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Sorption of Ni and Eu in a Multi-element System

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Abstract: Laboratory studies on the retardation of radionuclides in the far-field of a radioactive waste repository are often performed using a single metal in the presence of the solid surfaces in solution. However, in the event of failure in the engineered barrier system (EBS), groundwater flowing pass the EBS will likely contain more than one long live radionuclide. The aim of this paper is to understand sorption in systems containing more than one radionuclide in solution. The work presented is carried out to understand how the presence of Ni or Eu in solution will affect the sorption of each other. Static batch sorption experiments of Ni and Eu sorption to different granitic materials have been performed. Radiometric analysis was done using Cobra (II) Auto gamma for ^{152}Eu and TriCarb liquid scintillation for $^{Ni}63$. Experimental results were described initially using the empirical models from which R_d values were obtained for sorption in single systems of Ni and Eu, and of multi-element systems of Ni and Eu. The experimental data was fitted to the surface complexation using JChess Geochemical Code to obtained complexation constants for the interactions between Ni and Eu and the solid surfaces. The effect on sorption in a multi-element system was expressed by the ratio of the sorption capacity of one metal ions in the presence of the other metal ions Q_{mix} to the sorption capacity of same metal ions when it is present alone in solution Q_{sing}. $\frac{Q_{mix}}{Q_{sing}} > 1$, the sorption is promoted by the presence of other metal ions, whereas if: $\frac{Q_{mix}}{Q_{sing}} = 1$, there appears to be no observable effect, and if: $\frac{Q_{mix}}{Q_{sing}} < 1$, it would indicate that sorption is suppressed by the presence of other metal ions in solution. Results obtained showed that sorption was suppressed in systems containing Eu and Ni. Ratios of Q_{mix} and Q_{sing} were calculated as approximately 1 and Eu sorption to Muscovite Mica and for Ni sorption to Plagioclase Feldspar, showing that there was no effect on the sorption capacity. The ratio was calculated as < 1 for Eu sorption to Granite Adamellite, Rose Quartz, Plagioclase Feldspar and Muscovite Mica, showing that sorption of Eu in the presence of both Ni was suppressed. Results also showed suppression of Ni sorption in the presence of Eu with the most suppression occurring with for Ni sorption to Rose Quartz in the presence of Eu with a mixed/single ratio << 1. A correlation between the R_d and determined surface complexation constant is determined for the granitic minerals.

Key words: Multi-element sorption, nickel, europium.

1. Introduction

At present the immobilisation of high level waste (HLW) by vitrification followed by their burial in deep geological repositories, which are composed of natural and engineered barriers to isolate the long lived radionuclides from the biosphere is the most preferred procedure in many countries. Granitic rock formations are being considered as host rocks for such geological repositories [1]. The study of the sorption of radionuclides onto the geological media such as rocks or minerals is therefore an important part of the safety assessment of deep geological disposal of radioactive waste. When exposed to groundwaters, mineral surfaces undergo a variety of reactions which may include hydration, dissolution and precipitation, leaching and the sorption of protons, hydroxyl ions [2], which can affect the interactions of the host rock with radionuclides, and hence, their mobility.

A number of experiments and reviews on the sorption of radionuclides have been performed in the past, usually providing distribution coefficients (K_d and/or R_d values) for various radionuclides. Although these values have been used in performance assessments there has been little or no consideration on the effect of other radionuclides competing for the

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sorption sites at the wetted surfaces in the rock fractures. In scenarios resulting to the failure of the engineered barrier systems, the release of more than one long-lived radionuclide into the conducting fractures is possible. However, how one radionuclide might affect the sorption of another has not been fully studied as has been highlighted by Srivastava et al. in their study of sorption of different heavy metals to kaolinite [3]. For some important radionuclides such as Ni and Eu, only limited data are available for the sorption onto crystalline rock and on the primary and secondary minerals found in granitic rocks [4]. Most recently (2008) Prasad and colleagues have investigated the competitive effects of Pb(II), Cu(II) and Zn(II) on the sorption of each other [5]. The complexity of the sorption mechanisms resulting from solute-surface interactions and competition of metal ions with each other may explain the scarcity of papers on this topic [5].

Different approaches have been used to model whole-rock particle or bulk sediment sorption processes [6]. One of the several models commonly used to model sorption data is the Generalised Composite (GC) approach. It assumes that a mineral assemblage is too complex to be described as a superposition of the individual phases. In this approach, sorption is described using generic sites (called ≡SOH) and the values of the site densities and formation constants are obtained by fitting the experimental data [6].

Various empirical approaches, such as the distribution coefficient and Freundlich and Langmuir isotherm equations, have been used to represent adsorption. The empirical approaches are not capable of accounting for the effects of variable chemical conditions, such as pH, on adsorption reactions. This can be done using chemical models such as surface complexation models. These models define specific surface species, chemical reactions, equilibrium constants, mass balances, and charge balances, and their molecular features can be given thermodynamic

significance [7]. Surface complexation models were developed for single mineral phases but have now been applied to natural mineral assemblages using both component generalised composite (GC) approaches [7].

This work is aimed at modelling the sorption of [63]Ni and [152]Eu to granitic materials using the GC approach, when they are present in solution alone (single system) and when present simultaneously (mixed system) using empirical and surface complexation models. In this work static batch sorption experiments have been carried out using active [63]Ni serving as a representative member of divalent radionuclides relevant to nuclear waste such as [57]Co. [152]Eu has been selected also to serve as an analogue for trivalent radionuclides such as [241]Am.

1.1 Empirical Sorption Models

The "isotherm", a curve describing the retention of a substance on a solid at various concentrations, is a major tool to describe and predict the mobility of this substance in the environment [8]. This isotherm often cannot of itself provide information about the type of reaction involved. For example, the retention can be either due to surface retention without creating three-dimensional structure or to precipitation of a new solid phase [9, 10]. However, isotherms give general view of the distribution of radionuclides between the solid-liquid interphase.

The partition (or distribution) coefficient, K_d, is a measure of sorption of contaminants to geomedia and is defined as the ratio of the quantity of the adsorbate adsorbed per unit mass of solid (Q) to the amount of the adsorbate remaining in solution at equilibrium (C).

$$K_d = \frac{Q}{C} \qquad (1)$$

$$Q = \frac{V}{M}(C_{a0} - C) + Q_{a0} \qquad (2)$$

Most of the time, the concentration of the compound retained on the solid Q is calculated by difference between the initial solute concentration C_{a0} and the final solute concentration C. In the case of retention stage, the solid concentration at equilibrium Q (mol·g^{-1})

is given by Eq. with *V* being the volume of solution (L), m is the solid mass (g) and Q_{a0} (mol·g^{-1}) is the concentration of the compound initially retained by the solid, which must be measured or shown to be negligible [8].
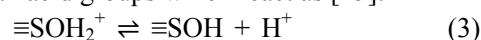
Values for K_d not only vary greatly between contaminants, but also vary as a function of aqueous and solid phase chemistry [11]. This model is used in describing results that showed a linear distribution. The distribution coefficient is a bulk parameter and cannot be used to represent the contributions of different uptake processes to contaminant retardation [7]. For rocks and minerals, contaminant adsorption can sometimes deviate from the linear relationship established by the distribution coefficient. In some circumstances, the amount of contaminant in solution contacting the solid will reach such a concentration that all adsorption sites would become saturated and the linear relationship between contaminant adsorbed to contaminant in solution would no longer hold.

Long-lived radionuclides and stable elements can be found in leachates and groundwaters near waste sources at concentrations large enough to affect the saturation of surface adsorption sites. The Freundlich equation [11, 12] and the Langmuir are mostly used to describe sorption in such situations.

1.2 Surface Complexation Models (SCM)

Mechanistic models have intrinsic advantages over empirical values when trying to justify sorption values chosen for safety assessment analysis and when it is necessary to predict sorption under a variety of different conditions [13]. In surface complexation models, ions and individual functional groups on the surface are considered to react to form coordination complexes and ion pairs [14]. Experimental data on interactions at the mineral-electrolyte interface can also be represented mathematically using mechanistic models such as the surface complexation models (SCM) [15], which are based on thermodynamic concepts such as mass action laws and material balance equations.

Three types of surface species are usually considered: protonated and hydrolysed surface sites; surface sites coordinated with major ions of the background electrolyte; and surface-sorbate complexes. The chemical reactions that take place can be described solely in thermodynamic terms, the detailed nature of the surface complexes being irrelevant [15]. Generally, the surface hydroxide groups are written as identical diprotic weak acid groups which react as [15]:

$$\equiv SOH_2^+ \rightleftharpoons \equiv SOH + H^+ \tag{3}$$

$$K_{a1} = \frac{[\equiv SOH]\{H^+\}}{[\equiv SOH_2^+]} \tag{4}$$
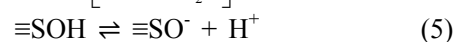
$$\equiv SOH \rightleftharpoons \equiv SO^- + H^+ \tag{5}$$

$$K_{a2} = \frac{[\equiv SO^-]\{H^+\}}{[\equiv SOH]} \tag{6}$$

1.3 Effect of Competition

The study of adsorption in multi-component systems shows a higher level of complexity than single radionuclide systems because of the solute-surface interactions and potential completion of metal ions with each other for sorption sites. The effect of ionic interactions on the sorption process may be represented by the ratio of the sorption capacity of one metal ion in the presence of the other metal ions Q_{mix} to the sorption capacity of same metal ion when it is present alone in solution Q_{sing} [5].

$\frac{Q_{mix}}{Q_{sing}} > 1$, the sorption is promoted by the presence of other metal ions, whereas if: $\frac{Q_{mix}}{Q_{sing}} = 1$, there appears to be no observable effect, and if: $\frac{Q_{mix}}{Q_{sing}} < 1$, it would indicate that sorption is suppressed by the presence of other metal ions in solution [5].

The above expressions make use of the maximum concentration of the metal bound, however, no information on the concentration of the metal remaining in solution is shown. The approached used in this paper is to compare the R_d in mixed and single systems, as the R_d are a true representation of the changes in solution and on the solid surfaces.

2. Experiment

The main constituents of silica-rich rock types such as granite are quartz, feldspars, and mica [16]. The sorption properties of intact rock will obviously depend on the constituents of the different individual components of the rock. Therefore, the present study did not only focus on granitic rocks, but also their individual components. The solids considered were Granite Adamellite (GA), Muscovite Mica (MM), Plagioclase Feldspar (PF) and Rose Quartz (RQ) were supplied by UK Geological Equipment as intact samples.

Firstly, the adsorbents were reduced in particle size. This size reduction was for the performance of batch equilibrium experiments, since sorption capacity is proportional to the total surface area available and the total surface area of non-porous particles is inversely proportional to the particle diameter [17]. In addition, the kinetics of processes controlled by diffusion in porous particles is directly related to particle size. Smaller adsorbents will require shorter equilibration times if any porosity is present [17]. Samples were crushed and pulverised using a ball mill and sieved to obtain a particle size range of 46 to 250 μm. 0.2 g of the pulverised samples were mixed with 40 cm^3 of non-active research-grade $NiCl_2$ or $EuCl_3$ solution (Aldrich), giving a solid-liquid ratio of 1:200. Three replicates of varying concentrations (1×10^{-13} to 1×10^{-4} mol dm^{-3}) of Ni^{2+} or Eu^{3+} were prepared and spiked with ^{63}Ni or ^{152}Eu to give an activity of 25.3 KBq per 40 cm^3 reaction vial. After adding the spike, the vials were shaken for between 5 to 7 days to reach steady-state. 1 cm^3 of the supernatant was removed, filtered (using 0.2 micron Whatman filter paper) and mixed with 10 cm^3 of High Flash-point Universal liquid scintillation cocktail and the samples counted in a TriCarb liquid scintillation counter after light adjustment. Control samples were taken to correct for wall and filter sorption, both of which were found to be negligible. All experiments were conducted at ambient laboratory temperature. The equilibration pH of the solid-solution mixtures were at *ca.* 7.5.

In the mixed systems, the activities of both Eu and Ni were adjusted to 5.3 KBq per 40 cm^3. The concentration of inactive Eu and Ni was also adjusted to be the same as that used in a single element system. The experiments were allowed to equilibrate for 7 to 10 days. Separation of the supernatant was carried out by filtration using 0.2 micron Whatman filter paper.

For experiments in which both ^{152}Eu and ^{63}Ni were present, ^{63}Ni was counted as described above while Eu was analysed using the Cobra (II) Auto gamma counting between 100 to 1500 KeV at 2 sigma. When analysing ^{63}Ni in the presence of ^{152}Eu, it was important that the Eu did not influence the counts for ^{63}Ni. This was possible because upon analysis the mixed system for Eu, it was found that the counts were mostly background, (230 to 250 CPM). The implication was that upon corrections for wall sorption all Eu was removed from solution. Thus, it was possible to analyse the ^{63}Ni neglecting the effect of Eu.

2.1 Effect of Surface Area

Sorption strongly depends on the specific surface area which varies significantly for different materials, especially for heterogeneous substances such as granitic rocks. Alonso and co-workers [18] have proposed the use of a new parameter R_{d*} to describe the dependence of sorption on surface area. This methodology has been adopted by the present study. The R_d calculated from static batch sorption is corrected for effective surface area to give R_{d*}. R_{d*} is defined as the R_d per surface area.

$$R_{d*} = \frac{Measured R_d}{BET Surface Area} \qquad (7)$$

BET surface areas used are mean values calculated from individual measurements for different granitic rocks and minerals.

2.2 Radionuclide Speciation in Solution

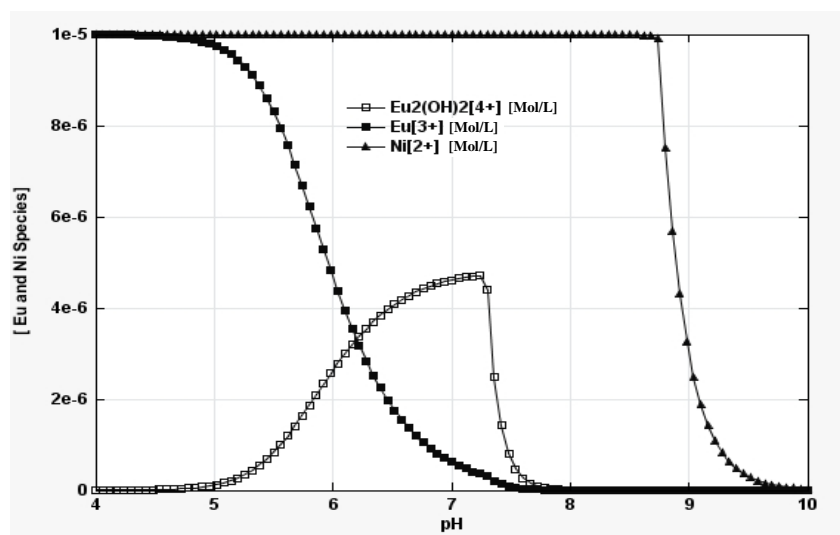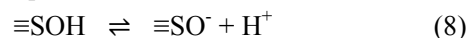JChess [19] speciation software indicated that Ni^{2+}

Fig. 1   Ni and Eu speciation in water calculated from JChess Code [19].

was the predominant species in solution over the concentration range of 1×10^{-5} to 1×10^{-14} mol·dm^{-3}. Below pH of *ca* 7.5, the major species, of Eu species were Eu$_2$(OH)$_2$$^{4+}$ and Eu^{3+}. The high positive charge on both species plays an important role for Eu sorption to negatively charged surfaces in solution (Fig. 1).

2.3 Proton Exchange Capacity Measurement

The proton exchange capacity (PEC) is an important input parameter for SCM modelling with the JCHESS speciation code [19]. Using Metrohm 857 Titrando auto-titrator, coupled with Metrohm 6.0258.010 pH probe and Metrohm 800Dosino dosimeter, the equivalent points for the granitic rock (Granite Adamellite,) and three granitic minerals (Rose Quartz, Plagioclase Feldspar and Muscovite Mica) were determined, after titrating with 2 M NaOH (NaOH pellets ≤ 1.0% sodium carbonate supplied from Sigma Aldrich were used, and purified a the method described by Sipos et al. [20], at a dosing rate of 0.1 cm^3 per minute, stirring at 60 rpm. The total number of protons released at the mineral-water inter phase depends on the hydrolysis of surface groups and the electrostatic interactions of hydrated cations with the mineral surface. The formation of negative surface charge on minerals corresponds to the concentration of protons

released from -OH functional groups by the reaction as shown by the equations below [21, 22].

$$\equiv SOH \;\rightleftharpoons\; \equiv SO^- + H^+ \qquad (8)$$

$$\equiv SOH + nH_2O.M^{Z+} \rightleftharpoons \equiv SO^- + nH_2O.M^{Z+} + H^+ \ (9)$$

where ≡SOH is a surface bound species responsible for proton exchange.

The surface charge that develops at silica surfaces corresponds to the concentration of protons released from silanol functional groups by Eqs. (8) and (9). The total surface charge does not distinguish between contributions made by both equations above. Thus the proton exchange capacity is thus, calculated by determining the difference of the total proton concentration and the free proton and hydroxyl concentrations from the potentiometric measurements and normalising to the surface area of the mineral in the titration vessel [21].

3. Results and Discussion

3.1 Modelling with Empirical Models

3.1.1 Granite Adamellite

Sorption isotherms for Ni and Eu on Granite Adamellite in both single and mixed systems are shown in Fig. 2. Best fit sorption models have been calculated and are shown in Table 1. The results showed a shift in the best-fit sorption model from Linear, for the single systems of Ni and Eu, to Langmuir for mixed systems
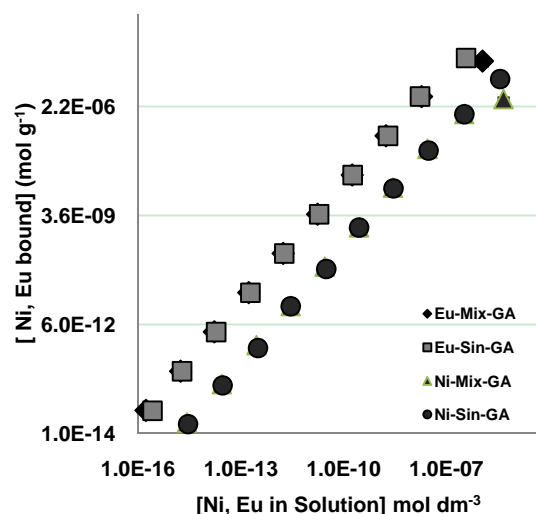
Fig. 2 log[Ni, Eu] bound as a function of log[Ni, Eu] in solution, in a Ni and Eu mixed system.

of Ni and Eu. Using the Linear model, the R_d values were derived from the gradients of the sorption isotherms of the concentration of metal bound as a function of the concentration of metal in solution. Table 1 shows the sorption parameters after fitting the sorption data to the Langmuir and the Linear models. The R_d values for Eu were 101.1 and 27.0 mL·g⁻¹ for single and mixed systems respectively. The results show that Eu sorption is suppressed in the presence of Ni. Thus, Ni could be competing for the free sites on the mineral surface. For Ni, the process was also suppressed in the presence of Eu in solution as shown by the R_d values of 0.7 and 1.3 mL·g⁻¹ obtained for Ni sorption to GA in mixed and single systems respectively. It is therefore, possible that the presence of two or more radionuclides in solution could suppress

Table 1   Sorption parameters for statistic batch sorption experiments for Eu and Ni sorption to granitic materials in mixed and single systems.

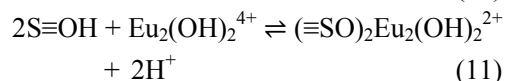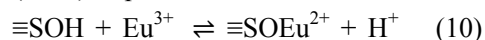|	Langmuir		Linear K$_d$		Mean R$_d$	
	K (dm⁻³·meq⁻¹)	R2	Rd (ml·g-1)	R2	*Rd (ml·g-1)	Rd* (ml·g-1m-2)
Eu mixed system						
Granite adamellite (GA)	6.4 × 106	0.99	27	0.99	205.4	7
Rose quartz (RQ)	-	0.43	0.45	0.98	1.2	110.0
Plagioclase feldspar (PF)	3.0 × 105	0.88	1.4	0.99	3.1	53.2
Muscovite Mica (MM)	-	0.79	147	0.99	195.1	89.0
Eu single system						
Granite adamellite (GA)	-	0.76	101	0.99	192.9	1700
Rose quartz (RQ)	1.1 × 105	0.99	1.3	0.89	93.5	2690
Plagioclase feldspar (PF)	3.5 ×105	0.99	10.8	0.97	85.1	1370
Muscovite mica (MM)	-	0.20	174	0.99	151.3	2220
Ni mixed system						
Granite adamellite (GA)	1.8 × 106	0.99	0.74	0.87	5.7	66.5
Rose quartz (RQ)	-	0.74	0.4	0.99	0.9	1.0
Plagioclase feldspar (PF)	-	0.04	0.6	0.99	0.5	0.3
Muscovite mica (MM)	2.2 × 107	0.99	16	0.97	349.9	205.8
Ni single system						
Granite adamellite (GA)	2.4 × 104	0.82	3.0	0.99	5.3	0.18
Rose quartz (RQ)	-	0.01	0.8	0.99	0.9	1.0
Plagioclase feldspar (PF)	-	0.02	61	0.99	1.0	0.6
Muscovite mica (MM)	7.7 × 106	0.96	1530	0.98	332.0	195.3

- means model is not applicable

the sorption of a particular radionuclide. The R_d values calculated for Ni is within the range 2.4 to 660 mL·g^{-1} as found by Ticknor [4], using different synthetic groundwaters and granite.

The main assumption of the Langmurian model is that the sorption process occurs with eventual saturation of sorption sites. The good fit of the sorption data to the Langmuir model for both Ni and Eu sorption in mixed systems would, suggest that there is a decrease in available sorption sites due to competition. For single systems containing Ni or Eu, sorption data fitted best to the Linear model shown by the fit parameter R^2 of 0.99 for Ni (Table 1).

Modelling the effect of competition as shown in Table 2 showed that the presence of Ni and Eu in a mixed system affected the sorption processes of each other, as shown by the enhancement/suppression factor calculated. Suppression factors of 0.2 and 0.3 are calculated for Ni and Eu respectively. The results indicate that in a multi-element system Ni immobilisation could be reduced compared to that of Eu in the same system. The reason for the suppressed sorption for Ni and Eu in mixed systems could be due to the arrangement of the metal ions on the surface. It is noted that the sorption mechanism changes from Linear to Langmuir for sorption in both systems. The Langmuir model permits a monolayer sorption mechanism with an upper bound to the amount of metal ions sorbed at the experimental conditions. The Linear model has no upper limit within the concentration. Despite the considerable knowledge acquired about radionuclide retention at the atomic scale, the prediction of radionuclide sorption at the whole-rock/mineral scale is still a challenge because of the mineralogical complexity of natural rocks [6].

Eu sorption to GA is greater compared to that of Ni as shown by R_d values (Table 1). The reason for this difference could be explained by the speciation of both metals in solution. Between pH 7 and 8, Ni remains in solution as Ni^{2+}. However, this is not the case with Eu,

the main Eu species in solution are Eu^{3+} and Eu$_2$(OH)$_2$$^{4+}$. The presence of the highly positively charge species results in enhanced sorption to the surface sites (SOH) as postulated below.

$$\equiv SOH + Eu^{3+} \rightleftharpoons \equiv SOEu^{2+} + H^+ \quad (10)$$
$$2S\equiv OH + Eu_2(OH)_2^{4+} \rightleftharpoons (\equiv SO)_2Eu_2(OH)_2^{2+} + 2H^+ \quad (11)$$

3.1.2 Rose Quartz

Quartz is an important mineral in granitic rocks and has been studied in an attempt to understand the different sorption properties of the constituent minerals of granitic rocks. Fig. 3 shows the sorption isotherms for Ni and Eu sorption in mixed and single system. The sorption isotherm for Eu sorption in Ni-free system showed saturation of sorption sites at concentration 6.0 $\times$ 10^{-6} mol dm^{-3} with data fitting best to the Langmuir model ($R^2 = 0.99$). Fitting the data to the Linear model, sorption data showed good fits for Eu and Ni sorption in a mixed system, and for Ni sorption in a Eu-free system (Sorption parameters are shown in Table 1).

No change in the best-fit sorption model was observed for Ni sorption in both systems, however, a change from Langmuir (Single system) to Linear (Mixed system) is observed for Eu sorption as shown by data in Table 3. Modelling the effect of competition
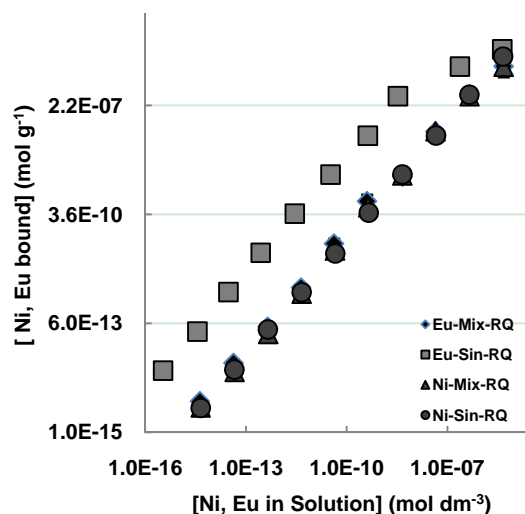

Fig. 3 Log[Ni, Eu] bound as a function of log[Ni, Eu] in solution, in a Ni and Eu mixed system.

Table 2 Sorption parameters for statistic batch sorption experiments for Eu and Ni sorption to granitic materials in mixed and single systems. Data obtained from modelling using the Linear model.

	Eu				Ni			
	R_{dsing} (ml g^{-1})	R_{dmix} (ml g^{-1})	R_{dmix} /R_{dsing}	Remarks	R_{dsing} (ml g^{-1})	R_{dmix} (ml g^{-1})	R_{dmix} /R_{dsing}	Remarks
Granite adamellite	101.1	27	0.3	suppressed	3.0	0.7	0.2	suppressed
Rose quartz	1.3	1.0	0.7	suppressed	0.8	0.4	0.5	suppressed
Plagioclase feldspar	10.8	1.4	0.1	suppressed	0.8	0.6	0.8	suppressed
Muscovite mica	174	147	0.8	suppressed	61	16	0.3	suppressed

Table 3 Variation of sorption models, for Eu and Ni sorption to different granitic materials in mixed and single systems.

Sample	Eu$_{Sing}$	Eu$_{Mix}$	Ni$_{Sing}$	Ni$_{Mix}$
Granite adamellite (GA)	Linear	Langmuir	Linear	Langmuir
Rose quartz (RQ)	Langmuir	Linear	Linear	Linear
Plagioclase feldspar (PF)	Linear	Linear	Linear	Linear
Muscovite mica (MM)	Linear	Langmuir	Linear	Linear

showed that Eu and Ni sorption was suppressed in both mixed and single systems, as shown by the calculated suppression factors of 0.8 and 0.5 for Eu and Ni respectively. The results show Ni sorption in the presence of Eu is lower than that of Eu in terms of the calculated R_d. R_d values were calculated as 1.3 and 1.0 mL·g^{-1} for Eu in single and mixed systems respectively while for Ni, the R_d was 0.8 and 0.4 mL·g^{-1} for single and mixed systems respectively. The fact that Ni is weakly sorbing to quartz has been shown by Ticknor [4], who reported R_d values in the range 0.05 to 3.6 mL·g^{-1} for Ni sorption to quartz in different synthetic groundwater systems. Cornell and Aksoyoglu [23] had shown earlier (1992) the low sorption ability of quartz. They obtained an R_d of 1.6 mL·g^{-1} for an initial metal concentration of 1.1×10^{-7} mol·dm^{-3}. The results obtained in this work for Ni sorption in a single system, differ from previous work mentioned, however, sorption of Ni in a mixed system gave R_d value (11 mL·g^{-1}) in the range determined by the authors mentioned above. The mean R_d values and the R_d values obtained from the linear model are in the range 0.50 to 2 mL·g^{-1}, which is in good agreement with values measured by previous authors as seen above.

3.2 Modelling with Surface Complexation Models

Mechanistic models have intrinsic advantages over empirical values when trying to justify sorption values chosen for safety assessment analysis and when it is necessary to predict sorption under a variety of different conditions [13]. In surface complexation models, ions and individual functional groups on the surface are considered to react to form coordination complexes and ion pairs [14]. The general equation for the interaction of the metal ion with an oxide substrate may be expressed by the following equation [24, 25].

$$M^{n+} + x(\equiv SOH) = [M(\equiv SOH)_x]^{(n-x)+} + xH^+ \quad (12)$$
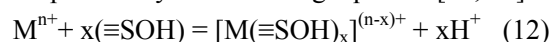
Using the JChess code, with the input parameters shown in Table 4, modelled values were fitted to experimental data. LogK values for the complexation of metal to surface sites at the mineral surfaces were determined as shown in Table 4 for mixed and single systems. Complexation constants give an indication of the strength of the metal-solid complex and are analogous to the Langmuir constant K or the R_d. In this study, a parallel comparison is made for the non-electrostatic correction models (Linear) and the electrostatic correction model (using the double layer theory for electrostatic correction term) [19].

3.2.1 Quartz-Ni-Rose Quartz-Single System

Correlating experimental data, to values obtained from the model, showed that the experimental data were in agreement with the model as shown in Fig. 4. The SCM did not agree with experimental data at concentrations greater 1×10^{-6} mol·dm^{-3}. At 1×10^{-6} mol·dm^{-3}, saturation of sorption sites is attained for the

Table 4 Surface complexation parameters for Ni and Eu sorption to different granitic minerals.

Solid-volume ratio	0.005 g·mL^{-1}					
Concentration of metal	1×10^{-14} to 10^{-4} mol·dm^{-3}					
BET surface area	Quartz (0.85 m^2·g^{-1}) Feldspar (1.6 m^2·g^{-1}) Mica(1.7 m^2·g^{-1})					
Particle radius	Quartz (1.4 nm) Feldspar (2.7 nm) Mica (2.8)					
Solution pH	7.5					
Dissolution	disabled					
Precipitation	disabled					
Temperature	Room temperature					
Sample	Surface complexation	System	Exchange capacity (μmol·m$^{-2)}$	Complexation constant	Concentration of surface sites (mol·g^{-1})	
Quartz	≡Quartz-O-Ni$^+$ ≡(Quartz-O)$_2$Ni	Ni-single system	5.88	LogK = -4 LogK = -5.2	8.2×10^{-7} 70×10^{-11}	
	≡Quartz-O-Eu^{2+} (≡Quartz-O)$_2$-Eu$^-$	Eu single system		LogK = -6 LogK= -10	5.6×10^{-8} 1.4×10^{-8}	
Feldspar	≡Feldspar-O-Ni$^+$ (≡Feldspar-O)$_2$-Ni	Ni-single system	3.14	LogK = -3 LogK = -3.2	4.5×10^{-16} 1.7×10^{-22}	
	≡ Feldspar -O-Eu^{2+} (≡Feldspar -O)$_2$-Eu$^-$	Eu single system		LogK = -2.5 LogK = -2.5	8.5×10^{-8} 3.8×10^{-13}	
Mica	≡Mica-O-Ni$^+$ (≡Mica-O)$_2$-Ni	Ni-single system	74	LogK = -3 LogK = -3	1.7×10^{-8} 7.0×10^{-6}	
	≡Mica-O-Eu^{2+} (≡Mica-O)$_2$-Eu$^-$	Eu single system		LogK = -2.1 LogK = -2.1	1.5×10^{-7} 1.3×10^{-9}	
	≡Mica-O-Ni$^+$ (≡Mica-O)$_2$-Ni	Ni-Mixed system		LogK = -4 LogK = -4	2.0×10^{-7} 1.0×10^{-14}	
	≡Mica-O-Eu^{2+} (≡Mica-O)$_2$-Eu	Eu single system		LogK = -5 LogK = -5	1.4×10^{-7} 6.7×10^{-10}	
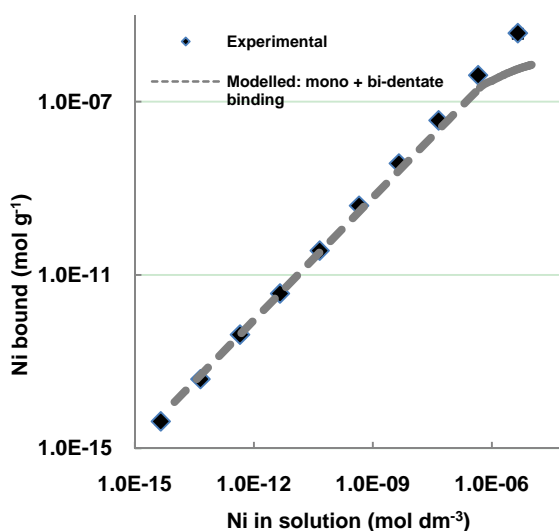
Fig. 4 Log-log sorption isotherms for Ni sorption to rose quartz.

model. Based on the calculated concentration of sorption sites, the surface complexation of Ni to quartz, in a single system is predominantly monodentate bonding.

3.2.2 Ni and Eu Sorption to Plagioclase Feldspar-Single System

The SC model for Plagioclase Feldspars showed a similar pattern to that of RQ. Results from JChess modelling (JCM) showed sorption to Plagioclase Feldspar occurred by the formation of monodentate complex with Ni (Fig. 5).

Fig. 6 shows poor fit between experimental data fitted with the SC model at lower concentrations (< 1 $\times 10^{-10}$). The reasons for the deviation between the model and the experimental can be attributed to the purity of the solid sample (Plagioclase Feldspar). Due to limited knowledge of the exact purity of the samples, the mineral sample can not be considered pure as compared to that used by the model. The presence of impurities in the sample can affect the sorption profile of the same mineral used by the model, also, due to the complexity of Eu speciation in water, the interaction of the different species with the solid can complex
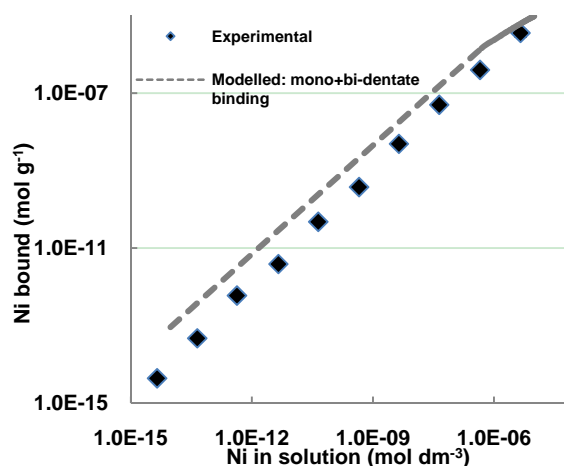
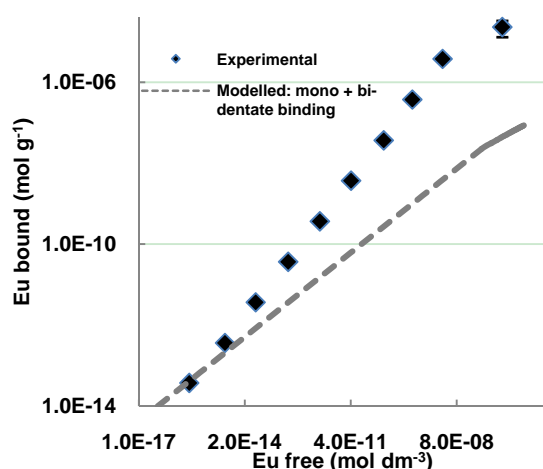**Fig. 5   Log-log sorption isotherms for Ni sorption to plagioclase feldspar in Eu-free system.**

Fig. 6   Log-log sorption isotherms for Eu sorption to plagioclase feldspar.

Resulting to deviation from theoretically defined sorption profiles.

3.2.3 Muscovite Mica-Ni single and Mixed Systems

SC modelling in mixed and single systems is shown in Figs. 6 and 7. From the results, the JCM fitted the experimental model with saturation attained at higher metal loading.

3.3   Contextualising   Empirical   and   Surface Complexation Models

An analogy has been drawn between the calculated r_d and the surface complexation constant logK, based on parameters shown in Tables 1 and 4. Results   from
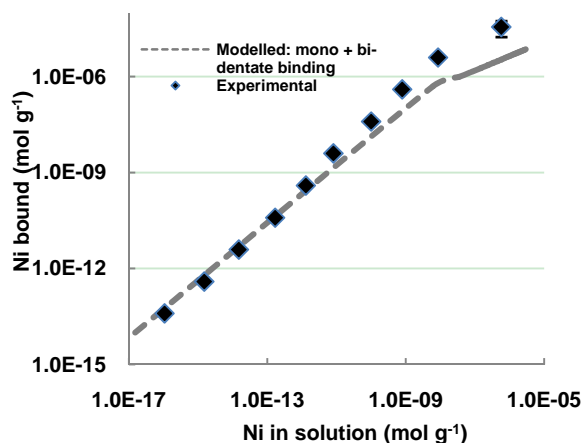

Fig. 7   Log-log sorption isotherms for Ni sorption to Muscovite mica.

SCM and the empirical models showed a general relationship. For most of the systems studied the higher the sorption capacity the higher the surface complexation constant. Considering Ni sorption to mica, a LogK value of -2.1 ($R_d = 61$ cm^3 g^{-1}) and -4 ($R_d = 16$ cm^3 g^{-1}) were obtained for Ni sorption in single and mixed systems respectively (Table 5).

3.4 Eu and Ni Sorption Summary to Granitic Rocks and Minerals

When comparing sorption capacities of different samples, the effect of   the   net   surface   area   of the

Table 5   Surface complexation constants and R_d values for Ni and Eu sorption in mixed and single systems showing the general variation between the R_d and the SC constants.

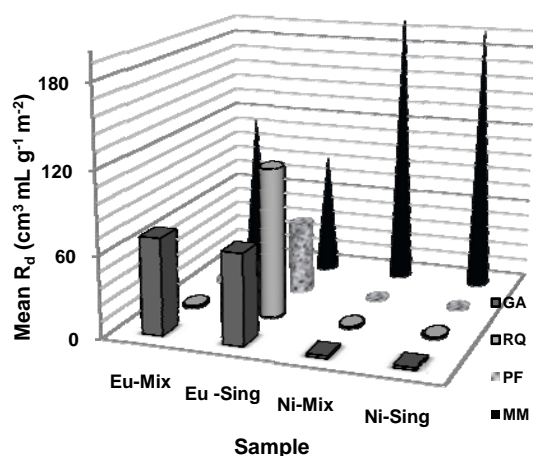| Sample	System	Complexation constant	R_d (mL g^{-1})
Quartz	Ni-single system	LogK = -4 LogK = -5.2	0.8
	Eu single system	LogK = -6 LogK= -10	1.3
Feldspar	Ni-single system	LogK = -3 LogK = -3.2	0.8
	Eu single system	LogK = -2.5 LogK = -2.5	1.4
Mica	Ni-single system	LogK = -3 LogK = -3	61
	Eu single system	LogK = -2.1 LogK = -2.1	174
	Ni-Mixed system	LogK = -4 LogK = -4	16
	Eu mixed system	LogK = -5 LogK = -5	147

Fig. 8   Variation of R_d for Eu and Ni sorption to different granitic materials in mixed and single systems showing effect of the effective surface area on the sorption capacity.

mineral/rock particles exposed in solution is important. A comparative analysis of the granitic materials studied is shown in Fig. 8 taking into consideration the R_d values corrected for surface area. It can be seen that the major constituent in the retardation of radionuclide in granitic rocks is mica. However, the high sorption values of the rocks could not be attributed solely to electrostatic sorption process, intermolecular diffusion and diffusion into dead end pores contribute to the bulk sorption.

4. Conclusions

The following deductions could be made based on the application of the Linear model to the experimental data: Eu and Ni sorption is, in terms of R_d corrected for surface area affect in the following order.

Eu_{mix}: MM > GA > PF > RQ,

Eu_{sing}: MM > GA > PF > RQ

Ni_{mix}: MM > GA > PF > RQ

Ni_{sing}: MM > RQ > GA > PF

From the ranking above it is evident that sorption to MM plays a significant role in the overall bulk sorption of granitic samples. Results showed a relationship between R_d and surface complexation constants (The higher the R_d the high the surface complexation constant). Fitting data to the Linear model showed that

sorption of Ni and Eu in mixed systems was suppressed for GA, MM, and RQ, while no effect was observed for PF. Using JChess code, it was possible to attribute logK values to sorption processes in the different systems. Results thus far indicate that the effect of multi-element sorption cannot be disregarded in safety assessments of radionuclides in the far-field.

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