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Modelling the Sorption of $^{63}$Ni to Granitic Materials:
Application of the Component Additive Model

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Abstract: The component additive modelling approach is based on summing the results from models already calibrated with pure mineral phases. The summation can occur as the sum of results for thermodynamic surface speciation models or as the sum of pseudo-thermodynamic models for adsorption on individual mineral phases. Static batch sorption experiments of $^{63}$Ni are with different granitic rocks and component minerals. XRD analyses have been used to calculate the percentage mineralogical composition of the granitic rocks. Sorption data has been modelled using non electrostatic correction models to obtain $R_d$ for the granitic rocks and mineral. $R_d$ values for the granitic rocks predicted from the component additive model have been compared to experimental values. Results showed that predicted $R_d$ values for granite adamellite, biotite granite and rapakivi granite were identical to the experimentally determined values, whereas, for graphic granite and grey Granite, the predicted and experimentally determined $R_d$ values were much different. The results also showed a greater contribution to the bulk $R_d$ by feldspar while quartz showed the least contribution to the $R_d$.

Key words: Radionuclide sorption, $^{63}$Ni, component additive model.

1. Introduction

In several countries, Sweden and Finland, low permeability crystalline rocks (e.g. Granite) are under consideration as potential hosts for radioactive waste repositories. In such formations groundwater flow occurs predominantly in specific fractures rather than being a general porous flow through the entire rock matrix. In the evaluation of radionuclide retardation therefore, the effect of sorption on secondary minerals must be clearly considered. Despite the enormous amount of efforts to understand the possible behaviour of escaped radionuclides, great uncertainty remains mostly highlighted by the problem of time. Time constitutes one of the greatest limitations into understanding future scenarios because one integrated experiment that captures all the relevant mechanisms for the times of interest is not possible. It needs to understand all important processes and how they integrate over > 100,000 years [1]. Geological matrices surrounding a waste repository are expected to act as natural barrier to both water flow and radionuclide migration. Granite rock formations as the host media and bentonite alone or its mixture with sand quartz or crushed granite as the backfill are the favourite materials [2]. Granite which is the most common igneous rock appears to be an excellent candidate for a repository area [3, 4]. Physical properties lending uniqueness to granite are porosity/permeability. Granite has almost negligible porosity with high thermal stability. Granite is impervious to weathering from temperature and even from the air borne chemicals and has very small co-efficient of expansion. Many studies on granite reveal the main composition to be quartz, plagioclase feldspars and Biotite [5-8]. Granitic rocks are metagranite with high content of quartz with high thermal conductivity and high mechanical strength and rock stress. The rocks contain tectonic plates with

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gentle sloping sub vertical zones with different fracture domains [9].

1.1 Objectives

The Rd concept when applied to describe the bulk sorption properties of granite can be very sensitive to the composition of heterogeneous samples. The overall bulk property may be expected to be the summation of the bulk properties of the individual minerals that make up the granite sample. The component additivity approach [10] is based on summing the adsorption by the individual component minerals of sample to obtain a measure of the total sorption of the bulk sample. The summation can occur as the sum of results from thermodynamic surface speciation models or as the sum of pseudo-thermodynamic models for adsorption on individual mineral phases. Pseudo-thermodynamic models include models without electrostatic correction terms, sometimes called NEMs (non-electrostatic models non-electrostatic models). Thus, this work will test if the bulk Rd is a summation of the bulk properties of the individual minerals. Rd values were determined for different granitic rocks and minerals, and the CAM (component additive model) applied to the sorption data. Sorption data has been modelled using empirical models to obtain Rd values and sorption parameters.

1.2 Nickel

The isotope 63Ni is an artificial radionuclide. The presence of 63Ni in the environment results mainly of the activities of man. 63Ni is formed by neutron capture of stable 62Ni. 63Ni is a pure β-emitter with a half-life of 100.1 years [11]. Naturally occurring nickel is composed of 5 stable isotopes: 58Ni, 60Ni, 61Ni, 62Ni and 64Ni with 58Ni being the most abundant (68.077% natural abundance). Eighteen radioisotopes have been characterized with the most stable being 59Ni with a half-life of 76,000 years, 63Ni with a half-life of 100.1 years, and 56Ni with a half-life of 6.077 days. All of the remaining radioactive isotopes have half-lives that are less than 60 hours and the majority of these have half-lives that are less than 30 seconds. Nickel can be transported as particles released into the atmosphere or as dissolved compounds in natural waters [12]. Three main sources are responsible for the presence of 63Ni in the environment. These sources are nuclear weapon tests, radioactive effluents from nuclear installations and accidental releases of nuclear power plants (e.g. Chernobyl) [11]. 63Ni is a weak beta-emitting radionuclide of $E_{\text{max}} = 67$ keV. It exists in the coolant water of nuclear power reactor and is formed by neutron capture of nickel released from steel piping and so on due to corrosion. It is included in the list of low-level long-lived radioactive waste from nuclear power reactor [13].

1.3 Sorption Models

1.3.1 Linear $K_d$ Model

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 to the amount of the adsorbate remaining in solution at equilibrium. Values for $K_d$ not only vary greatly between contaminants, but also vary as a function of aqueous and solid phase chemistry [14]. Some adsorption studies are conducted in a systematic fashion to evaluate the effects of various parameters (such as pH, and ionic strength) on $K_d$. The results of a suite of experiments evaluating the effect of contaminant concentration on adsorption, while temperature is held constant, are called an “adsorption isotherm”. Among all phenomena governing the mobility of substances in aqueous porous media and aquatic environments, the transfer of substances from a mobile phase (liquid or gaseous) to a solid phase is a universal phenomenon. That is the reason why 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 [15]. 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 [16, 17]. However, isotherms give a general view of the distribution of radionuclides between the solid-liquid phases. Isotherm models are used to describe the case where sorption relationships deviate from linearity. For many short-lived radionuclides, the mass present never reaches quantities large enough to start loading surface adsorption sites to the point that the linear $K_d$ relationship is not accurate. However, 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 partition (or distribution) coefficient, $K_d$, is expressed mathematically 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 ($C$).

$$K_d = \frac{Q}{C}$$

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. (2) with $V$ being the volume of solution (dm³), $M$ 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 [15]. The use of a distribution coefficient in describing nuclide migration requires some assumptions:

- The sorption process during migration is reversible;
- The ratio of solute concentration between the solid and solution phases also remains constant [7].

A more realistic approach to the concept of $K_d$, which is a thermodynamically determined value, is the $R_d$ (Distribution ratio) of the solute between the solid and liquid phases, at the stated experimental conditions and it is not thermodynamically determined. This paper thus makes use of $R_d$ rather than $K_d$.

1.3.2 The Freundlich Isotherm

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, Eq. (3) [18, 19] is one of the various models that have been employed for the study of metal adsorption. It expresses relation between the adsorbed quantity $Q$ and the remained solute concentration.

$$Q = K C^{\frac{1}{n}}$$

The equation is expressed in the linear form as:

$$\log Q = \log K + \frac{1}{n} \log C$$

where, $Q$ is the concentration of metal sorbed (mol·g⁻¹), $C$ is the concentration of metal in the equilibrium solution (mol·dm⁻³), $K$ (dm³·g⁻¹) and $n$ (dimensionless) is a parameter that describes the heterogeneity of the sorption sites. A graph with $\log C$ as x-axis versus $\log Q$ as y-axis provides a line of slope $1/n$ and intercepts the y-axis at $\log K$. According to the Freundlich equation, the isotherm does not reach a plateau as $C$ increases.

As $1/n$ tends to unity the surface becomes more uniform. Intact and crystalline minerals have higher $1/n$ values than pulverised and non-crystalline minerals. The constants are usually derived from a
plot of sorbed concentration \((Q)\) against concentration in solution \((C)\). The Freundlich equation assumes that the surface of the solid is covered with a monolayer of sorbed species. The monolayer is not covered by any other layer. The Freundlich model does not account for finite adsorption capacity at high concentrations of solute [20].

1.3.3 Langmuir Isotherm

Sorption by the Langmuir assumes the solid has a limited adsorption capacity \(Q_{\text{max}}\). All the adsorption sites:

- Adsorption occurs up to the extent of one monolayer;
- All adsorption sites are identical;
- Occupation of a site is independent of the occupation of neighbouring site(s);
- The temperature is constant;
- The surface is uniform and homogeneous;
- The process is reversible;
- Each site retains one molecule of the given compound;
- All sites are energetically and sterically independent of the adsorbed quantity [21].

The reversibility/irreversibility of the sorption process is of fundamental importance for the understanding of the fate of radionuclides in the geological systems. If the process is reversible, the same isotherm should be valid for sorption and desorption under the same experimental conditions [22]. The Langmuir Model equation takes the form as shown in Eq. (5) [23]:

\[
Q = \frac{K b C}{1 + K C}
\]  

(5)

The linearised form of the equation is represented as [24]

\[
\frac{C}{Q} = \frac{1}{K B} + \frac{C}{B}
\]  

(6)

where, \(b\) is the maximum adsorption capacity of the substrate \((\text{mol} \cdot \text{g}^{-1})\) and \(K\) is a constant representing the strength with which the solute is bound to the substrate \((\text{dm}^{3} \cdot \text{meq}^{-1})\). Values of \(b\) and \(K\) can be determined by plotting the linearised Eq. (6) [24].

The Freundlich and the Langmuir models have been used in describing results that showed deviations from a linear distribution. Empirical models like those mentioned are mathematical description of the experimental data without any particular theoretical basis [25]. Because adsorption isotherms at very low solute concentrations are often linear, either the Freundlich isotherm with \(n\) equalling 1 or the Langmuir isotherm with \(KC\) much greater than 1 fits the data. The value of \(n\) for the adsorption of many radionuclides is often significantly different from 1, such that nonlinear isotherms are observed. In such cases, the Freundlich model is a better predictor than the Langmuir model.

1.4 The Component Additive Model

The component additive modelling approach is based on summing the results from models already calibrated with pure mineral phases. Thus, the CA approach is a predictive tool [26] rather than for safety case assessment purposes. Extending the models to natural samples necessitates certain approximations and modifications. For example, the assumption is usually made that adsorption occurs through interaction with the hydroxyl groups at the edges of the mineral particles and constituent minerals are uncoated and do not interact [26]. Considering granitic rocks, the \(K_d\) for a rock type with different component minerals will be a contribution from the \(K_d\) value of independent minerals constituting the rock. Granite has three main mineral components (feldspars, quartz and Mica). The fraction of a mineral in the main rock and the molecular structure of the mineral will determine how much effect each mineral has to the overall \(K_d\) value of the rock type. The distribution ratio of a rock type is given by: \(K_d = C_{\text{soln}}/C_{\text{sat}}\) as earlier defined. If the additivity rule is applicable for the rock type, the distribution ratio based on the rock type is
expressed by a linear combination of $K_d$ and the rock mineral component by Eq. (2) [20].

$$K_d = \sum_i K_{di} \times p_i \tag{7}$$

$K_{di}$ is the distribution ratio for the $i$-th component of the rock type and $p_i$ is the content of the $i$-th component.

2. Experiment

Analytical grade water with purity up to 18.2 MΩ produced from a Barnstead NANOpure water purification system was used throughout. Analytical grade NiCl$_2$ was supplied from Sigma Aldrich as anhydrous, powder with 99.99% trace metals basis. $^{63}$Ni isotope was provided by the Radiochemistry Laboratory at Loughborough University supplied from Eckert and Ziegler Isotopes Products Valencia California, with original activity at 74 mBq. Sample separation was performed by filtration using Whatman filters (0.2 μm) and by centrifugation at 6,000 rpm for 30 min. The liquid scintillation cocktail used was Goldstar (Meridian, Surrey, UK). All rock and mineral samples were supplied by UK Geologist Equipment as intact samples (Granite Adamellite—GA, Biotite Granite—BG, Rapakivi Granite—RG, Grey Granite—GrG, and Graphic Granite—GG). The component minerals include feldspar, quartz and mica. Sorption phenomena that took place over a period of less than one year were considered. During this time both fast reactions that involve oxidation-reduction reactions and physical diffusion into the micropores of the sorbents can be observed, and long-term process such as weathering of the solid phase and the re-distribution of the sorbed species have yet to occurred, as such it can be assumed that the physiochemical nature of the rock particles remained the same during this time.

2.1 Preparation of $^{63}$Ni Solutions

An original $^{63}$Ni stock solution of known activity (926, 1.1 mBq) was provided in the Radiochemistry Laboratory of the University (High Level Lab). From this stock 30 μL were pipetted, using a 50 μL pipette, into a 100 cm$^3$ volumetric flask, and deionised water added to the 100 cm$^3$ mark. After shaking the solution was kept for 24 h to equilibrate. This formed a new working stock (926-J). The activity of the stock solution was 0.2 kBq·cm$^{-3}$, so that 0.1 cm$^3$ of the spike solution gave approximately 1,200 counts·min$^{-1}$. Upon adding the spike the vials were allowed to shake for between 5 to 7 days. The supernatant, 1 cm$^3$ was mixed with 10 cm$^3$ of scintillation cocktail (High Flash-point, Universal LSC cocktail) and samples counted in a Tri Cab liquid scintillation counter. The counts for 0.1 cm$^3$ of the new stock were taken as counts for the standards to which other measurements were compared. The standard was counted for every set of experiments in order to present the same set of experimental conditions for the standard and the actual samples. Background corrections to the measured counts were made by counting blank samples without added radioactivity. The measured value for the blank sample (sample without added radioactivity mixed with liquid scintillation cocktail) is then subtracted from the measured counts of the sample. Corrections for wall and filter sorption were made by washing the filters and vials with nitric acid. The solution with the leached metal was counted. The results obtained from filter sorption were less than 1% of the total counts of the sample.

All rock and mineral samples were supplied by UK Geologist Equipment as intact samples. Samples were crushed and pulverised using a bore mill and sieved to obtain a particle size range of 46 to 250 μm. 0.1 g of the pulverised samples were mixed with 20 cm$^3$ of non active NiCl$_2$ solution. Three replicates of each of varying concentration ($1 \times 10^{-14}$ to $1 \times 10^{-4}$ mol·dm$^{-3}$) of Ni$^{2+}$ were prepared. $^{63}$Ni stock solution was prepared and allowed to equilibrate over 24 h and the activity of the solution was diluted to 0.2 kBq·cm$^{-3}$ so that 0.1 cm$^3$ of the spike solution should give approximately 1,200 counts·min$^{-1}$. Upon adding the spike the vials were allowed to shake for ca. 7 days.
cm$^3$ of the supernatant was mixed with 10 cm$^3$ of scintillation cocktail (High Flash-point, Universal LSC cocktail) and samples counted in a TriCarb liquid scintillation counter.

Sample separation was performed by centrifugation at 6,000 rpm for 30 min. The separated sample was mixed with 20 cm$^3$ of DI water and allowed to shake for between 5 and 7 days, upon which 1 cm$^3$ of the supernatant was filtered and counted in the energy range of 0 to 67 keV at 2$\sigma$ at a counting time of 20 min per sample. Three replicates of each stable Ni solution at each concentration were prepared. Vials containing stable Ni$^{2+}$ solutions were also prepared and counted for background corrections. The pH of all the samples was monitored so that the equilibration pH was ca 7.5. At this pH, the dominant Ni species is Ni$^{2+}$ as shown in Fig. 1.

2.2 Characterization of Granite Samples

The mineralogical composition of the different granitic rocks used was characterized at XRD laboratory of the British Geological Survey [27]. The aim was to confirm samples were of granitic origin, based on the elemental composition as shown in Fig. 2. A representative $c.25$ g sub-sample of each ground sample was removed for clay mineral analysis. The remaining material was tema-milled to < 125 $\mu$m in the BGS Sample Preparation Facility. In order to provide a finer and uniform particle-size for powder XRD analysis, a 4.5 g portion of each tema-milled sample was micronised under deionised water for 10 minutes with 10% (0.5 g) corundum (American Elements-PN:AL-OY-03-P). The addition of an internal standard allows to validate quantification results and also to detect any amorphous species present in the samples. Corundum was selected as its principle XRD peaks are suitably remote from those produced by most of the phases present in the samples. The samples were then spray-dried following the method and apparatus described by Hillier [28]. The spray-dried materials were then frontloaded into a standard stainless steel sample holders for analysis. XRD analysis was carried out using a PANalytical X’Pert Pro series diffractometer equipped with a cobalt-target tube, X’Celerator detector and operated at 45 kV and 40 mA. Following identification of the mineral species present in the samples, mineral quantification was achieved using the Rietveld refinement technique [29], using PANalytical Highscore Plus software. This method avoids the need to produce synthetic mixtures and involves the least squares fitting of measured to calculated XRD profiles using a crystal structure databank.

2.3 XRD Results for the Different Granitic Rocks

The results of quantitative powder XRD analyses are summarised in Table 1. Powder X-ray diffraction
Table 1  Summary of quantitative whole-rock XRD analysis.

<table>
<thead>
<tr>
<th>Mineralogical percentage composition</th>
<th>kaolinite</th>
<th>K-feldspar</th>
<th>'mica'</th>
<th>plagioclase</th>
<th>quartz</th>
</tr>
</thead>
<tbody>
<tr>
<td>GG</td>
<td>&lt; 0.5</td>
<td>49.4</td>
<td>0.5</td>
<td>21.6</td>
<td>28.3</td>
</tr>
<tr>
<td>GA</td>
<td>nd</td>
<td>32.9</td>
<td>3.1</td>
<td>25.7</td>
<td>38.1</td>
</tr>
<tr>
<td>BG</td>
<td>nd</td>
<td>17.2</td>
<td>7.4</td>
<td>40.0</td>
<td>28.1</td>
</tr>
<tr>
<td>GtG</td>
<td>nd</td>
<td>22.6</td>
<td>4.3</td>
<td>34.4</td>
<td>38.6</td>
</tr>
<tr>
<td>RG</td>
<td>&lt; 0.5</td>
<td>32.1</td>
<td>1.6</td>
<td>29.2</td>
<td>33.3</td>
</tr>
</tbody>
</table>

nd = not detected, ‘mica’ = undifferentiated mica species including muscovite, biotite, illite and illite/smectite etc. [27]. Further elemental characterisation and identification of the granite samples were carried out using energy dispersive spectroscopy. The elemental composition of elements present confirmed samples to be granites. GG = Graphic Granite, GA = Granite Adamellite, BG = Biotite Granite, GtG = Grey Granite, RG = Rapakivi Granite.

3. Results and Discussion
3.1 Modelling $^{63}$Ni Sorption

The distribution of trace concentrations of ionic species between solid and aqueous phases in groundwater is generally considered to be a linear relationship, with the process governed by the partition law. However, as the concentrations of ionic species in groundwater increase, the partition law becomes less valid in describing the distribution between the solid and the aqueous phases. Thus, different models such as those studied below are commonly used in order to take into consideration deviations that might be observed.

3.1.1 $^{63}$Ni Sorption to Granitic Rocks and Minerals by the Langmuir Model

Data obtained from static batch sorption experiments with GG (graphic granite), RG (rapakivi granite), (OF) orthoclase feldspar and (PF) plagioclase feldspar were fitted to different empirical models, the best fit sorption model was used to analyse the data. The best fit model is statistically determined as the root mean square value for a set of data. These values are shown as $R^2$ in the different sorption parameter tables. Results showed sorption occurred with saturation of sorption sites (Fig. 3) with metal loading above $5 \times 10^{-7}$ mol·dm$^{-3}$.

For PF, saturation was attained at a lower Ni concentration compared to GG, RG and OF. Saturation of sorption sites is also evident from the decrease in $R_d$ with metal loading above $5 \times 10^{-7}$ mol·dm$^{-3}$. At low metal concentration the sorption isotherm is linear with constant $R_d$. The $R_d$ decreases at higher metal concentration. Fig. 4 is a plot of $R_d$ as a function of metal concentration in solution.
Table 2 shows the sorption parameters, and $R_d$ values corrected for surface area effect. The differences in the results for GG and RG can be due to the inherent difference in the constitution of the component minerals. However, taking into consideration the effect of surface area, $R_d$ values were in the range 2 to 7 cm$^3$·g$^{-1}$·m$^{-2}$ as shown in Table 2. Based on the fact that most $R_d$ values in literature are not quoted in terms of surface area, it is not possible to make comparisons. However, Ticknor [31] obtained $R_d$ for granite from Lac du Bonnet batholith in Manitoba, using different synthetic groundwaters in the range 2.4 to 660 cm$^3$·g$^{-1}$. $R_d^*$ is obtained from corrections for effective surface area of the different samples. $B$ is the Langmuir parameter also known as the adsorption capacity relating to the maximum amount of sorbable cations. Application of the Langmuir model to sorption data is often done with the calculation of the favourability factor $F$ [32] (also known as the separation factor [33]) as:

$$F = \frac{1}{1 + KC_e} \quad (8)$$

where, $K$ is the adsorption constant (dm$^3$·mol$^{-1}$), $C_e$ is the amount in solution in mol·dm$^{-3}$. Values for $F$ were calculated within the range 0 < $F$ < 1.0, confirming the saturation of the sorption sites.

This value as shown in Table 3 is calculated by using the gradient and the intercept of the linearised Langmuir Eq. (6) $K$, which is a measure of the binding strength for the sorption process. This relates to the strength with which the metal ions are held in a monolayer.

### Table 2 Sorption parameters for $^{63}$Ni sorption to granitic rocks and minerals

<table>
<thead>
<tr>
<th>Sample</th>
<th>$B$ (mol·g$^{-1}$)</th>
<th>$K$ (dm$^3$·meq$^{-1}$)</th>
<th>$R^2$</th>
<th>Mean $R_d$ ± SD (cm$^3$·g$^{-1}$)</th>
<th>$R_d^*$ (cm$^3$·g$^{-1}$·m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphic Granite—GG</td>
<td>$1.59 \times 10^{-5}$</td>
<td>$1.23 \times 10^6$</td>
<td>0.99</td>
<td>$17.2 \pm 2.6$</td>
<td>$6.1 \pm 0.9$</td>
</tr>
<tr>
<td>Rapakivi Granite—RG</td>
<td>$1.89 \times 10^{-5}$</td>
<td>$3.57 \times 10^5$</td>
<td>0.98</td>
<td>$6.64 \pm 0.85$</td>
<td>$2.3 \pm 0.2$</td>
</tr>
<tr>
<td>Orthoclase Feldspar—OF</td>
<td>$1.46 \times 10^{-5}$</td>
<td>$4.15 \times 10^5$</td>
<td>0.98</td>
<td>$6.14 \pm 1.0$</td>
<td>$4.0 \pm 0.6$</td>
</tr>
<tr>
<td>Plagioclase Feldspar—PF</td>
<td>$5.6 \times 10^{-6}$</td>
<td>$4.5 \times 10^5$</td>
<td>0.98</td>
<td>$4.71 \pm 0.79$</td>
<td>$2.5 \pm 0.5$</td>
</tr>
</tbody>
</table>

$R_d^*$ is obtained from corrections for effective surface area of the different samples. $B$ is the Langmuir parameter also known as the adsorption capacity relating to the maximum amount of sorbable cations. This value is calculated using the gradient and the intercept of the linearised Langmuir equation. $K$ is a measure of the binding strength for the sorption process. This relates to the strength with which the metal ions are held in a monolayer. $SD$ is the standard deviation from three replicates.
Table 3  Values depicting how the Langmuir models fits to sorption data. Unfavourable = Langmuir model is invalid, Favourable = Langmuir model is valid.

<table>
<thead>
<tr>
<th>Value of $F$</th>
<th>Type of adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F &gt; 1.0$</td>
<td>Unfavourable</td>
</tr>
<tr>
<td>$F = 1.0$</td>
<td>Linear</td>
</tr>
<tr>
<td>$0 &lt; F &lt; 1.0$</td>
<td>Favourable</td>
</tr>
<tr>
<td>$F = 0$</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

Fig. 5  Log-log plot of Ni bound and free in solution showing Ni distribution for grey granite, and rose and milky quartz and minerals.

calculated for RQ and MQ respectively. Work done by Ticknor [31] concerning Ni sorption to different geologic materials using synthetic groundwaters as the background electrolyte gave $R_d$ values for quartz between -0.20 and 3.6 cm$^3$·g$^{-1}$ for a particle size range of 106-180 microns. Thus, the results obtained in this work for quartz support the fact that quartz is low sorbing in synthetic groundwater and deionised water. A high $R_d$ value (37 cm$^3$·g$^{-1}$) was obtained for GrG (Table 4) as compared to values obtained for GG and RG. However, no sorption data for Ni sorption to GrG were found in the literature to confirm the obtained result. One important characteristic of the constant Linear $K_d$ model applied to the sorption data was that the $R_d$ stayed constant within the concentration limits used in the experiment. One important characteristic of the constant Linear $K_d$ model applied to the sorption data is that the $R_d$ is constant within the concentration limits used in the experiment.

3.1.3 $^{63}$Ni Sorption to Granitic Rocks and Minerals by the Freundlich Model

Protonation/deprotonation reactions at the surfaces of minerals create surface structures such as $\equiv$SO$^-$, $\equiv$SOH, and $\equiv$SOH$^+$. The adsorption of cations and anions from the inert electrolyte leads to the formation of surface complexes which have the character of ion pairs. Each of these surface complexes has its own sorption energy as a result of surface heterogeneity. Surface heterogeneity causes variation of this sorption energy across the surface from one oxygen site to another [5]. This heterogeneity is taken into account by the Freundlich model. The Freundlich model, like the linear $K_d$ model, has no upper limit for the sorption process in the concentration range studied. Sorption can be described by a multilayer addition mechanism. Experimental data obtained for Ni sorption to BG (biotite granite) and GA (granite adamellite) were fitted to the linearised Freundlich isotherm (Eq. (4)) as the best fit model. From the intercept and gradient of the linearised isotherm, the Freundlich sorption parameters are calculated as shown in Table 5. The result fitted well to the model ($R^2 = 0.99$ for both BG and GA), a Freundlich parameter $N$ (also called the heterogeneity factor) is calculated as 1.13 and 1.03 for BG and GA respectively. When the heterogeneity factor = 1, then the sorption isotherm is linear. When the heterogeneity is greater or less than unity, the sorption is non-linear with no saturation attained within the concentration range studied.

Table 4  Sorption parameters for $^{63}$Ni sorption to grey granite, milky and rose quartz.

<table>
<thead>
<tr>
<th>Material</th>
<th>$R_d$ (cm$^3$·g$^{-1}$)</th>
<th>Mean $R_d \pm SD$ (cm$^3$·g$^{-1}$)</th>
<th>$R_d^* \pm SD$ (cm$^3$·g$^{-1}$·m$^{-2}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GrG</td>
<td>37.3</td>
<td>21.8 $\pm$ 4.2</td>
<td>13.2 $\pm$ 1.5</td>
<td>0.99</td>
</tr>
<tr>
<td>RQ</td>
<td>0.02</td>
<td>0.04 $\pm$ 0.001</td>
<td>4.7 $\pm$ 0.01</td>
<td>0.98</td>
</tr>
<tr>
<td>MQ</td>
<td>0.02</td>
<td>0.049 $\pm$ 0.006</td>
<td>5.7 $\pm$ 0.07</td>
<td>0.99</td>
</tr>
</tbody>
</table>

GrG = grey granite, RQ = rose quartz, MQ = milky quartz.
Table 5  Sorption parameters for $^{63}\text{Ni}$ sorption to BG and GA. $R_d^*$ is the mean $R_d$ corrected for surface area per gram. $N$ is a dimensionless factor related to the heterogeneity of the sorption sites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean $R_d$ ± SD (cm$^3$·g$^{-1}$)</th>
<th>$R_d^*$ ± SD (cm$^3$·g$^{-1}$·M$^{-2}$)</th>
<th>$N$</th>
<th>$R^2$</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>BG</td>
<td>10.8 ± 1.02</td>
<td>3.8 ± 0.36</td>
<td>1.13</td>
<td>0.99</td>
<td>$Q = 25C^{0.03}$</td>
</tr>
<tr>
<td>GA</td>
<td>13.90 ± 2.6</td>
<td>4.9 ± 0.94</td>
<td>1.03</td>
<td>0.99</td>
<td>$Q = 108C^{3.13}$</td>
</tr>
</tbody>
</table>

BG = Biotite Granite, GA = Granite Adamellite.

3.2 Application of the Component Additive Model to Sorption of Ni to Granitic Rocks and Minerals

Two approaches have been applied to describe sorption onto heterogeneous materials: the CA (component additivity approach) and the GC (generalised composite approach) approach [36]. The CA approach is based on summing the adsorption by the individual component minerals of a heterogeneous sample to obtain a measure of the total adsorption of the mixture. The summation can occur as the sum of results for thermodynamic surface speciation models or as the sum of pseudo-thermodynamic models for adsorption on individual mineral phases [26]. In this section sorption parameters derived from the application of NEM models such as the linear and the Langmuir models are used in the application of the CA approach to the sorption data obtained from static batch sorption experiments (results discussed above). One of the methods in the evaluation of the retention capacity of radionuclides is by use of a retardation factor. The main input parameter in determining the retardation factor is the $R_d$ obtained mainly from batch sorption experiments. For heterogeneous samples such as granite, the sorption properties of the constituent minerals may vary. Based on the additivity principle, the bulk property (such as $R_d$) is a summation of the properties of the component minerals [20]. However, this concept has little or no experimental data to back it up in published literature for Ni or Eu sorption to granitic rocks. This section therefore aims at investigating the CAM based on the results obtained from static batch sorption experiments performed on component minerals of granite.

Deductions from XRD analysis shown in Table 1 showed that the main constituents of the granitic rocks studied were quartz, feldspar and mica. Feldspar and quartz constituted more that 95% of the mineralogical composition of all the granite samples while mica and other mica related minerals constituted between 1 to 10 percent. To investigate the CAM, mean $R_d$ values for the different sets of minerals are used (mean value for RQ and MQ, mean value for OF and PF and MM and BM). Also, because the different samples fitted to different sorption models within the concentration of metal studied, average values for the $R_s$ are used. The mean $R_d$ values obtained and the analyzed mineralogical composition are related to the bulk percentage composition, to obtain a predicted value. The predicted value for the minerals is summed to obtain a predicted bulk $R_d$ value for the granite samples. The predicted bulk $R_d$ value is compared with the experimental bulk $R_d$ value obtained.

The contribution to the bulk $R_d$ of each granitic mineral from its percentage composition was calculated (as shown in column 4, 6, 8, 10 and 12 of Table 6). To show that the CAM applied to a granitic rock sample, the ratio

$$\frac{R_d \, \text{predicted}}{R_d \, \text{calculated}} = 1 \quad \text{(9)}$$

Applying Eq. (9) to sorption data showed that the CAM was applicable more to Ni sorption to BG. The CAM was thus applicable in the following order; BG (1) > GA (0.7) > RG (0.5) > GG (0.2), GrG (0.2)

Values in brackets represent the ratio of $R_d$ predicted and $R_d$ calculated.

Looking at Table 6 it can be seen that the summation of the $R_s$ of the individual minerals of the different granitic rocks varied from 3.9 to 22 cm$^3$·g$^{-1}$. The results showed a fit between the predicted values for GA, BG and RG, as shown in Table 6. Thus, the
Table 6  Application of the CAM for Ni sorption to granitic rocks at constant pH and variable metal concentration.

<table>
<thead>
<tr>
<th></th>
<th>Measured $R_d$ ($cm^3 g^{-1}$)</th>
<th>Graphic granite $%_{com}$</th>
<th>Granite adamellite $%_{com}$</th>
<th>Biotite granite $%_{com}$</th>
<th>Grey granite $%_{com}$</th>
<th>Rapakivi granite $%_{com}$</th>
<th>Contribution to bulk $R_d$ %</th>
<th>Contribution to bulk $R_d$ %</th>
<th>Contribution to bulk $R_d$ %</th>
<th>Contribution to bulk $R_d$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>$4 \times 10^{-2}$</td>
<td>28</td>
<td>$1.3 \times 10^{-2}$</td>
<td>28</td>
<td>$1.7 \times 10^{-2}$</td>
<td>28</td>
<td>38.6</td>
<td>38.6</td>
<td>38.6</td>
<td>38.6</td>
</tr>
<tr>
<td>Mica</td>
<td>4.59</td>
<td>1</td>
<td>$4.6 \times 10^{-2}$</td>
<td>3</td>
<td>0.14</td>
<td>15</td>
<td>0.7</td>
<td>4.3</td>
<td>5.4</td>
<td>4.3</td>
</tr>
<tr>
<td>Feldspar</td>
<td>5.46</td>
<td>71</td>
<td>3.9</td>
<td>59</td>
<td>3.2</td>
<td>59</td>
<td>3.2</td>
<td>57</td>
<td>61.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Predicted $R_d$</td>
<td>4</td>
<td>3.35</td>
<td>3.9</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Measured $R_d$</td>
<td>4</td>
<td>3.8</td>
<td>3.8</td>
<td>21.8</td>
<td>21.8</td>
<td>21.8</td>
<td>6.6</td>
<td>6.6</td>
<td>6.6</td>
<td>6.6</td>
</tr>
</tbody>
</table>

% Com = percentage mineralogical composition of a granite sample.

CAM is shown to be applicable to sorption data obtained from Ni sorption to BG based on the experimental condition used. However, application of the CAM to GG and GrG showed a disparity between the predicted and the calculated values. The reason for this disparity is not obvious and requires further investigation at the metal-surface interphase. The CAM thus depends on the detailed elucidation of the composition of the heterogenous sample [26].

$R_d$ measured $\approx$ $(R_d$ predicted from CAM) when Eq. (9) is valid as shown with BG.

Deductions from Table 6 include:

1. Quartz and mica contribute less to the overall Ni sorption capacity of intact granite. This is probably due to the small percentage composition of mica in the intact sample and the observed low sorption capacity of quartz. Sorption to feldspar is thus very significant in terms of the overall sorption ability of granites, probably due to the high percentage contribution and also the high sorption as observed in Table 6.

2. The sorption capacity of intact granite sample will not only depend on the composition of the granitic materials, it will also depend on the effective surface area of the mineral that is in contact with the solution. However, for the above analysis it is considered that an average mineralogical composition is proportional to the effective surface area of the mineral in contact with the solution ions.

4. Conclusions

Modelled data showed that quartz and mica contribute less to the overall Ni sorption capacity of intact granite. This is probably due to the small percentage composition of mica in the intact sample and the observed low sorption capacity of quartz. Sorption to feldspar is thus very significant in terms of the overall sorption ability of granites, probably due to the high percentage contribution. Applying the effect of BET surface area, the sorption capacity of intact granite sample will not only depend on the composition of the granitic materials, it will also depend on the effective surface area of the mineral that is in contact with the solution.

References

Modelling the Sorption of $^{63}$Ni to Granitic Materials: Application of the Component Additive Model