Na}_2\text{SO}_4$  solution (positive steps) and *vice-versa* (negative steps). The conductivity of  
160 the outflow was used for the calculations. Measuring the RTD permitted to measure the porosity of the bed  $\epsilon$  the  
161 porous volume  $V_p$ , defined as defined as  $V_p = \epsilon \times BV$ . The number of mixing cells  $J$  was estimated conventionally  
162 with  $J = (\bar{t} / \sigma)^2$ , where  $\bar{t}$  is the mean residence time, and  $\sigma$  the variance of the RTD.

164 Before the experiments, the resin bed endured five cycles of pre-equilibration, Ni loading, and elution. For all  
 165 experiments, the resin bed was pre-equilibrated with the same Na<sub>2</sub>SO<sub>4</sub> solution (pH 2) until the output conductivity  
 166 and pH were identical to the input. It was then rapidly rinsed with deionized water at 10 mL/min for 8 min (2.2 bed  
 167 volumes) and then fed with a Ni-rich solution (Table 2). After rinsing under the same conditions, elution was carried  
 168 out with a concentrated sulfuric acid solution. The concentration of the eluting solution was 2 mol/L and decreased  
 169 to 1.25 mol/L for the leachate 2 experiment in an attempt to save reagents.

170 During loading and elution, fractions were collected for analysis and weighted. The exact volume pumped was  
 171 then calculated from the weights and densities of the fractions. The size of the fractions was chosen to have the best  
 172 compromise between the representativeness of the effluent and an acceptable number of fractions. Small fractions  
 173 (2 mL) were collected when the composition of outflow varied the most and larger fractions (up to 10 mL) when it  
 174 varied the least. When it was known to be constant, intermediate samples were not analyzed.

175

176 **Table 2.**

177 Feed solutions for loading column experiments.

Feed solutions	$c_{\text{Ni}}$ (mol/L)	$c_{\text{SO}_4}$ (mol/L)	$c_{\text{Na}}$ (mol/L)	pH
Pre-equilibration	-	1.02	2.21	2
Sol. ref	0.31	0.95	1.15	2
Sol. -	0.31	0.60	0.64	2
Sol. +	0.30	1.12	1.85	2
Leachate 1	0.25	1.68	2.00	2
Leachate 2	0.37	1.09	-	2

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181

182 3. Theory

183 3.1. Equilibrium model

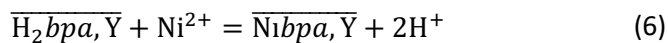
184 A simple equilibrium model has been built to highlight the dominant mechanisms of the sorption process. To start-  
185 off, the dissociation and complexation reactions occurring in the solution are considered (Eqs (1)-(5)). They are  
186 assumed to follow a mass action law, with the corresponding stability constants (Table 3) extracted from the CHESS  
187 database at 25 °C and zero ionic strength [25]. No attempt was made to convert them to match the experimental  
188 conditions.



189

190 In the vicinity of the resin functional groups, nickel cations compete with protons for chelation (Eq. (6)). Here, the  
191 overbar represents the species in resin phase; Y stands for the counter anion, and *bpa* for the bis-picolylamine  
192 functional group.

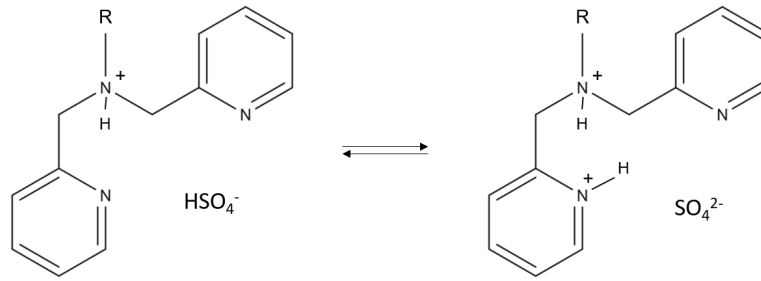
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194

195 For the selected pH region, it was assumed that the functional groups were all doubly protonated. This is ensured  
196 by pre-equilibrating the resin with a concentrated Na<sub>2</sub>SO<sub>4</sub> solution at pH 2. Indeed pH 2 is between the reported pK<sub>a1</sub>  
197 and pK<sub>a2</sub> of the resin [19,23]. Furthermore, the once protonated *bpa*H<sup>+</sup>,HSO<sub>4</sub><sup>-</sup> form is a tautomer of *bpa*H<sub>2</sub><sup>2+</sup>,SO<sub>4</sub><sup>2-</sup> (Fig.  
198 2). Thus, the first form can be treated equally as a doubly protonated form.

199



200

201

202 Fig. 2. Tautomerism of the protonated *bpa* group in a sulfate medium.

203 Assuming that the contribution of the sorbed counterion Y can be neglected, the reaction can be rewritten as Eq.  
 204 (7), which is similar to a classical cation exchange reaction.

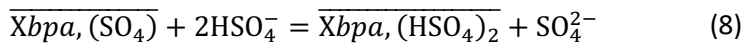
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206

207 Whether Ni is chelated or the resin protonated, anion exchange can occur as the functional group is positively  
 208 charged (Eq. (7)). In our conditions (pH 2), sorption of the  $\text{HSO}_4^-$  anion is practically inexistent. The sorption of the  
 209  $\text{NaSO}_4^-$  complex is assumed to be negligible in comparison to  $\text{SO}_4^{2-}$ : because of its net double charge, it should be  
 210 preferred for sorption [24]. For simplification, competition between  $\text{HSO}_4^-$  and  $\text{NaSO}_4^-$  was neglected. Hence, anion  
 211 exchange reactions were reduced to the exchange of  $\text{SO}_4^{2-}$  with two  $\text{HSO}_4^-$  (Eq. (8)):

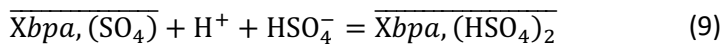
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213

214 where X is indifferently 2H or Ni. This reaction can be rewritten as in Eq. (9) to better highlight its role as an acid  
 215 adsorption in the column.

216



217

218 This property is well-known for anion-exchanger with polyvalent functional groups in contact with polyacids and  
219 has been called “site-sharing” [24]. The selectivity constant  $K_9$  is related to  $K_8$  via Eq. (10).

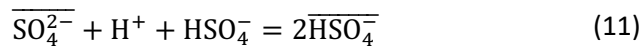
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$$K_9 = K_3 * K_8 \quad (10)$$

221

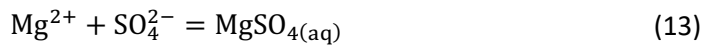
222 For simplification, Eq. (9) can be rewritten to yield Eq. (11), with the selectivity constant  $K_{11} = K_9$ . The ion exchange  
223 reactions considered are summarized in Fig. 3.

224

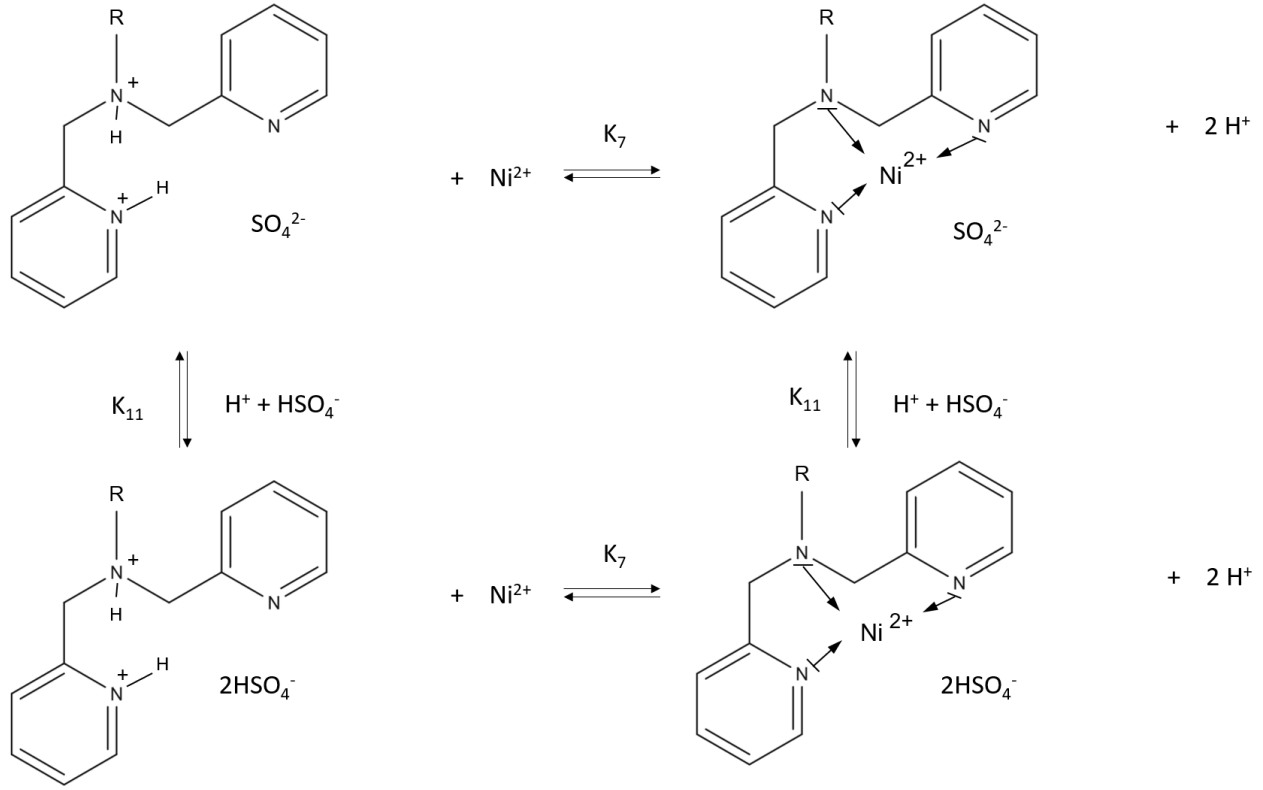


225 To simulate the breakthrough curves of the ash leachates, the reactions described by Eqs (12)-(15) taking place in  
226 the aqueous phase were added. Sorption of the other anions and cations was not considered to limit the complexity  
227 of the model and the number of estimated parameters.

228



229



230

231 Fig. 3. Ion exchange reactions considered.

232 The cationic exchange capacity (CEC) and anionic exchange capacity (AEC) are defined by Eqs(16)-(17):

233

$$\text{CEC} = n(\overline{\text{H}^+}) + 2n(\overline{\text{Ni}^{2+}}) \quad (16)$$

$$\text{AEC} = n(\overline{\text{HSO}_4^-}) + 2n(\overline{\text{SO}_4^{2-}}) \quad (17)$$

234

235 where  $n(A_i)$  is the quantity of fixed species  $A_i$  per unit of bed volume (in mol/L).

236 *3.2. Transport model*

237 Column hydrodynamics were modeled using the conventional model of mixing cells in series. Each cell is composed

238 of a stationary phase (resin) and a flowing phase (aqueous solution). To do so, the computer code IMPACT [26] was

239 used. As described in previous works [27–29], the code relies on the following assumptions:

- 240 - The cell geometry is constant, no shrinking or swelling of the resin is considered.

- 241 - Axial dispersion is accounted for in the number of mixing cells J, the Peclet number being equal to 2(J-1).
- 242 - Equilibrium is attained in each cell.
- 243 - The system is isothermal.
- 244 - Each phase is electrically neutral.
- 245 - No activity correction is performed.

246 **Table 3.**

247 List of the reactions implemented in the model.

Reactions in the aqueous phase	Equilibrium constant (25°C)	Reaction#
$\text{H}_2\text{O} = \text{H}^+ + \text{HO}^-$	$K_w = 10^{-14}$	(R1)
$\text{H}_2\text{SO}_{4(\text{aq})} = \text{H}^+ + \text{HSO}_4^-$	$K_2 = 10^3$	(R2)
$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$	$K_3 = 10^{-1.9}$	(R3)
$\text{Na}^+ + \text{SO}_4^{2-} = \text{NaSO}_4^-$	$K_4 = 10^{0.82}$	(R4)
$\text{Ni}^{2+} + \text{SO}_4^{2-} = \text{NiSO}_{4(\text{aq})}$	$K_5 = 10^{2.13}$	(R5)
$2\overline{\text{H}^+} + \text{Ni}^{2+} = \overline{\text{Ni}^{2+}} + 2\text{H}^+$	$K_7$	(R7)
$\overline{\text{SO}_4^{2-}} + \text{H}^+ + \text{HSO}_4^- = 2\overline{\text{HSO}_4^-}$	$K_{11}$	(R11)
$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_{4(\text{aq})}$	$K_{12} = 10^{2.11}$	(R12)
$\text{Mg}^{2+} + \text{SO}_4^{2-} = \text{MgSO}_{4(\text{aq})}$	$K_{13} = 10^{2.41}$	(R13)
$\text{K}^+ + \text{SO}_4^{2-} = \text{KSO}_4^-$	$K_{14} = 10^{-0.88}$	(R14)
$\text{H}_3\text{PO}_{4(\text{aq})} = \text{H}^+ + \text{H}_2\text{PO}_4^-$	$K_{15} = 10^{-2.16}$	(R15)

248

249 *3.3. Calculations*

250 Equilibria are calculated in each cell by minimizing the Gibbs enthalpy, using a Newton-Raphson algorithm. Inputs

251 are the number of mixing cells J, composition of the pre-equilibrating feed solution, and the composition and injected

252 volume of subsequent feed solutions. The washing and loading steps are successively modelled in the same simulation

253 with the corresponding volumes.

254 The CEC and AEC are set by the user by defining the total amount of initially fixed species (Eqs(16)-(17)). The  
255 anionic capacity was set equal to the cationic one - determined experimentally - to maintain electroneutrality in the  
256 resin phase.

257 The program delivers the user the breakthrough curves for each defined species, expressed in mol/L, calculated  
258 as the outflow of the last mixing cell. Increments of 0.1 Vp were used for all the calculations. The concentrations of  
259 the different species were appropriately summed in a separate worksheet to allow comparison with experimental  
260 results (elemental concentrations) provided by ICP. The computed concentration of free H<sup>+</sup> in the column output  
261 ( $c_{H^+}$ ) was converted to pH without activity correction (Eq. (18)).

$$\text{pH} = -\log (c_{H^+}) \quad (18)$$

262 The elution curves for the two leachates were treated as follows: a hypothetical pool was calculated by summing  
263 only the fractions with  $c_{Ni} > 0.1$  mol/L. The term “pool” or “pooled fractions” refers to the solution resulting from the  
264 addition of the considered fractions together. The value of 0.1 mol/L value was arbitrarily chosen to ensure that the  
265 purification of the eluates benefits from sufficiently high Ni concentration (*e.g.*, facilitating precipitation or  
266 electrowinning). The concentrations in the pool were conventionally calculated by integration of the elution curve  
267 between the chosen cuts. The integration step was defined by the fraction size of 2 mL, representing 0.1 Vp. The  
268 purity of the pooled solution was calculated as follows:

$$\text{NiSO}_4 \text{ Purity} = \frac{c_{Ni,pooled}}{c_{Ni,pooled} + \sum_j c_{j,pooled}} \quad (19)$$

269 Where  $j$  belongs to {Na, Mg, Ca, K, PO<sub>4</sub>, Zn, Mn, Fe}, and with all the concentrations in mol/L. Obviously, neither  
270 sulfate nor H<sup>+</sup> were considered as impurities because the medium is sulfuric acid. Solution purity was also calculated  
271 excluding Na to allow comparison between the two leachates.

## 272 4. Results and discussion

### 273 4.1 Determination of the model parameters



274 The residence time distribution (RTD) of the packed bed was determined from the results of the tracing  
275 experiments. Integration of the response curve revealed that the porosity  $\epsilon$  of the bed was  $\epsilon = 0.55$ , therefore the  
276 porous volume was  $V_p = 20.4$  mL. The number of mixing cells in series was  $J = 56$ , which corresponds to a Peclet  
277 number of 110. The porous volume  $V_p$  was thus of 20.4 mL.

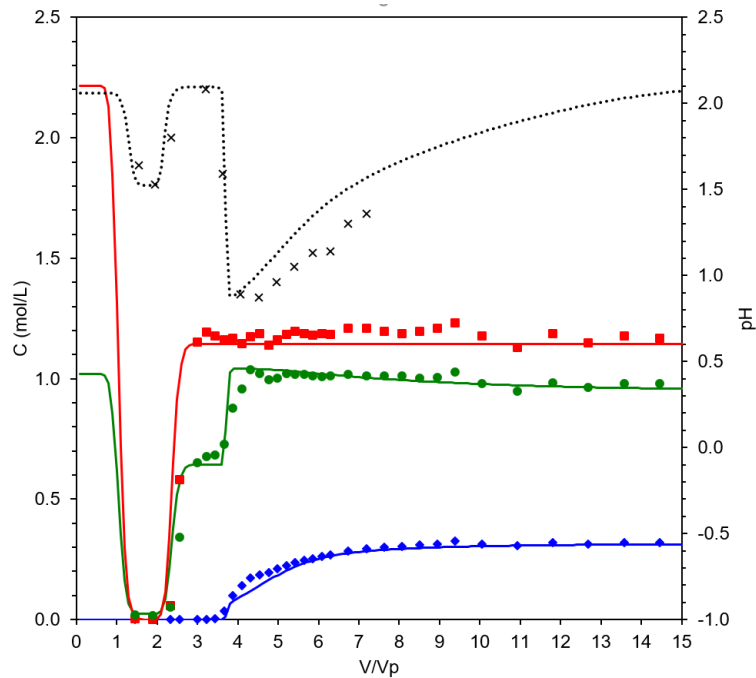
278 The resin bed capacity was determined by integrating the three breakthrough curves presented here (Figs 4 and  
279 5). The Ni loading capacity was  $0.53 \pm 0.04$  mol/L, or  $1.06 \pm 0.08$  eq/L which is consistent with the manufacturer  
280 information concerning Cu [30]. Therefore,  $CEC = AEC = 1.06 \pm 0.08$  eq/L.

281 The breakthrough curves obtained when the column is fed with 1  $V_p$  of water for rinsing, then fed solution Sol.  
282 Ref (Table 2) are displayed in Fig. 4 with calculated results in continuous lines. Firstly, the interstitial volume filled  
283 with pre-equilibrating solution is flushed. Then, the rinsing water breaks through, and from  $V/V_p = 1$  the breakthrough  
284 curve of the feed solution Sol. Ref can be observed:

- 285 • at  $V/V_p = 2$ , the normality front appeared, corresponding to the sharp breakthrough of  $\text{Na}^+$ , not retained  
286 by the resin, accompanied by sulfate, the molar ratio  $\text{Na}/\text{SO}_4$  being  $2.0 \pm 0.01$  (on  $n = 6$  data points).
- 287 • The second front started at  $V/V_p = 3.6$ , where Ni broke through sharply, consistently with a rapid pH  
288 decrease (down to pH 1). The nickel release rate was significantly slower after  $V/V_p = 4.4$  as the pH of the  
289 effluent was stabilizing towards the nominal value of the feed solution. The release of Ni and  $\text{H}^+$  was  
290 accompanied by that of sulfate.

291 These experimental breakthrough curves were used to determine the selectivity constants  $K_7$  and  $K_{11}$ . These  
292 parameters were adjusted to fit the location of the Ni breakthrough and the shape of the sulfate concentration curve.  
293 The best fits were obtained by trial-and-error yielding  $K_7 = 0.05$  and  $K_{11} = 0.0003$ . These values were kept for all  
294 subsequent simulations.

295 Despite the simplicity of the model and the many assumptions, the calculated breakthrough curves were in  
296 excellent agreement with the experimental ones. The first front, as well as the values of sulfate and sodium  
297 concentrations and pH on the plateau between 2 and 3.6  $V_p$  were successfully predicted, as well as the shape of the  
298 front for Ni and total sulfate. The rise of pH to its nominal value was somewhat overestimated.



299

300 Fig. 4. Total nickel (blue diamonds), sulfate (green circles), and sodium (red squares) outlet concentration of the  
 301 resin bed while injecting the Sol. ref feed. pH values (crosses) are displayed with respect to the secondary axis.  
 302 Flowrate was of 1 mL/min (corresponding to 0.05 Vp/min) and the temperature was of 20 °C.

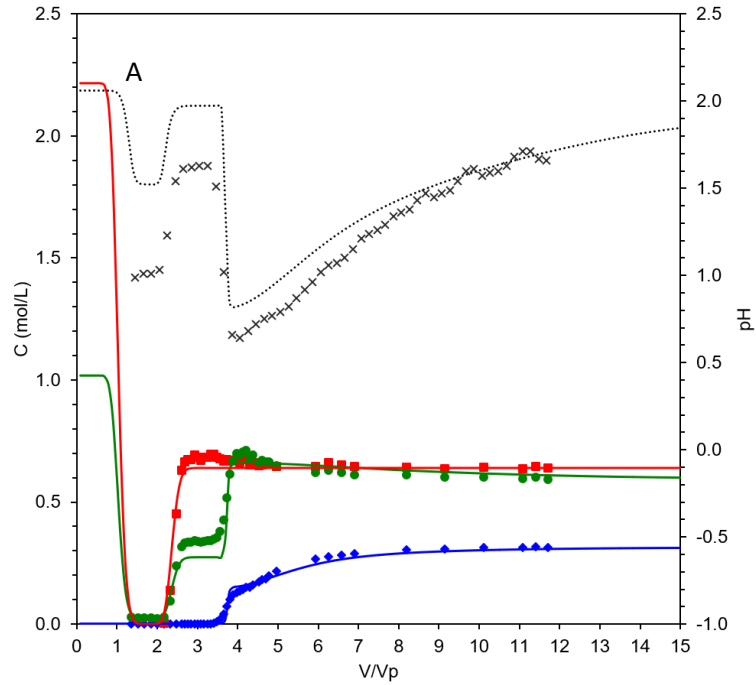
303 *4.2. Validation of the model with synthetic solutions*

304 *4.2.1. Loading curves*

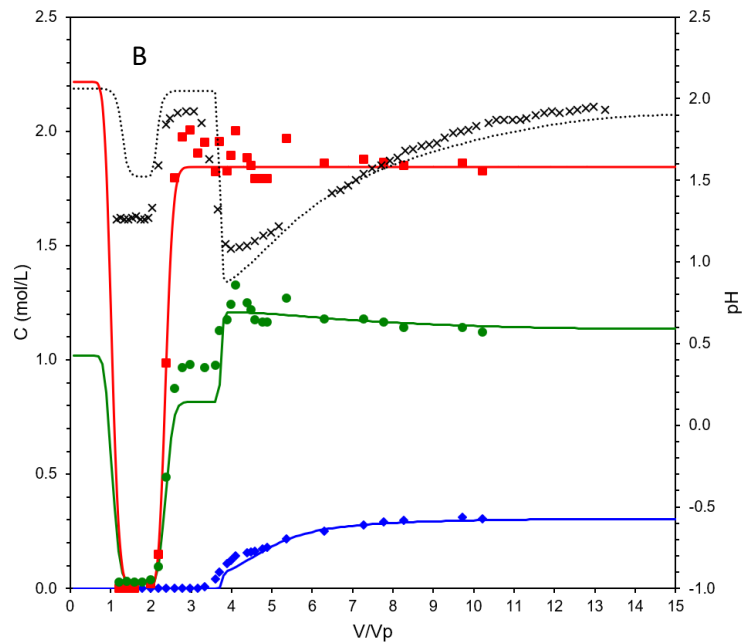
305 The objective of the experiments with the Sol.+ and Sol.- feed solutions was to determine the influence of the  
 306 Na<sub>2</sub>SO<sub>4</sub> background concentration. The breakthrough curves presented in figure 5 show that, in the considered  
 307 domain, this concentration did not affect Ni sorption. Indeed, the Ni breakthrough curves are practically identical in  
 308 the three cases. This later fact confirmed the reversibility of the sorption. Narrower pH variations were observed with  
 309 increasing Na<sub>2</sub>SO<sub>4</sub> concentration, most likely related to the pH buffering capacity of the electrolyte.

310 The model performed equally for both Sol. + and Sol. – breakthrough curves, predicting fairly well the location of  
 311 the fronts and plateaus (Fig. 5). However, in both cases, the total sulfate concentration on the intermediate plateau  
 312 was underestimated by *ca.* 20%.

313 As observed experimentally, the predicted Ni front appears to be decomposable into a first slightly sharp front,  
314 followed by a broader one. Although this trend was not observed in practice, the predicted Ni profile was markedly  
315 sharper for the Sol. – feed (Fig. 5A) and broader for the Sol. + feed (Fig. 5B). In both cases, the pH rise for the second  
316 front is better predicted than in the previous case.



317

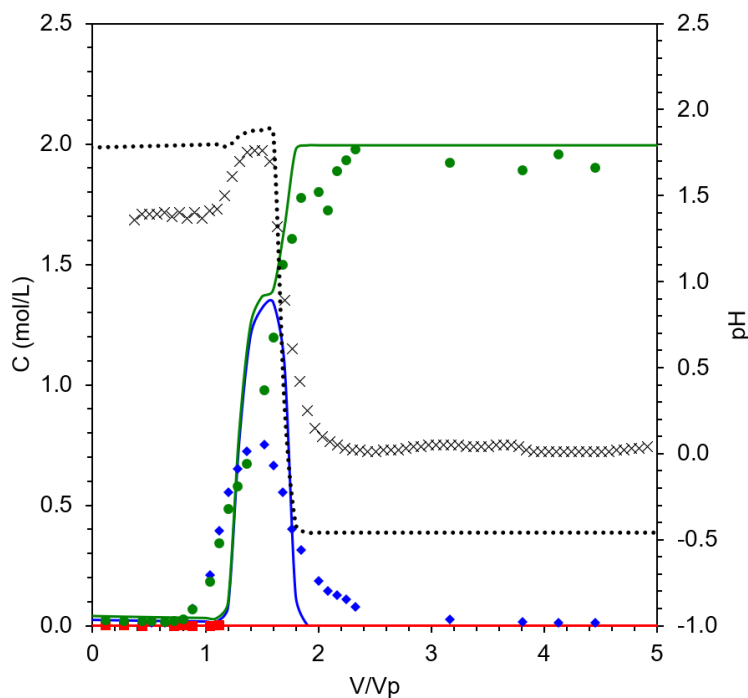


318

319 Fig. 5. Breakthrough curve for the feeds Sol. - (A) and Sol + (B). Total nickel (blue diamonds), sulfate (green circles),  
320 and sodium (red squares) outlet concentration of the resin bed. pH values (crosses) are displayed with respect to the  
321 secondary axis. Flowrate was of 1 mL/min (corresponding to 0.05 Vp/min) and the temperature was of 20 °C.

#### 322 4.2.2. Elution curves

323 In all experiments, the elution performed with 2 mol/L H<sub>2</sub>SO<sub>4</sub> permitted the recovery of all retained Ni. The elution  
324 after the loading with Sol. - is given as an illustration (Fig. 6). The model approximated the shape of the elution curves,  
325 yet, the experimental fronts were more diffuse than the calculated ones. Because the model has no activity correction  
326 implemented, the dissociation of the acids in presence (H<sub>2</sub>SO<sub>4</sub> and HSO<sub>4</sub><sup>-</sup>) was most likely overestimated, resulting in  
327 the overestimation of the free H<sup>+</sup> concentration (negative pH). Therefore, Ni is displaced more sharply than  
328 experimentally observed. Another possibility is the third protonation of the resin, the latter taking up more protons  
329 than the model predicts.



330  
331 Fig. 6. Elution curve of resin bed with 2 mol/L H<sub>2</sub>SO<sub>4</sub> after loading with the Sol. - feed. Total nickel (blue diamonds),  
332 sulfate (green circles), and sodium (red squares) outlet concentration of the resin bed. pH values (crosses) are  
333 displayed with respect to the secondary axis. Flowrate was of 1 mL/min (corresponding to 0.05 Vp/min) and the  
334 temperature was of 20 °C.

335 Even though the shape of the modeled elution curve differed from the experimental one, the amount of Ni eluted  
336 (calculated by integration) was rather consistent. The relative difference was of 5%, 12% and 12% for the elution  
337 after loading with Sol. –, Sol Ref, and Sol. +, respectively.

#### 338 *4.4. Application to multicomponent leachates*

339 This work was undertaken in view of understanding and predict the loading and elution behavior of the resin bed  
340 with hyperaccumulator ash leachates with different characteristics, especially regarding their Na<sub>2</sub>SO<sub>4</sub> concentration.  
341 The leachates also contained other cations (Mg, K, Fe) as well as notable amounts of phosphate (most likely in the  
342 form of phosphoric acid). Breakthrough and elution curves are presented Figs. 7 and 8.

343 Thanks to extremely favorable selectivity of the resin for Ni, and in the absence of Co and Cu, the other unwanted  
344 metals had little effect on Ni sorption. The breakthrough curves were highly similar to those obtained with the  
345 synthetic solutions, even when sodium was absent from the medium.

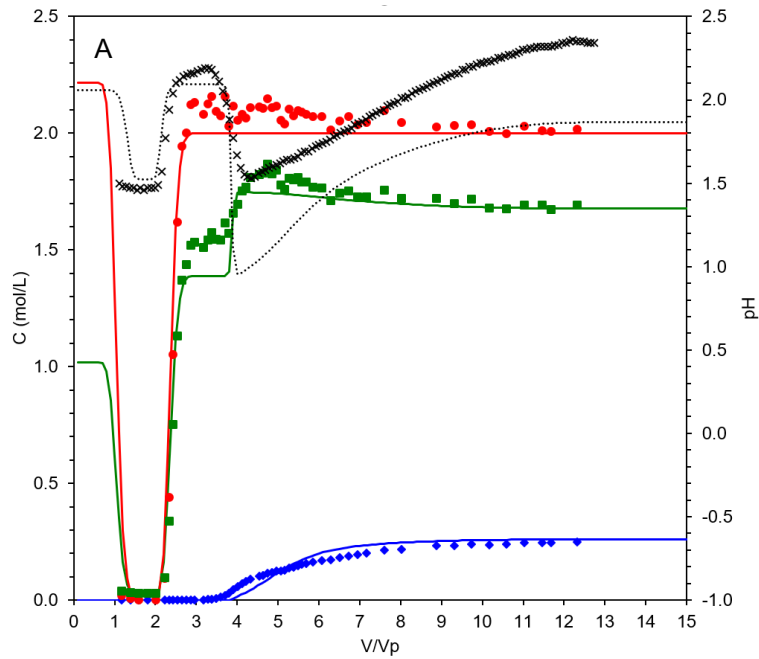
346 Interestingly, small amounts of Na were eluted during the loading of the resin with leachate 2 (Fig. 7B). This  
347 revealed that some NaSO<sub>4</sub><sup>-</sup> was bound to the resin during pre-equilibration, representing an uptake of 0.02 eq/L, but  
348 remained in minority (2% of the total capacity). It was easily replaced by HSO<sub>4</sub><sup>-</sup> and/or SO<sub>4</sub><sup>2-</sup>, thus confirming the  
349 assumption made in section 3.

350 In a first attempt, the complexation and dissociation reactions described by Eqs (12)-(15) were not implemented  
351 in the model and calculations resulted in poor fitting (not shown here). A good adequacy between calculated and  
352 experimental breakthrough curves was achieved after supplementing the model with the missing reactions (Fig. 7).  
353 The implementation was easy as stability constants were readily available. It quickly appeared that the pH buffering  
354 role of these reactions was determining at such a high ionic strength.

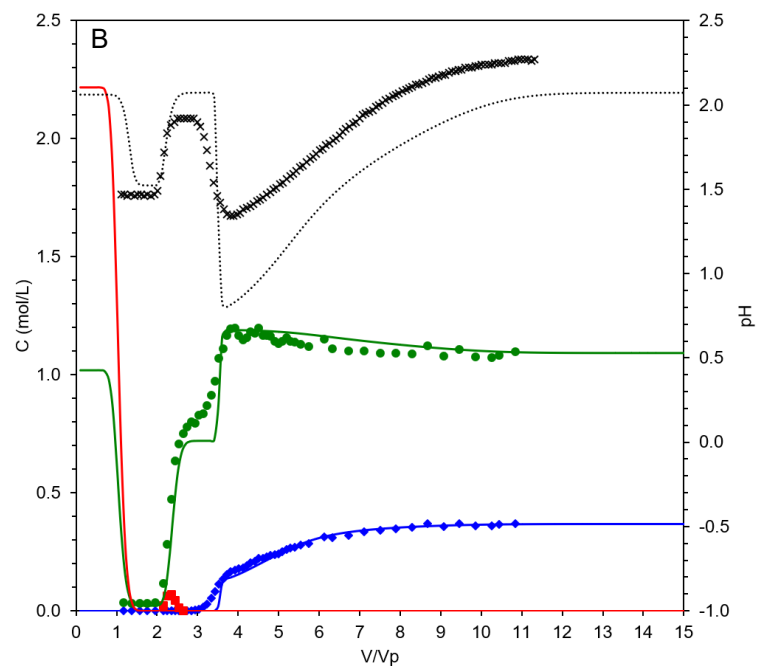
355 The calculated pH values varied much more than the experimental ones, and were underestimated during the Ni  
356 breakthrough ( $\Delta\text{pH} \approx 0.2 - 0.4$ ). For both leachates, experimental Ni breakthrough was observed slightly earlier than  
357 predicted, with the same order of magnitude as for Feed Sol. + (Fig. 5B).

358 Similarly, to the experiments with synthetic solutions, retained Ni from the ash leachates was eluted by H<sub>2</sub>SO<sub>4</sub>. The  
359 elution curves are displayed in Fig. 8. Sodium in the eluate was searched for in the eluate fractions, but levels were  
360 extremely low. Lower acid concentration of the flushing solution resulted in peak broadening (Fig. 8B). Nonetheless,  
361 more than 96% of the fixed Ni was recovered by V/Vp = 4.

362



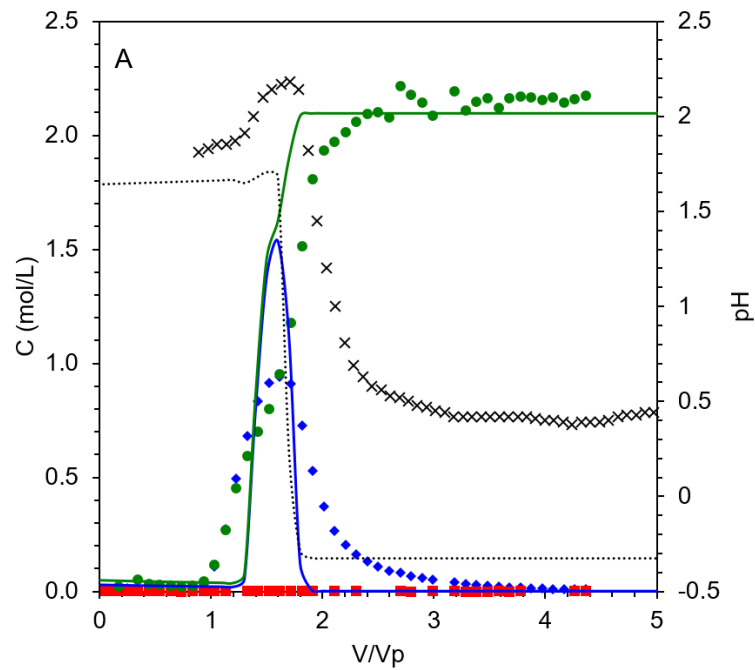
363



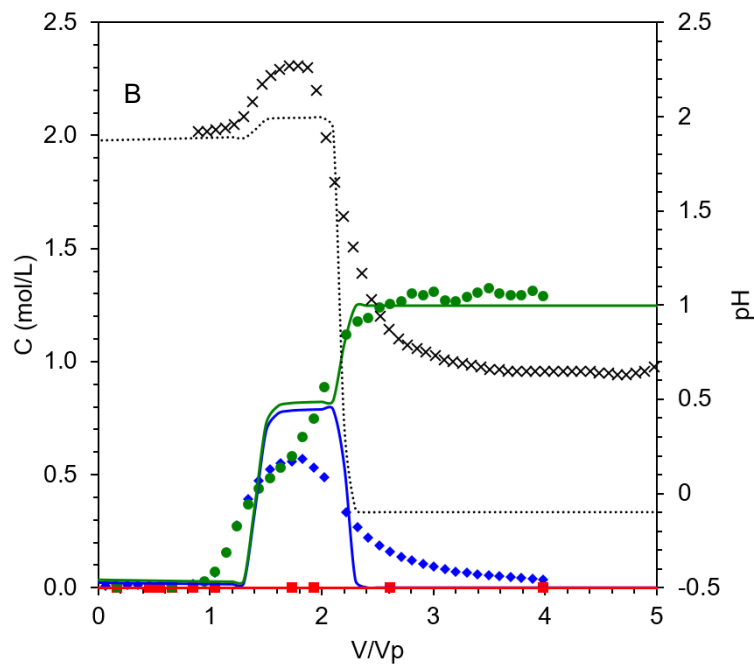
364

365 Fig. 7. Total nickel (blue diamonds), sulfate (green circles), and sodium (red squares) outlet concentration of the  
366 resin bed while injecting leachate 1 (A) and leachate 2 (B). pH values (crosses) are displayed with respect to the  
367 secondary axis. Flowrate was of 1 mL/min (corresponding to 0.05 Vp/min) and the temperature was of 20 °C.

368 Again, the model predicted correctly the location of the elution peak, the variation of the sulfate concentration  
369 and the pH variation. This time though, it failed to calculate precisely their shape, and the pH of the outflow was  
370 underestimated.



371



372

373 Fig. 8. Elution curves of the loaded resin with (A) Leachate 1, and (B) Leachate 2. Total nickel (blue diamonds),  
374 sulfate (green circles), and sodium (red squares) outlet concentration of the resin bed. pH values (crosses) are  
375 displayed with respect to the secondary axis. Flowrate was of 1 mL/min (corresponding to 0.05 Vp/min) and the  
376 temperature was of 20 °C.

#### 377 4.5. Performance of the developed model

378 The model developed here using the IMPACT software confirmed that the dominating mechanisms were those  
379 that were already hypothesized. Quantitative prediction of the pH in the column is the primary driver, as pH is the  
380 main driver of Ni – H<sup>+</sup> exchange. The implementation of the site-sharing reaction in the model resulted in an overall  
381 excellent prediction of the pH and Ni concentrations at the column outlet. The overall reaction scheme is based on a  
382 set of known reactions, whose constants are available, only two reactions and two parameters were added (selectivity  
383 constants  $K_7$  and  $K_{11}$ ). Moreover, this reaction scheme, even if it only includes reactions at equilibrium, allowed for a  
384 quantitative prediction of the number of elution fronts, their position and concentration variations. Finally, the  
385 calculated concentrations values were in excellent agreement with the experimental ones.

386 The approach proposed here is straightforward and easily reproducible: the equilibrium constants are input from  
387 readily available databases, then, specific selectivity constants are fit using a single reference experiment. Finally, the  
388 model can be applied to predict the loading behavior of a resin bed. The good fit also depends on the choice and  
389 number of assumptions (*e.g.*, protonation of the resin, isolation of the dominant mechanism involved, local  
390 equilibrium is reached at each step), that may not be valid in other experimental domains.

391 The model accuracy decreased when simulating the elution of the resin bed. This could be caused by several  
392 factors. Additional protonation of the resin was implemented using *bpa* dissociation reactions and the reported  $pK_{ai}$   
393 values from the literature. However, no significant improvement was observed. The Donnan exclusion effect could  
394 have played a certain role in the loss of exactness. If the positive charge of the sorption sites ( $Ni bpa^{2+}$ ) is not entirely  
395 masked by the counter anion ( $SO_4^{2-}$  or  $2HSO_4^-$ ), the diffusivity of H<sup>+</sup> in the pores could be limited. This would result in  
396 H<sup>+</sup> not displacing chelated Ni not as sharply as the model predicts. In contrast, Ni approaches the sites in its neutral



397 complexed form ( $\text{NiSO}_4$ ), it is therefore not subject to electrostatic repulsion. The most obvious reason for a decrease  
 398 in model accuracy would stem from incorrect prediction of activity. When the sulfuric acid concentration increases  
 399 up to 2 mol/L, dissociation of the acid (particularly bisulfate) appears to be overestimated, resulting in a negative pH  
 400 and thus a sharp displacement of the chelated Ni by  $\text{H}^+$ . In forthcoming versions of the model, the implementation of  
 401 activity coefficient models suited for high ionic strength will address this issue. Lastly, from a more practical aspect, it  
 402 is conceivable that the online pH cell, situated after the column outflow, causes recirculation to the fluid, generating  
 403 the tail of the Ni elution peak. Finally, assays are to be conducted to verify the effects of the flowrate. If required, the  
 404 model could be modified to account for sorption kinetics, and/or mass transfer limitations (intra- and extra- particle  
 405 diffusion).

#### 406 4.6. Obtention of a $\text{NiSO}_4$ solution of high purity

407 Elution cuts defined by  $c_{\text{Ni}} > 0.1$  mol/L (see section 3.3) represented a volume of 1.47 and 1.57 Vp for leachate 1  
 408 and 2 respectively. Their mean Ni concentration was 0.38 and 0.51 mol/L respectively (corresponding to 22 and  
 409 30  $\text{g}_{\text{Ni}}/\text{L}$ ). The purities of the leachates and of the hypothetically pooled solutions are presented in Table 4.

410 **Table 4.**

411 Purity characteristics of the leachates before and after purification with the conducted procedure

Solution	Leachate 1	Leachate 2	Leachate 1	Leachate 2
	Before purification		After purification	
$\text{NiSO}_4$ purity (%)	$9 \pm 1$	$29 \pm 2$	$98.8 \pm 0.3$	$96.9 \pm 0.7$
$\text{NiSO}_4$ purity (%)*	$32 \pm 2$	$29 \pm 2$	$99.1 \pm 0.2$	$96.9 \pm 0.7$
Impurity #1	Na	Mg	$\text{PO}_4$	$\text{PO}_4$
Impurity #2	Mg	K	Na	Ca

\*: Excluding Na from impurities

412 Most of the impurities present in the leachate, namely Ca, Mg, K, Na, Fe, and Mn, were entirely removed during  
 413 the rinsing step, prior to elution. The poor affinity of the resin for those elements can explain this result. Additionally,  
 414 rinsing with DI water could have shifted the site-sharing equilibrium (Eq. 11), leading to the release of diluted  $\text{H}_2\text{SO}_4$   
 415 [24], the latter eluting poorly-sorbed cations.

416 Phosphate is an important component of the leachate, and could rise issues if  $\text{Ni}(\text{OH})_2$  was to be precipitated  
417 directly from the leachates. Nickel phosphate ( $\text{Ni}_3(\text{PO}_4)_2$ ) is quite insoluble ( $K_s = 4.74 \cdot 10^{-32}$ ) and should precipitate  
418 around pH 4-5, while  $\text{Ni}(\text{OH})_2$  precipitates in the pH 7-8 region [31]. As an illustration, raising the pH of the leachate  
419 2 would result in the stoichiometric precipitation of 78% of the Ni as  $\text{Ni}_3(\text{PO}_4)_2$ .

420 With the conducted separation, phosphate concentration was reduced from 0.030 and 0.167 mol/L to 0.002 and  
421 0.009 mol/L for leachate 1 and 2 respectively. The majority of the content has been removed, most likely displaced  
422 by the excess sulfate via ion-exchange during loading. A non-negligible fraction remains sorbed after the rinsing step,  
423 and is co-eluted with  $\text{NiSO}_4$  becoming the first impurity in both eluates. Given the molar concentration in the purified  
424 solution, the resulting Ni losses through precipitation would however be minor (comprised between 1% and 4%, for  
425 leachate 1 and 2 respectively) and might be even further decreased. Phosphate removal could be conducted directly  
426 onto the loaded resin by circulating a concentrated  $\text{Na}_2\text{SO}_4$  solution (at pH 2), the sulfate would displace the bound  
427 phosphate. Then, rinsing with water would remove lightly bound  $\text{NaSO}_4^-$  and the interstitial solution. Finally,  $\text{NiSO}_4$   
428 could be recovered at purities higher than those displayed in Table 4.

429 In the scenario of recovering Ni through electrowinning, phosphate precipitation should not be an issue as it is  
430 typically conducted around pH 3.5 or lower in sulfate media [10,32]. Comparable Ni and  $\text{PO}_4$  concentration levels  
431 (0.2 mol/L and 0.007 mol/L respectively) were met in the electrowinning experiment conducted by Lee [33] in which  
432 Ni is successfully recovered, although no information is given regarding the phosphate content of the produced  
433 cathode. In this case, the challenging impurity is likely to be Fe, even though its concentration in the purified solution  
434 does not exceed  $5 \cdot 10^{-4}$  mol/L. A sequential elution with dilute  $\text{H}_2\text{SO}_4$ , or with a scrubbing solution of  $\text{NiSO}_4$ , are  
435 conceivable answers to further improve purity.

436 The method permitted the isolation of Ni from the main leachates' impurities, and relatively high purities were  
437 obtained ( $\geq 97\%$ ). This was also possible because of the high affinity of the resin for Ni and the absence of metals with  
438 higher or comparable affinities (Cu, Co, U). The procedure paves the way for the production of a high value-added Ni,  
439 whether in the Ni hydroxide or ASNH salt form [9], or even cathodic Ni by electrowinning [10]. By avoiding the use of  
440 stoichiometric precipitants, cost savings were achieved regarding impurity removal, compared to published work. The

441 reusability of the resin is a key feature and should be monitored overtime. Our results, in consistency with other  
442 previously published studies [15,16], suggest that a high number of sorption/desorption cycles can be performed  
443 without capacity deterioration.

444 In the case of processing plant ash leachates, resin poisoning by metals that bind more strongly than Ni is unlikely.  
445 Ni-specific hyperaccumulator plants (and their derived ash) contain trace amounts of Cu (generally on the order of  
446 ppb). Contamination could only occur if important amounts of soil were retained with the treated biomass. It is  
447 suggested that Cu contamination would result in a decrease in capacity, without affecting the purity of the produced  
448 solution. Indeed, Cu elution on *bpa* resins has been reported to be almost impossible with sulfuric acid (up to 2 mol/L)  
449 [20,34]. If detected, resin poisoning by Cu could be solved by eluting the resin bed with ammonia [34].

## 450 5. Conclusions

451 One objective of this work was to better understand the functioning of the Dowex M4195 resin during the  
452 adsorption/desorption of Ni in sulfate medium at pH 2 in the presence of  $\text{Na}_2\text{SO}_4$ . Column experiments with synthetic  
453 solutions allowed to understand the dominant mechanisms involved: Ni competes with  $\text{H}^+$  for sorption on *bpa* groups,  
454 while sulfate sorption on the resin plays a crucial role in pH regulation and significantly affects Ni sorption, by limiting  
455  $\text{H}^+$  activity. These hypotheses were tested by comparing experimental breakthrough curves with results calculated  
456 using the IMPACT computational code, combining column transport and chemical reactions at thermodynamic  
457 equilibrium. The reaction scheme with only two optimized constants, was found to be sufficiently accurate to  
458 calculate the number and location of fronts, as well as concentration variations. Overall, a very good agreement was  
459 obtained between the experimental and calculated values.

460 The use of this resin allowed the isolation of Ni sulfate from hyperaccumulator plant ash leachate to high purity  
461 levels (up to 99%). The interest of this resin in the context of Ni valorization by the agromining chain of processes has  
462 thus been confirmed. Compared to purification by precipitation, this technique has the advantage of saving expensive  
463 reagents, in particular soda.

464

465 The approach proposed here aims at isolating the dominant sorption behavior, and secondarily consider the other  
466 elements. The complexity of the multi-metallic solution was reduced to a minimum, consisting of only the main metal  
467 (Ni), and the electrolyte ( $\text{Na}_2\text{SO}_4$ ). Modelling the biphasic equilibrium, and especially pH, is crucial but can be easily  
468 conducted by equilibrium models as this work has highlighted. Then, the addition of the secondary elements (other  
469 cationic metals, but also anions such as phosphate) were subsequently considered. In this work, modelling their  
470 behavior properly in the solution, attained a good agreement between the calculated values and experimental values.

471 This work opens perspectives for the improvement of the process. Parameters critical for operation remain  
472 unexplored such as temperature and flowrates and need to be considered for higher throughput. Since feasibility has  
473 been proven and key mechanisms identified, more advanced process configuration has to be studied.

#### 474 Declaration of competing interest

475 The authors declare that they have no competing financial interests or personal relationships that could have  
476 influenced the work reported in this paper.

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481 of remediation technologies for degraded and polluted lands (Groupement d'Intérêt Scientifique sur les Fiches  
482 Industrielles - <http://www.gisfi.univ-lorraine.fr>). The authors wish to thank the GISFI platform and technical staff for  
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