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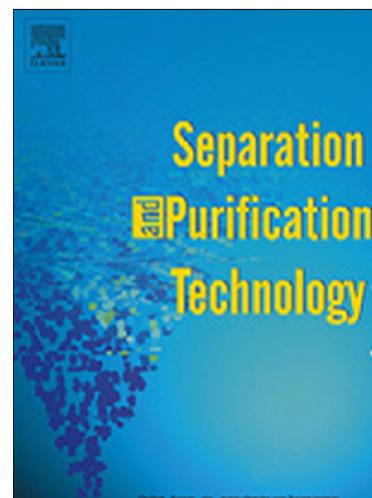
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Selective Recovery of Germanium with N-methylglucamine -functional Resin from Sulfate Solutions

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Abstract

Growing demand of germanium and uncertainties in supply create a need for research into efficient separation methods. Ion exchange recovery of germanium from sulfate solutions was studied with equilibrium experiments, column experiments, and modeling. Based on screening of four commercial resins by equilibrium experiments, a bifunctional N-methylglucamine resin was selected for dynamic adsorption studies and modeling. The adsorption of germanium onto the resin depended strongly on pH. The first pK_a value of germanic acid, $\text{Ge}(\text{OH})_4$, is 9 and its anionic dissociation products (oxoanions) were adsorbed to the nitrogen containing groups by anion exchange mechanism. The germanium species were all adsorbed to glucose sites. Other metal ions in the studied multimetal feeds decreased the Ge adsorption directly by competition, and indirectly by acting as buffers to prevent pH increase and the dissociation of germanic acid. Iron was found to have a particularly detrimental effect on the adsorption.

A competitive adsorption model was used to describe the sorption equilibrium of germanic acid and its dissociation products to glucose sites and to amine groups. A transport-dispersive model with a solid film linear driving force model was employed for the dynamic modeling. Authentic and simulated feed solutions were used to study the effect of competing metals. The feed solutions contained 63-490 mg/L Ge and metal sulfates so that ionic strengths were between 0.58 and 5.82 mol/L. The constructed

simulation model predicted the equilibrium isotherms and the breakthrough curves of germanium well.

Keywords

Germanium; N-methylglucamine; Dynamic adsorption; Competitive adsorption isotherm; Transport-dispersive model

Nomenclature

List of symbols

c_i	concentration of i in solution (mol/L)
D_L	axial dispersion coefficient (m^2 L/s·mol)
D_s	diffusion coefficient (m^2 /s)
F	phase ratio between solution and resin (-)
I_c	ionic strength (mol/L)
K_{diss}	1 st dissociation constant of germanic acid (L/mol)
K	affinity constant (L/mol)
k_L	lumped mass transfer coefficient, Eq. (6) (1/s)
m_{ads}	adsorbed mass (g)
n	parameter in Eq. (4) (-)
Q	capacity of the resin (mol/L resin)
q	concentration in resin phase (mol/L resin or mg/g resin)
R_p	radius of resin particle (mm)
T	temperature ($^{\circ}$ C)
t	time (s)
u	mobile phase velocity (m/s)
V_{bed}	volume of the resin bed (L)
z	spatial coordinate (m)

Greek letters

ϵ	void fraction of the resin bed (-)
ρ	density of the resin (g/mL swollen resin)

Superscripts and subscripts

0	initial
eq	equilibrium
H	proton
i	component
j	measuring point in column experiments

Abbreviations

BV	unit (bed volume)
ICP-AES	inductively coupled plasma atomic emission spectroscopy
IDA	iminodiacetic acid
PS-DVB	polystyrene divinylbenzene copolymer

1. Introduction

Germanium is a valuable semimetal, that is used in semiconductors, optical devices, polymerization catalysts and solar cells [1], and worldwide demand is expected to grow within this decade [2,3]. The current market price for elemental Ge is 1650 USD/kg and for GeO₂ 1380 USD/kg [4]. Worldwide refinery production of germanium in 2010 was estimated to be 120 tons. 30% of germanium is produced from secondary raw materials, which include window blanks from decommissioned military devices and scrap from manufacturing optical devices. Approximately 60% of the germanium used in optical device manufacture is recycled [5].

Despite its relatively high price, germanium is not very rare. It is evenly distributed in the earth's crust (abundance 0.0007%) without large individual deposits. Although Ge minerals exist, the element usually occurs among sulfide ores of copper, zinc, silver and lead. Most commonly, germanium is recovered as a side product of zinc processing. Coal deposits may also contain germanium, which can be recovered from fly ashes, for example in power plants [1].

The most important oxidation state of germanium is IV. The Ge⁴⁺ -ion rarely occurs in aqueous solutions but it is easily hydrolyzed. Germanic acid, Ge(OH)₄, and its dissociation products in the form of Ge-oxoanions thus dominate the aqueous chemistry of germanium. Dissociation of germanic acid takes place in slightly basic solutions; the first p*K*_a value is about 9 and varies slightly depending on the medium and reference (Fig. 1). Consequently, germanium occurs as an electrically neutral germanic acid species in the neutral and acidic solutions that are commonly found in hydrometallurgical processes. At higher concentrations, germanium may also form polynuclear species [6].

Figure 1. Dissociation of germanic acid. Values for pK_a are from the Hydra-database [7].

According to the literature, conventional anion exchangers, cation exchangers and several common chelating resins have previously been tested for recovery of germanium. However, very specific functional groups are needed to achieve desired capacity and selectivity over other metals [8].

Anion exchangers with different functionalities have been studied extensively in the former Soviet Union. AN-31, which is a condensation polymer of epichlorohydrin, ammonia and polyethylene polyamine, has been suggested as suitable in several studies [9–12]. EDE-10P and AV-16 have been cited as other applicable resins [10,13–15]. Omarov [16] found the strong cation exchanger KU-2 to be effective at pH 4-6.

The adsorption mechanism of germanium is not totally clear, although it seems to involve anion exchange at least to some extent. Matvejeva *et al.* found that hydroxyl groups in the resin enhance adsorption [9] and it is known that Ge compounds form stable complexes with polyols [17]. N-methylglucamine –functional resin, generally used for boron removal, has been applied successfully for adsorption of germanic acid dissociation products by Schilde and Uhlemann [17,18] and Yasuda and Kamazu [19–21]. Of the chelating resins, iminodiacetic acid (IDA), chitosan, or a combination of these and vinylamidoxime functionalities have been used for adsorption of germanium [22–26].

The purpose of this research is to develop a selective and effective separation method for germanium from various sulfate based multimetal solutions based on the use of commercially available ion exchange resins. Equilibrium studies were done to determine a suitable resin (functional groups in Fig. 2) and to study pH dependency. Dynamic adsorption experiments in columns with different types of multimetal solutions were done to study kinetic phenomena and the effect of other metals on the adsorption of germanium.

A mathematical model was constructed for simulation of the adsorption. The main purpose of the modeling was to enhance understanding of the adsorption mechanism of germanium on multifunctional resins, thus providing tools for designing recovery processes.

2. Experimental

2.1. Reagents

Four resins were selected for the screening experiments: Amberlite IRA-743, Amberlite IRA-67, WP-2, and Lewatit TP-260 (Table 1). The resins are from different categories as regards functional group, matrix and support. The common feature of these resins is a functional group with an N-donor atom (Fig. 2). IRA-743, WP-2 and TP-260 are chelating resins and IRA-67 is a weak anion exchanger.

Table 1. Characteristics of the resins in screening experiments [27–30].

Figure 2. Functional groups of the resins used in screening experiments.

The following chemicals were used in the experiments: pure GeO_2 from OMG Kokkola Chemicals, and the analytical grade chemicals: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, ZnSO_4 from Riedel-de-Haën, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ from Sigma Aldrich, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ from J.T. Baker, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, H_2SO_4 , HCl , HNO_3 , NH_4OH from Merck, and NaOH -pellets from Eka Chemicals,

Germanium solutions were prepared by dissolving GeO_2 in 0.1 M NaOH at a ratio of 20g/L. The solutions were then diluted to the desired concentration with deionized water and pH was adjusted with concentrated H_2SO_4 . The multimetal solutions were obtained by mixing the germanium solutions with the respective metal sulfate salt solutions.

2.2. Analytical techniques

All metal analyses of aqueous samples were carried out from 10% HNO₃-media using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.3. Equilibrium experiments

In the resin screening phase, adsorption isotherms were determined for the resins in the base form by equilibrating 0.5 g of the dry resin with 10 mL of the Ge solutions at different concentrations in glass test tubes. For each resin, a series of experiments were done at two initial pH values, 0.8 and 3.0 respectively. For IRA-743 and TP-260 similar isotherms were obtained with acid form resins. All these equilibrium experiments were done at 25°C and samples were equilibrated for 2-3 days. The concentration of Ge was analyzed in the aqueous phase.

Based on the screening experiments, IRA-743 was chosen for further research, because of its superior adsorption capacity in the initial pH 3.0. To avoid neutralization costs in full-scale applications, tests were carried out to find the lowest applicable pH where adsorption is sufficient. This was done by performing six series of equilibrium experiments in the same way as described above. The initial pHs were 0.8, 1.4, 1.8, 2.2, 2.6, and 3.0. These experiments also gave equilibrium model parameters to describe the pH effect.

2.4. Column experiments

Dynamic adsorption of germanium with IRA-743 was studied by conducting a series of column experiments with different feed solutions at different conditions. A 16 mm diameter column was used. The ionic strength, temperature and flow rate were varied to cover a wider range of solutions and conditions, and to study the effect of these parameters on adsorption. The experiments were done at 25°C and 40°C. The flow rates

were 1.0 and 2.0 cm/min. The volume of the resin bed varied between 20.1 and 28.8 mL. The volumetric phase ratio between resin and solution was 0.552, which was calculated based on measured resin bead density, mass of the resin in the bed and the bed volume. The experimental conditions and the feed solutions of the column experiments are presented in Table 3.

Dynamic adsorption capacities in each experiment were calculated with the following equation:

$$m_{ads} = \left(\sum_j \{0.5 \cdot [(c_0 - c_i) + (c_0 - c_{i-1})] \cdot (V_i - V_{i-1})\} - \varepsilon \cdot c_0 \right) \cdot V_{bed} \quad (1)$$

where m_{ads} is the adsorbed mass of metal, j is the number of sampling points, c is the analytical concentration of i and ε is the void fraction of the bed.

3. Modeling

In the literature, Jevdokimov and Kostjuk used the Freundlich isotherm to describe germanium adsorption to an AV-16 anion exchanger [14]. Yasuda and Kawazu also used this approach for Ge adsorption to an N-methylglucamine -functional resin [19]. Dzhelassi et al. [11,31,32] utilized the Box-Wilson method [33] to study the effect of pH, phase ratio and feed concentration on the adsorption capacity and recovery yield of anion exchangers.

In this study, a model is constructed for germanium adsorption in an N-methylglucamine -functional resin (IRA-743). A competitive adsorption isotherm model is used to describe the equilibrium behavior and a transport-dispersive model with a solid film linear driving force model is used for the dynamic behavior.

3.1. Equilibrium model

Dissociation of germanic acid through the following reaction is taken into account:



Based on the reaction above, the fractions of both germanic acid and its first dissociation product in solution are calculated (activity coefficients are neglected) from the equilibrium

$$K_{\text{diss}} = \frac{[\text{GeO(OH)}_3^-][\text{H}^+]}{[\text{Ge(OH)}_4]}, \quad (3)$$

where K_{diss} (mol/L) is the dissociation constant of germanic acid. The value used for $\log K_{\text{diss}}$ is -9.31, which was taken from the Hydra-database [7].

Matvejeva *et al.* [9] and Schilde and Uhlemann [17] state that hydroxyl groups and an increasing OH/NH-ratio in the resin enhance adsorption and that the germanic acid complexates with polyol groups. On the other hand, it is also known that amine groups themselves adsorb germanic acid weakly [14]. It would be expected that protonated amine groups also adsorb the dissociation products of germanic acid by anion exchange mechanism. In the model used in this work, the N-methylglucamine group is considered to consist of two different types of functionalities; weakly basic amine functionality and glucose functionality. The following competitive adsorption model is employed as an isotherm model [34]:

$$q_i = Q \frac{(K_i c_i)^{n_i}}{1 + \sum (K_i c_i)^{n_i}}, \quad (4)$$

where q_i is the concentration of component i in the resin (eq/L resin), and Q is the amount of active sites in the resin (eq/L resin). K (L/mol) and n (-) are parameters dependent on the adsorption properties of the component i onto the functional group. K is the affinity of component i onto the functional group, and n describes the non-ideality of the adsorption due to stoichiometric effects and/or lateral interactions. For the amine group, only $\text{GeO}(\text{OH})_3^-$ is adsorbed subsequently after adsorption of the proton, and for the glucose group $\text{GeO}(\text{OH})_3^-$ and $\text{Ge}(\text{OH})_4$ compete. Equilibrium parameters for Ge species are determined by a least squares method in which the target value is the total concentration of the Ge species, q_{Ge} , in the resin. Input values for this fitting are the measured analytical Ge and H^+ concentrations, c_{Ge} and c_{H^+} , in the liquid phase.

The effect of other metals on the adsorption of germanium is taken into account via speciation chemistry of different solutions, which was studied with the MEDUSA computer program [7] and via direct competition with proton adsorption. An assumption was made that the affinity for other metals is low, and thus the selectivity was studied in column experiments and lumped parameters were used in the modeling.

3.2. Dynamic model

A transport-dispersive model is used in this work. The general mass balance equation for the cross section of the column is written [35]:

$$\frac{\partial c_i}{\partial t} + F \frac{\partial q_i}{\partial t} + u \frac{\partial c_i}{\partial z} = D_{L,i} \frac{\partial^2 c_i}{\partial z^2}, \quad (5)$$

where c (mol/L) and q (mol/L resin) are, respectively, concentrations in the liquid and solid phase, F (-) is the phase ratio between the stationary and mobile phase, u is the mobile phase velocity (m/s), z (m) is a spatial coordinate along the column, and $D_{L,i}$ ($\text{m}^2 \text{ L/s}\cdot\text{mol}$) is the axial dispersion coefficient. Assumptions in this model are that u and $D_{L,i}$ are constant along the column. In this work, $D_{L,i}$ is assumed to be zero, so the term on the right hand side of the Eq. (5) equals zero. To calculate the temporal derivative of the solid phase concentration, a solid film linear driving force model was employed [35]:

$$\frac{\partial q_i}{\partial t} = k_L (q_{eq,i} - q_i), \quad (6)$$

where $q_{eq,i}$ (mol/L resin) is the solid phase concentration at equilibrium and k_L (1/s) is a lumped mass transfer coefficient, for which the following relationship is used [35]:

$$k_L = \frac{15D_{s,i}}{R_p^2}, \quad (7)$$

where $D_{s,i}$ (m^2/s) is the diffusion coefficient in the resin pore and R_p (m) is the mean radius of the resin particle.

4. Results and discussion

4.1. Adsorption isotherms for germanium

Of the four resins studied, the adsorption of germanium was higher at initial pH 3.0 than at pH 0.8 for all resins except TP-260 (Fig. 3). This result is due to the fact that at initial pH 3.0 the equilibrium pH is high enough for germanic acid to dissociate according to Eq. (2). The results are in agreement with those of Matvejeva *et al.* [9], who report that hydroxyl groups enhance adsorption. At low Ge concentrations, IRA-743 showed superior performance compared to the other resins, but at pH 0.8 its capacity was very low. The polyamine functional IRA-67 resin showed strong Ge adsorption at pH 3.0 in higher Ge concentrations, but the adsorption was weak at lower Ge concentrations. This result could be due to the formation of polynuclear Ge species at higher concentrations, which IRA-67 may be able to adsorb.

Figure 3. Adsorption of germanium onto four ion exchange resins (IRA-743, IRA-67, WP-2 and Lewatit TP-260) from sulfate solutions.

The aminomethylphosphonium functional chelating resin, Lewatit TP-260, behaved differently from the above-mentioned resins. Lewatit TP-260 had a much higher adsorption capacity at initial pH 0.8 compared to pH 3.0 and it is clearly the best adsorbent at pH 0.8. At initial pH 0.8, all the phosphonium groups, which enhance the adsorption, are in protonated form, which is not totally the case at initial pH 3.0. Furthermore, at both initial pH 3.0 and initial pH 0.8, the amino groups do not adsorb enough protons to affect the dissociation of germanic acid.

4.2. Effect of pH on adsorption of germanium onto N-methylglucamine resin

When the pH was decreased from 3.0 to 2.6, 2.2 and 1.8, the germanium adsorption decreased slightly in each step (Fig. 4). From pH 1.8 to 1.4, the adsorption decreased abruptly. This result is consistent with the fact that in these last two series (initial pH 1.4 and 0.8) the pH in the equilibrium also remained much lower, leaving more germanic acid undissociated. It can be concluded that pH has a significant effect on adsorption behavior of germanium in N-methylglucamine resins via the dissociation equilibrium of germanic acid. This conclusion is well verified by the equilibrium model, which predicts the adsorption very well. The fitted parameters obtained based on these experiments are presented in Table 2.

Figure 4. Effect of initial pH on adsorption of germanium onto N-methylglucamine resin from sulfate solutions. Solid lines are modeled with the competitive adsorption model (Eq. (4)).

Table 2. Model parameters (Eq. (4)) for Ge species and H^+ fitted to the equilibrium data.

4.3. Dynamic adsorption

Dynamic adsorption of germanium onto N-methylglucamine resin was studied with five different solutions; four multimetal solutions and one pure Ge solution. In all solutions, the initial pH was 3.0 and the temperature in the column was 25°C or 40°C (Table 3). The equilibrium parameters of binding were not determined at 40°C since Matvejeva *et al.* [9] report that temperature has no significant effect on Ge adsorption with oxygen groups containing polyamine resins, and thus the same equilibrium parameters are used as in calculations for 25°C.

Table 3. Feed solutions and conditions for the five dynamic adsorption experiments.

Table 4. Model parameters for competitive adsorption fitted based on dynamic adsorption experiments. The K values for the Ge species are as in Table 2. Subscript *other* refers to the lumped parameter for other metals.

As can be seen from Table 3, the feed solutions cover a wide ionic strength range, which affects the resin bead size since the resins shrink when the salt concentration increases. It is also known that the diffusion coefficients in the resin pores increase with increasing temperature [36]. The effect of these two variables is seen in the values of the lumped mass transfer coefficient defined in Eq. (7) and shown in Table 4.

Although the N-methylglucamine -functional resin has significantly lower affinity for the other elements, adsorption parameters for the amine group are given to these elements. These parameters are presented in Table 4.

When several metals are present together with germanium in the solution, they are capable of forming hydroxide complexes and thus act like buffers. The theoretically calculated equilibrium curves (Fig. 5) illustrate that the pH remains constant when the total proton concentration in the solution decreases (the effect of precipitation is ignored in the

calculations). Such a decrease takes place, for example, when a basic resin is added to the solution. And the more hydroxide complexes of metals there are present in the solution, the more acid is needed to lower the pH. It is assumed that in all solutions used in this study the equilibrium is at the plateau part of the curve, and thus the dynamic modeling can be simplified by assuming that the pH is constant in all the multimetal cases. In the case of Experiments 1, 2 and 3, this assumption leads to a small error because in the final part of the experiment, the resin can no longer uptake further protons and the pH drops below the constant value of the plateau part of the curve.

Figure 5. Modeled dependency of pH on total proton concentration in solutions used in dynamic adsorption studies. Calculations were performed with the MEDUSA computer program [7].

The buffering effect of other metals in the solution is dramatic. Fig. 6 presents breakthrough curves for two column experiments (Experiment 4 and 5 in Table 3). In the former, only germanium was present, and in the latter, there was a multimetal feed. As discussed earlier, pH has a great effect on the Ge adsorption. In the case of the multimetal solution, the pH in the outlet was between 3 and 4, whereas with the pure Ge solution it was around 11. For this reason, breakthrough for the pure Ge case is not achieved within 35 BV (40 BV according to the model simulation) and in the multimetal case it is at around 5 BV. Dynamic adsorption capacities for Ge were 26.5 and 3.0 mg/(g wet resin), respectively. From the multimetal solution, 26 and 8 mg/(g wet resin) of Cd and Al were adsorbed, respectively. When there was only 8.6 g/L Co as an impurity (Fig 7.) breakthrough was after 30 BV. The dynamic adsorption capacity of the resin for Ge in this case was 29.3 mg/(g wet resin). The model predicted these breakthrough curves of germanium well.

Figure 6. Dynamic column adsorption of germanium with N-methylglucamine resin from pure Ge and multimetal sulfate solutions (initial pH 3.0). Lines are modeled. The experiments are numbers 4 and 5 in Table 3.

Figure 7. Dynamic adsorption of germanium with N-methylglucamine resin from sulfate solution (initial pH 3.0) containing 8.6 g/L Co as an impurity. The line is modeled. The experiment is number 1 in Table 3.

It has been stated in the literature that Fe^{3+} poisons resins with amine groups, thus interfering with the adsorption of germanium [8]. Fe^{3+} is known to precipitate at pH \sim 3, and since one of the original feed solutions contained 630 mg/L of iron, presumably as Fe^{3+} , two methods were employed to overcome this problem. Firstly, the Fe^{3+} was reduced to Fe^{2+} with SO_2 (Experiment 2 in Table 3.) and secondly, most of the Fe^{3+} was precipitated with NaOH leaving 93 mg/L of Fe to the solution (Experiment 3 in Table 3.). The latter method was found to work better (Fig. 8). Breakthrough for germanium with the reduced solution took place at around 10 BV, while breakthrough of the precipitated solution was a little before 20 BV. The dynamic adsorption capacities for Ge were 1.5 and 4.3 mg/(g wet resin), respectively. This result suggests that iron in any form is detrimental to germanium adsorption. According to Gil *et al.* [37], when pH is below ca. 3.7, Fe^{3+} forms an anionic compound, $\text{Fe}(\text{SO}_4)_2^-$, which competes in adsorption with anionic Ge species. Neither Fe^{3+} nor Fe^{2+} form other anionic species in sulfate media [37]. The speciation chemistry of Fe^{3+} and Fe^{2+} in sulfate media was also verified with the MEDUSA computer program [7]. As 1.8 and 11.9 mg/(g wet resin) of iron were adsorbed, respectively, it would appear that the adsorbed amount does not explain the detrimental effect. A possible reason for the better Ge adsorption with the precipitated solution may be that the Fe^{2+} was partly oxidized back to Fe^{3+} in Experiment 2 (Table 3). Sulfuric acid is released in the oxidation reaction, lowering the pH and leading to decreased Ge adsorption. In Fig. 5, both solutions have similar calculated pH vs. $c_{\text{tot},\text{H}^+}$ -curves.

The modeled breakthrough curves in Fig. 8 were calculated with the same parameters. The curves diverge in different directions and it seems that the lumped mass transfer coefficients should be varied to get better fits. The ionic strengths of these solutions are similar (1.52 and 1.38 mol/L), meaning that the size of the resin particles are similar, and the reason for the difference can be expected to be found in the diffusion coefficients in the resin pores.

Figure 8. Effect of prevention methods for Fe poisoning on dynamic adsorption of germanium with N-methylglucamine resin from multimetal sulfate solutions. Lines are modeled. Experiments 2 and 3 in Table 3.

The elution of germanium using H_2SO_4 , and HCl solutions was briefly tested at different concentrations. Both acids were found to be applicable and higher concentrations resulted in sharper elution peaks.

5. Conclusions

When the initial pH was 3.0, the N-methylglucamine functional resin (IRA-743) proved to be superior for germanium removal from sulfate solutions containing several base metals compared to other commercial resins containing functional groups with nitrogen donor atoms. However, at a low pH (< 1) the aminomethylphosphonium resin (Lewatit TP-260) showed higher adsorption capacity.

The N-methylglucamine resin was chosen for closer consideration in terms of modeling and column experiments for recovery of germanium from multimetal sulfate solutions. The strong effect of pH on adsorption capacity is explained by the dissociation of germanic acid due to the pH increase in the solution which results from protonation of the amine group. Anionic dissociation products in the form of Ge-oxoanions are then adsorbed by an anion exchange mechanism. The promoting effect of glucose groups is

explained with adsorption of all Ge species to hydroxyl groups. Since increasing pH does not increase the affinity for competing metals, the selectivity of N-methylglucamine for germanium improves with increasing pH.

In the dynamic adsorption experiments to study the adsorption of germanium from multimetal solutions, the other metals in the solution have a diminishing effect on germanium adsorption because of competing and buffering effects. The buffering effect means that cations form hydroxide complexes, thus preventing pH increase to the range in which germanic acid dissociates. This observation was validated by running parallel experiment with Ge only. Furthermore, it was found that iron, both Fe^{3+} and Fe^{2+} , has a negative effect on the Ge adsorption.

The competitive adsorption model described the effect of pH on the germanium adsorption equilibrium accurately. The transport-dispersive model coupled with a solid film linear driving force model described well the dynamic behavior, although the fit was only satisfactory in modeling of iron-containing solutions. It is suggested that this may be due to Fe^{3+} poisoning the resin, thus affecting kinetic phenomena inside the resin pores.

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References

- [1] R.R. Moskalyk, Review of germanium processing worldwide, *Miner. Eng.* 17 (2004) 393–402.
- [2] M. Buchert, D. Schuler, D. Bleher, *Critical Metals for Future Sustainable Technologies and their Recycling Potential*, Germany, 2009.
- [3] European Commission, The Ad-hoc Working Group, *Critical raw materials for the EU*, <http://ec.europa.eu/enterprise/policies/raw-materials/>, 2011.
- [4] Metal pages, <http://www.metal-pages.com/>, 2012.
- [5] D.E. Guberman, *Germanium 2011*, U.S. Geological Survey 2011.
- [6] S.A. Wood, I.M. Samson, The aqueous geochemistry of gallium, germanium, indium and scandium, *Ore Geology Reviews* 28 (2006) 57–102.
- [7] KTH - Chemistry / Chemical Equilibrium Diagrams, 2010.
- [8] D.A.D. Boateng, D.L. Ball, G.M. Swinkels, *Recovery of germanium from aqueous solutions*, U.S. Patent 4525332, 1985.
- [9] Z.I. Matvejeva, P.D. Novikov, Use of the AN-31 anion-exchanger in germanium extraction technology, *Cvetnye Metally* 44 (1971) 46–48.
- [10] N.M. Sobinyakova, S.I. Balikhina, E.I. Vasil'chikova, L.L. Grachev, A.F. Chetverikov, Y.V. Samborskii, Use of ion exchange for germanium recovery from semiconductor device production refuse, *Miner. Syr'e. No. 23* (1972) 129–139.
- [11] A.F. Dzhelassi, A.M. Egorov, E. Miva, Use of the Box-Wilson method for determining the degree of effect some factors have on the adsorption of germanium by AN-31 resin, *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 13 (1970) 1286–1289.
- [12] L.E. Slobtsov, Sorption of germanium from Waelz sublimates in the copper industry., *Tsvetn. Met.* (1990) 20–22.
- [13] G.M. Esirkegenov, U.F. Kasymkhanova, Extraction of germanium from solutions by an ion exchange method, *Tr. Kaz. Politekh. Inst. No. 26* (1967) 384–386.
- [14] D.J. Jevdokimov, A.P. Kostjuk, Ion-exchange resin sorption of germanium from solutions, *Zhurnal Prikladnoi Khimii* 3 (1969) 511–516.
- [15] V.P. Meleshko, G.E. Dubrovskaya, L.I. Kadaner, Recovery of germanium from aqueous solutions by ion-exchange resins and electrolysis, *Ionoobmen. Mater. Ikh Primen.* (1968) 141–144.
- [16] S.T. Omarov, Extraction of germanium by ion exchangers, *Khim. Khim. Tekhnol. No. 1* (1970) 96–100.
- [17] U. Schilde, E. Uhlemann, Separation of several oxoanions with a special chelating resin containing methylamino-glucitol groups, *React. Polym.* 20 (1993) 181–188.
- [18] U. Schilde, H. Kraudelt, E. Uhlemann, Separation of the oxoanions of germanium, tin, arsenic, antimony, tellurium, molybdenum and tungsten with a special chelating resin containing methylaminoglucitol groups, *React. Polym.* 22 (1994) 101–106.
- [19] S. Yasuda, K. Kawazu, Preconcentration of germanium(IV) from natural water by chelating resin with 1-deoxy-1-(methylamino)sorbitol groups, *Bunseki Kagaku.* 37 (1988) T67–T71.
- [20] S. Yasuda, K. Kawazu, Removal of trace germanium from concentrated zinc sulfate solution using N-methylglucamine resin, *Kyushu Kogyo Gijutsu Shikensho Hokoku.* (1989) 2739–2744.
- [21] S. Yasuda, K. Kawazu, Separation of germanium from ethylene glycol distillates by N-methylglucamine resin, *Sep. Sci. Technol.* 26 (1991) 273–277.

- [22] Y. Inukai, Y. Kaida, S. Yasuda, Selective Separation of Germanium(IV) by Iminodiacetic Acid-Type Chitosan Chelating Resin, *Anal. Sci.* 13 (1997) 339–344.
- [23] H. Masuda, Separation technology for rare metals. An example of separation from Kuroko deposits, *Kagaku Sochi.* 30 (1988) 95–99.
- [24] K. Sekine, A. Tanaka, H. Takahashi, M. Hirai, S. Tomoshige, K. Kondo, Recovery of germanium in leachate of nonferrous metal ore smelting residues, JP60145914A, 1985.
- [25] K. Sekine, A. Tanaka, H. Takahashi, M. Hirai, S. Tomoshige, K. Kondo, Process for concentration of germanium, JP60166225A, 1985.
- [26] A. Kataoka, K. Matsuda, M. Aoi, Chelating resins for recovery of germanium, 1985.
- [27] IRA-743 Product data sheet, DOW, www.dow.com, 2008.
- [28] IRA-67 Product detail, DOW, www.dow.com, 2000.
- [29] WP-2 Product data sheet, Purity Systems Inc., www.puritysystemsinc.com, 2010.
- [30] Lewatit TP-260 Product information, Lanxess, www.lanxess.com, 2010.
- [31] A.F. Dzhelassi, A.M. Egorov, Use of the Box-Wilson method for studying the sorption of germanium by the EDE-10P resin using tiron, *Zh. Prikl. Khim.* 44 (1971) 534–540.
- [32] A.F. Dzhelassi, A.M. Egorov, N. Shivgulam, Application of the Box-Wilson method to the study of germanium adsorption by the resin AN-18 with use of tiron, *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 13 (1970) 1116–1119.
- [33] G.E.P. Box, K.B. Wilson, On the experimental attainment of optimal conditions, *Journal of the Royal Statistical Society* (1951).
- [34] L.K. Koopal, W.H. van Riemsdijk, J.C.M. de Wit, M.F. Benedetti, Analytical Isotherm Equations for Multicomponent Adsorption to Heterogeneous Surfaces, *J. Colloid Interface Sci.* 166 (1994) 51–60.
- [35] G. Guiochon, A. Felinger, D.G. Shirazi, A.M. Katti, *Fundamentals of preparative and Nonlinear Chromatography*, 2nd ed., Amsterdam, Elsevier, 2006.
- [36] F. Helfferich, *Ion Exchange*, Dover Publications Inc., 1995.
- [37] A.F. Gil, L. Salgado, L. Galicia, I. González, Predominance-zone diagrams of Fe(III) and Fe(II) sulfate complexes in acidic media. Voltammetric and spectrophotometric studies, *Talanta* 42 (1995) 407–414.

Resin	Matrix	Functional group	Physical structure	Capacity	R _p	ρ
IRA-743	PS-DVB	N-methylglucamine	macroporous	0.70 eq/L	0.30 mm	1.23 g/mL ¹
IRA-67	crosslinked acrylic	amine	gel	1.60 eq/L	0.32 mm	45 lb/ft ³ ²
WP-2	silica	iminodiacetic acid	gel	13 g Cu/L	0.13 mm	0.50-0.56 ³
Lewatit TP-260	PS-DVB	aminomethylphosphonium	macroporous	2.30 eq/L	0.28 mm	0.72 g/mL ⁴

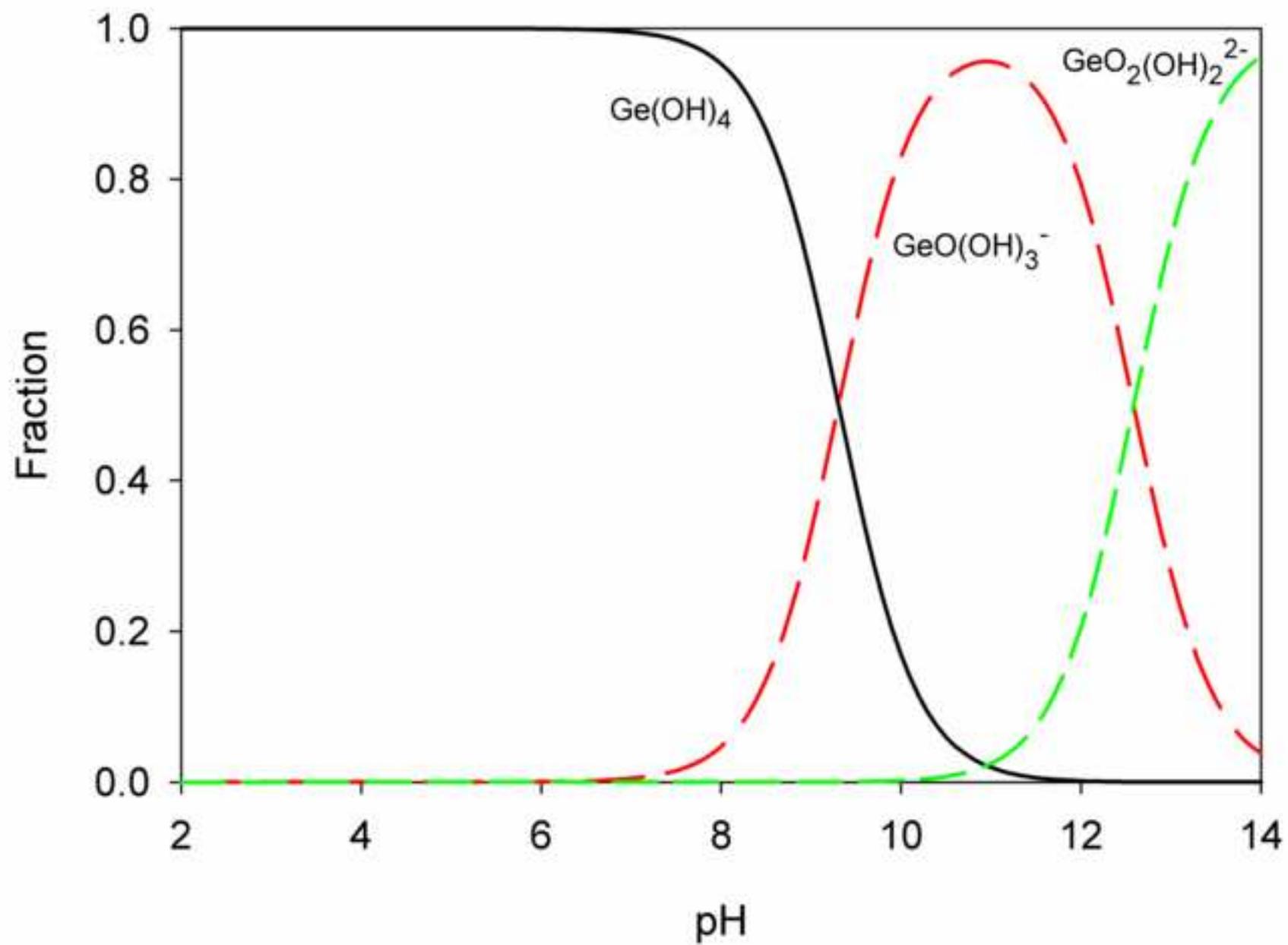
¹This work, ²Shipping weight, ³Specific gravity, ⁴Bulk density

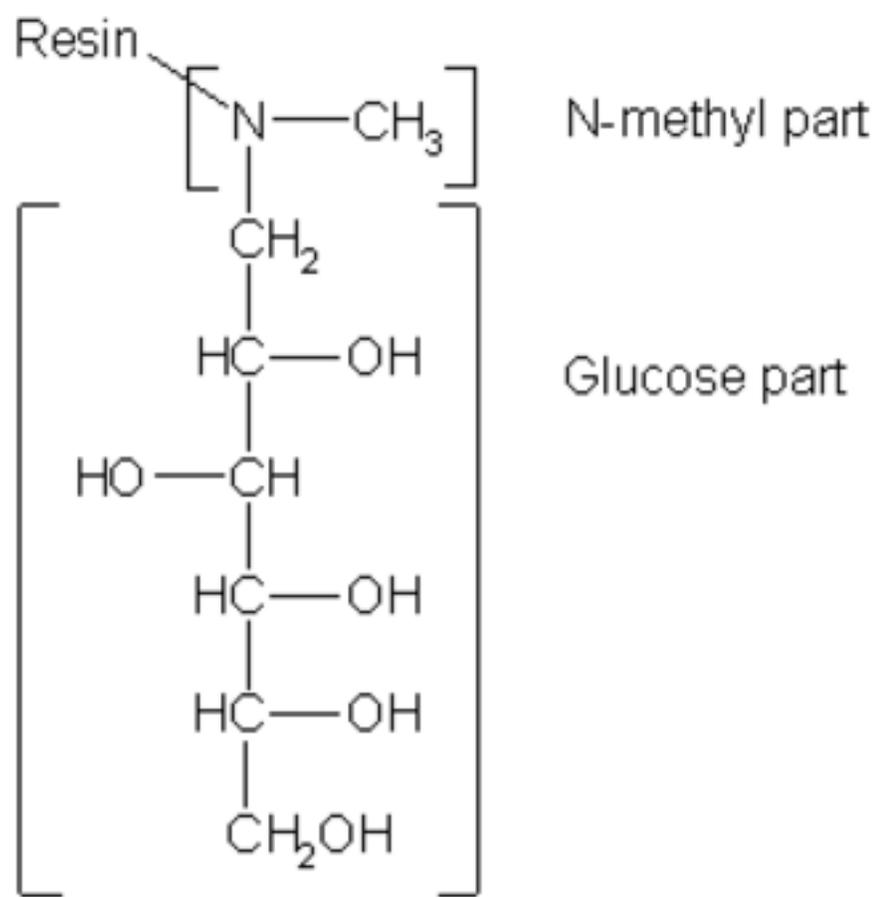
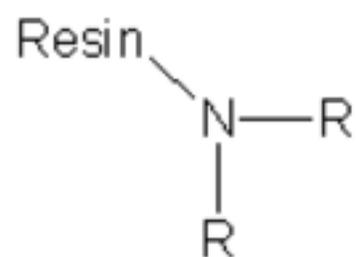
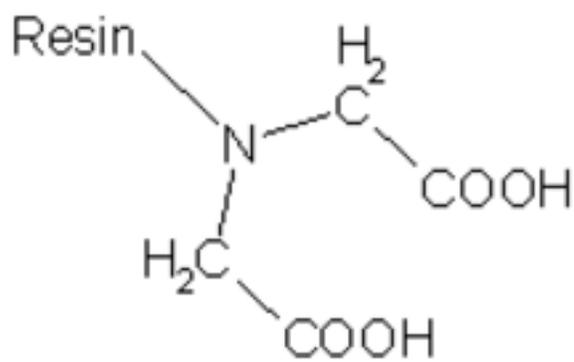
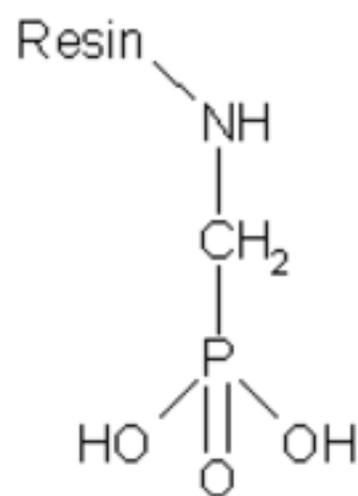
N-methyl group	Glucose group
$K_{\text{H}^+} = 1.4 \cdot 10^8 \text{ L/mol}$	$K_{\text{GeO(OH)}_3^-} = 7.3 \text{ L/mol}$
$n_{\text{H}^+} = 0.70$	$n_{\text{GeO(OH)}_3^-} = 1.72$
$K_{\text{GeO(OH)}_3^-} = 2.2 \cdot 10^6 \text{ L/mol}$	$K_{\text{Ge(OH)}_4} = 4500 \text{ L/mol}$
$n_{\text{GeO(OH)}_3^-} = 0.48$	$n_{\text{Ge(OH)}_4} = 0.62$

ACCEPTED MANUSCRIPT

		<i>Concentration in solution, g/L</i>					
Experiment	Zn	Al	Fe²⁺	Fe³⁺	Cd	Ge	
1	-	-	-	-	-	0.399	
2	1.20	-	0.629	-	-	0.063	
3	1.12	-	-	0.093	-	0.073	
4	33.2	7.68	-	-	14.0	0.300	
5	-	-	-	-	-	0.490	
		Cu	Mg	Mn	Co	As	Ni
1	-	-	-	8.60	-	-	
2	0.076	-	-	20.4	0.003	0.166	
3	0.202	-	-	18.9	0.008	0.117	
4	0.060	3.20	4.10	-	-	-	
5	-	-	-	-	-	-	
		<i>Other variables in the experiments</i>					
Experiment	I_c, mol/L	Initial pH	T, °C	u, cm/min	V_{bed}, mL		
1	0.58	3.0	25	2.0	27.1		
2	1.52	3.0	40	2.0	28.8		
3	1.38	3.0	40	2.0	28.8		
4	5.82	3.0	25	1.0	20.1		
5	-	3.0	25	1.0	20.1		

Experiment	K_{other} , L/mol	n_{other} , L/mol	k_L , 1/s		
			<i>Ge species</i>	<i>Proton</i>	<i>Other metals (lumped)</i>
1	-	-	$2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-2}$	-
2	10^6	0.48	$4.0 \cdot 10^{-4}$	$4.0 \cdot 10^{-2}$	$4.0 \cdot 10^{-4}$
3	10^6	0.48	$4.0 \cdot 10^{-4}$	$4.0 \cdot 10^{-2}$	$4.0 \cdot 10^{-4}$
4	10^6	0.48	$1.2 \cdot 10^{-3}$	$1.2 \cdot 10^{-1}$	$1.2 \cdot 10^{-3}$
5	-	-	$1.2 \cdot 10^{-3}$	$1.2 \cdot 10^{-1}$	-



**IRA-743****IRA-67****WP-2****Lewatit TP-260**

