

Modelling Desorption of ⁶³Ni from Granitic Rocks and Minerals

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Abstract

The reversibility or irreversibility of the sorption process is of fundamental importance for understanding the fate of radionuclides in geological systems. Desorption experiments with ⁶³Ni were carried out. Three replicates each of varying concentration $(1 \times 10^{-14} \text{ to } 1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3})$ of Ni²⁺ were prepared so that 0.1 cm³ of the spike solution should give approximately 1200 counts min⁻¹. One cm³ of the supernatant was mixed with 10 cm³ of scintillation cocktail (High Flash-point, Universal LSC cocktail) and samples counted in a TriCarb liquid scintillation counter, followed by centrifugation at 6000 rpm for 30 min. The separated sample was mixed with 20 cm³ of DI water and allowed to shake for between 5 and 7 days, upon which one cm³ of the supernatant was filtered and counted in the energy range of 0 to 67 keV at 2σ at a counting time of 20 min per sample. Hysteresis values were calculated for different granitic samples. Results showed that the hysteresis increases with R_d, as illustrated by GG $(R_d = 17.2 \text{ cm}^3 \cdot g^{-1}, H = 0.94)$ and PF $(R_d \ 6.1 \text{ cm}^3 \cdot g^{-1}, H = 0.79)$. These results highlight the ability of granitic materials to retard radionuclides in solution. The ability to retard radionuclides in the far field gives granitic rock systems an advantage in terms of repository considerations. Considering H, the following order is obtained; RG > OF > GG > PF. Taking into consideration the percentage desorption (average percentage desorption), the following values were obtained RG = 4.2%, OF = 3.4%, PF = 22.7%, these values show that the hysteresis increased as desorption decreased for the above samples.

Keywords

Sorption/Desorption, Hysteresis, Distribution Coefficient

1. Introduction

1.1. Desorption Phenomena

The reversibility/irreversibility of the sorption process is of fundamental importance for understanding the fate of radionuclides in geological systems. If the process is reversible, the same isotherm should be valid for sorption and desorption under the same conditions (Cui & Eriksen, 1997). Sorption-desorption hysteresis refers to the apparent asymmetry of sorption/desorption equilibrium and/or kinetics. It manifests itself as non-singular isotherms or different rates for sorption and desorption, where during desorption a higher affinity of a sorbate on a given sorbent and a longer time scale for release than adsorption is observed. Numerous studies have reported the phenomenon of hysteresis or non-singularity of sorption-desorption isotherms (Guohui, 2008). There are several causes of these observed hysteresis phenomena. Kinetic hysteresis could be due to different sorption and/or desorption rates arising from steric hindrance effects and sorbate entrapment in micropores. Non-linear sorption isotherms also lead to kinetic hysteresis, i.e. a self-sharpening concentration front during sorption and extended tailing during desorption. There are several examples of kinetic hysteresis reported in the scientific literature, in which sorption appears to be faster than desorption (Guohui, 2008).

The isotope ⁶³Ni is an artificial radionuclide. The presence of ⁶³Ni in the environment results mainly from activities such as; nuclear weapon tests, radioactive effluents from nuclear installations and accidental releases from nuclear power plants (e.g. Chernobyl) (Scheuerer et al., 1995). ⁶³Ni is formed by neutron capture of stable ⁶²Ni. ⁶³Ni is a β -emitter with a half-life of 100.1 years (Knol et al., 2008). 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). 18 radioisotopes have been characterised with the most stable being ⁵⁹Ni with a half-life of 76,000 years (decay mode is by electron capture to ⁵⁹Co and decay energy of 1072 MeV), ⁶³Ni with a half-life of 100.1 years, and ⁵⁶Ni with a half-life of 6.077 days. All 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. ⁶³Ni is a beta-emitting radionuclide of E_{max} = 67 keV. It exists in the coolant water of nuclear power reactors and is formed by neutron capture of nickel released from steel piping and so on due to corrosion.

 ${}^{62}\text{Ni} + {}^{1}\text{n} \rightarrow {}^{63}\text{Ni}$ neutron capture process (6.80 MeV) (Treado & Changnon, 1961)

It is included in the list of low-level long-lived radioactive waste from nuclear power reactors (L'Annunziata, 2004). Nickel can be transported as particles released into the atmosphere or as dissolved compounds in natural waters (Australian Government Department, 2008).

1.2. Objectives

This concerns the investigation of the tendency of radionuclides bound to solid

surfaces to desorb, i.e. to return to solution once the chemical environment, such as the ionic strength or pH is changed. For the sake of simplicity, desorption experiments were performed with deionised water, which has a different chemical potential with respects to the original electrolyte used in the sorption process. Work done by Ebong and Nick (Ebong & Nick, 2008, 2011, 2012) showed the extensive nature to which radionuclides can adsorb on silonal sites on different granitic materials through the adsorption coefficient. As a follow-up to the previous work that dealt with the sorption processes, this work looks at the reversible process of sorption quantitatively, for the sake of comparison.

1.3. Processes and Manifestations of Hysteresis

It is known that several metals show fast kinetic adsorption reactions by outersphere ion exchange followed by slow adsorptions with specific inner-sphere interactions, so it is sometimes difficult to know if thermodynamic equilibrium has been reached. If not, the superimposition between adsorption and desorption isotherms does not match (Limousin et al., 2007). This mismatch between adsorption and desorption isotherms is called "pseudo-hysteresis" (as shown in figure (Cui & Eriksen, 1997) or "kinetic hysteresis". A more convenient term could be "apparent irreversibility". The common term "irreversibility" can lead to the wrong conclusion that a part of the solute cannot be desorbed at all, whereas it could be just a matter of time. On the other hand, the saturation capacity of the solid during adsorption can be underestimated if equilibrium is not reached. The characteristic time of desorption can be several orders of magnitude different from the characteristic time of adsorption. The adsorbed species can react, in a second stage, with the solid by: slow diffusion inside the solid, inner-sphere surface complexation, or crystallisation of new solid phases. The duration of desorption is increased by the time needed to reverse these reactions. This highlights the importance of knowing the history of a system and considering any "ageing" effects (Limousin et al., 2007).



Figure 1. Processes and manifestations of hysteresis. Adapted from (Guohui 2008).

Pseudo-hysteresis due to experimental artefacts in the traditional batch sorption-desorption method can be classified mainly into two categories:

Desorption starting under non-equilibrium conditions (non-attainment of equilibrium due to rate limited diffusion) can lead to an underestimation of equilibrium sorbed concentration in the sorption direction, and an overestimation in the desorption direction.

Sorbate losses from the batch system and losses of sorbate to batch vial components, especially polymer liners and seals. If these losses are not considered, it could lead to incomplete mass balances used to construct the sorption isotherm, resulting in hysteresis due to overestimation of the sorbed concentrations.

Steric hindrances due to the molecular structure of particle-metal complex can result in limitations of the desorption process resulting in hysteresis.

1.4. Mechanisms of Desorption

The reversibility of sorption reflects the ability of the adsorbed radionuclides to be released to the aqueous phase by changing conditions. The most direct test of the reversibility of the sorption process is to use the same aqueous phase for both adsorption and desorption (Baik et al., 2004) The results are usually characterised using the hysteresis factor (H), a dimensionless parameter, calculated via:

$$H = \frac{\left(Q_{\text{bound}} + Q_{\text{Desorbed}}\right)}{Q_{\text{bound}}}$$
(1)

A common method of expressing the extent of desorption is by expressing the amount desorbed as a percentage of the amount bound initially.

$$\% \text{Desorbed} = \frac{\text{desorbed}}{\text{bound}} \times 100$$
(2)

where $Q_{bound} \text{ (mol} \cdot g^{-1})$ is the amount of metal bound and $Q_{desorbed} \text{ (mol} \cdot g^{-1})$ is the amount of metal desorbed upon desorption with DI water.

Hence, the larger the value of H (nearer to unity) the greater the resistance to desorption. Clear experimental evidence for the physical or chemical mechanisms proposed to lead to hysteresis is still lacking. Reasons for desorption hysteresis can be manifold (Guohui, 2008) More than a single mechanism may be responsible for the many observed desorption hysteresis phenomena. The most common experimental artefacts result from non-attainment of sorption/desorption equilibrium since the true equilibrium can require very long timeframes. Literature reported sorption/desorption experiments vary from hours to weeks and further up to more than a thousand days (Guohui, 2008). In addition, two other sources of artefacts due to sorbate mass loss are difficult to rule out using the traditional decant-and-refill batch method. To differentiate "pseudo-hysteresis" resulting from experimental artefacts from true hysteresis due to kinetic reasons or sorbent reconfiguration of the geological materials, a prerequisite for such experiments is to improve the experimental methodology to minimize or eliminate the artefacts. If, under these conditions, differences in the sorption and desorption isotherms are observed, kinetic reasons or irreversible sorption, as summarised in Figure 1, are likely.

The principal sorption mechanism is likely to vary during the sorption period. The often-observed variation in sorption mechanisms is transitions from relatively easily desorbable forms in earlier period to almost irreversibly sorbed or slowly desorbable forms in the later one. These transitions have been explained by the slow diffusion of elements onto internal surfaces and their subsequent occlusion in the structure of the minerals or by transition from outer-sphere complex to inner-sphere complex (Fujikawa & Fukui, 1997). The residence time plays a role in the desorption of radionuclides in the sense that, increased residence time could be attributed to different aging mechanisms such as rearrangements of surface precipitates (Pigna et al., 2006).

1.5. Sorption-Desorption Experiments with ⁶³Ni at Constant pH

All rock and mineral samples were supplied by UK Geologist Equipment as intact samples. Samples were crushed and pulverised using a ball mill and sieved to obtain a particle size range of 46 to 250 μ m. 0.1 g of the pulverised samples were mixed with 20 cm³ of non-active NiCl₂ solution. Three replicates each of varying concentration (1 \times 10⁻¹⁴ to 1 \times 10⁻⁴ mol·dm⁻³) of Ni²⁺ were prepared. ⁶³Ni stock solution was prepared and allowed to equilibrate over 24 h the activity of the solution was diluted to $0.2 \text{ kBq} \cdot \text{cm}^{-3}$ so that 0.1 cm^{3} of the spike solution should give approximately 1200 counts min⁻¹. Upon adding the spike, the vials were allowed to shake for ca. 7 days. One cm³ of the supernatant was mixed with 10 cm³ 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 6000 rpm for 30 min. The separated sample was mixed with 20 cm³ of DI water and allowed to shake for between 5 and 7 days, upon which one cm³ of the supernatant was filtered and counted in the energy range of 0 to 67 keV at 2σ at a counting time of 20 min per sample. Three replicates of each stable Ni solution at each concentration were prepared. Vials containing stable Ni²⁺ solutions were also prepared and counted for background corrections. For desorption experiments, the sample vials were centrifuged at 6000 rpm for 1 hour, and the supernatant discarded. DI water was added into the vials and allowed to equilibrate for 5 days after which separation and counting were performed as described in the sorption process. All experiments were performed within the equilibration pH of ca. 7.5.

2. Results and Discussion

To fully understand the hysteresis that is observed during desorption processes, it was important to perform both the sorption and desorption processes. Experiments were carried out with different granitic rocks and minerals to study the Sorption-Desorption Processes (SDP). The results have been arranged in terms of the sorption mechanisms by which the sorption processes occurred. Hysteresis is a sorption parameter that measures the extent to which the bound radionuclides are resistant to the desorption process. It is a dimensionless parameter, calculated using Equation (1).

2.1. ⁶³Ni Desorption from Granitic Rocks and Minerals for Those Whose Sorption Was Best Described by the Langmuir Model

Sorption by the Langmuir isotherm assumes the solid has a limited adsorption capacity Qmax. 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 and all sites are energetically and sterically independent of the adsorbed quantity (Langmuir, 1918). Application of the Langmuir model to sorption data is often done with the calculation of the favourability factor F (Alkan & Doğan, 2001) also known as the separation factor (Horsfall & Spiff, 2005) as shown below.

$$F = \frac{1}{(1 + KCe)}$$
(3)

where k is the adsorption constant ($dm^3 \cdot mol^{-1}$), Ce is the amount in solution in $mol \cdot dm^{-3}$.

Type of adsorption	
Unfavourable	
Linear	
Favourable	
Irreversible	
	Type of adsorption Unfavourable Linear Favourable Irreversible

Table 1. Values depicting how the Langmuir models fit to sorption data. The Favourability factor can take different values, with each value pertaining to different sorption scenarios. Unfavourable = Langmuir model is invalid, Favourable = Langmuir model is valid.

The separation factor (Favourability factor) is important in determining which model could be applied to sorption data collected from experiments. In cases where the Langmuir model is not applicable. 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 (Cui & Eriksen, 1997).

For Grey Granite (GrG), Rapakivi Granite (RG), Orthoclase Feldspar (OF) and Plagioclase Feldspar (PF), sorption took place with saturation of the sorption sites. One of the assumptions in applying the Langmuir model to sorption data is that the sorption process is reversible. The favourability constant (**Table 1**) is 0 < F <1, implying that the sorption data can be described by the Langmuir model. If the data fits to Langmuir model, the sorption process is expected to be reversible. Even though sorption data could be described by the Langmuir model, the process is usually not fully reversible. The reasons for hysteresis are discussed in Section 1.3. Thus, this section describes investigations of desorption profiles for different granitic rocks and minerals, to establish a link between the forward and reverse processes. Because the sorption experiments were done in deionised water as the electrolyte carrying the metal ions, it was important to use the same electrolyte without Ni present. Details of the experimental methodology are shown in Section 2 in the experimental section. Desorption experiments involving the solids mentioned above (with Ni²⁺ bound on the surfaces of the particles from the sorption experiments) were performed with deionised water. Results revealed a linear relationship between the concentration bound and the concentration desorbed as shown by the Log-Log plot (**Figure 2**). Desorption parameters are shown in **Table 2**. The implication of the linear relationship between the desorbed and the bound is that the amount desorbed increases as a function of the amount bound.

From **Table 2**, the hysteresis increases with R_d , as illustrated by GG ($R_d = 17.2 \text{ cm}^3 \cdot \text{g}^{-1}$, H = 0.94) and PF ($R_d 6.1 \text{ cm}^3 \cdot \text{g}^{-1}$, H = 0.79). These results highlight the ability of granitic materials to retard radionuclides in solution. The ability to retard radionuclides in the far field gives granitic rock systems an advantage in terms of repository considerations. Considering H, the following order is obtained; RG > OF > GG > PF. Taking into consideration the percentage desorption (average percentage desorption), the following values were obtained RG = 4.2%, OF = 3.4%, PF = 22.7%, these values show that the hysteresis increased as desorption decreased for the above samples. A significant difference in hysteresis between OF and PF is observed in terms of the percentage desorption. Even though both minerals are classified as feldspar, plagioclase forms a sub group of minerals with different concentrations of sodium and calcium; and aluminium and silicon, resulting in different structural patterns. Thus, the difference in hysteresis may be explained by structural differences.



Figure 2. Log-Log plot of Ni desorption profile for sorption processes described using the Langmuir model. Desorption experiments were performed using DI water and a single wash involving GG, RG, OF and PF at pH ca. 7.5.

Sample	Mean R _d (cm ³ ·g ⁻¹)	Hysteresis	$R_{d^{\star}}$ (cm ³ ·g ⁻¹ ·m ⁻²)
Graphic Granite-GG	17 ± 1.3	0.94	6.1 ± 0.9
Rapakivi Granite-RG	6.6 ± 0.8	0.98	2.3 ± 0.2
Orthoclase Feldspar-OF	6.1 ± 1.1	0.96	4 ± 0.7
Plagioclase Feldspar-PF	4.0 ± 0.8	0.79	2.5 ± 0.5

Table 2. Ni Sorption-Desorption parameters for granitic rocks and minerals for those whose sorption was best described by the Langmuir model.

 R_{d^*} is obtained from corrections for calculated effective surface area of the different samples. From the results it has been shown that one of the main assumptions of the Langmuir model (sorption reversibility) is not applicable in real systems like those studied in this work. Many systems have inherent properties (such as steric hindrances of molecular diffusion, chemisorption, heterogeneity of adsorption surfaces and most commonly loss of sorbate mass during batch systems) that do not allow the forward process to be equal to backward process, leading to isotherm non-linearity (the forward process does not interpose with the reverse process).

2.2. ⁶³Ni Desorption from Granitic Rocks and Minerals for Those Whose Sorption Was Best Described by the 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. K_d values are thermodynamically determined at stated equilibrium conditions as opposed to distribution ratios such as R_d which are not thermodynamically determined. In this thesis, R_d is preferred to K_d. Values for K_d not only vary greatly between contaminants, but also vary as a function of aqueous and solid phase chemistry (Atomic Mass data center, 2008). 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 (Limousin et al., 2007). 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 (Sparks, 2011, Veith & Sposito, 1977). However, isotherms give a general view of the distribution of radionuclides between the solid-liquid phases.

Previous work carried out by Ebong and Nick (Ebong & Nick, 2008, Ebong & Nick, 2011, Ebong & Nick, 2012) showed that sorption to Rose Quartz (RQ), Milky Quartz (MQ) and Grey Granite (GrG), was best described by the Linear K_d model. Desorbing with DI water in a single wash (Section 2) showed a linear relationship between the desorbed and the bound Ni, as shown in **Figure 3**. Hysteresis for both RQ and MQ was low, as expected, quartz is generally known to be low

sorbing, except in cases were incorporation into the structure through the dissolution of the Si-O-Si bound occurs. Due to the low sorption capacity, retention of metal ions on the surface is weak, as such, changes in the chemical environment (such as changes in the ionic strength of the solution) will affect the desorption process. Also, it was shown in Section 3.1 that the retention increases with the R_d. From **Table 3**, GrG showed high resistance to desorption (H = 0.98 with R_d = 13.2), while MQ showed low resistance (H = 0.68 with R_d = 0.06). The results once more showed a relationship between R_d and hysteresis. The high resistance to desorption for GrG was comparable to that shown by RG, GG, and OF as seen above.



Figure 3. Log-Log plot of Ni desorption profile for sorption processes taking place by the Linear K_d model. Desorption experiments were performed using DI water and a single wash involving RQ, GrG, and MQ. Equilibration pH ca. 7.5. Deviation from linearity is observed for GrG at higher metal loading to the surface.

It has thus, been shown that for these systems, the greater the degree of sorption, the greater the resistance to desorption, as shown in **Table 3**. However, deviation from linearity is observed with GrG. This can be attributed to some of the reasons mentioned in Section 1.3, such as; steric hindrance of molecular diffusion, truly bound residuals, chemisorption heterogeneity of adsorption surfaces or experimental artefacts (Pseudo-Hysteresis).

Table 3. Desorption parameters for sorption best described by the Linear K_d model, involving Ni, and GrG, MQ, and RQ, in a single wash process.

Sample	$\overline{\mathbf{R}_{d^{\star}}}$	R ²	Hysteresis
Grey Granite-GrG	13.2 ± 1.5	0.99	0.98
Rose Quartz-RQ	0.05 ± 0.01	0.98	
Milky Quartz-MQ	0.06	0.99	0.68

Due to the similarity in structure between MQ and RQ, and based on their sorption capacity, it is possible to conclude that RQ will show similar behaviour in terms of Ni desorption.

2.3. ⁶³Ni Desorption from Granitic Rocks and Minerals for Those Whose Sorption Was Best Described by the Freundlich Model

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; (Aksoyoglu, 1989, Atoniadis & Tsadilas, 2007) 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. Desorption experiments performed on Biotite Granite (BG) and Granite Adamellite (GA) showed that desorption increased with the concentration of metal bound. At higher metal concentrations, desorption decreased due to reasons mentioned in the previous section. Figure 4 shows desorption profile for BG and GA. Mean percentage desorption were <10% of the amount bound (3.8% and 9.1% for BG and GA respectively). The low desorption values thus, reflect the high hysteresis values recorded for BG and GA. Table 4 shows the various sorption parameters obtained.

Table 4. Desorption parameters for sorption best described by the Freundlich model, involving Ni, with GA and BG in a single wash process. Sorption parameters for Ni sorption to BG and GA. R^2 values are those for the sorption model. Q and C are amounts bound and present in solution respectively (Q mol·g⁻¹ and C mol·dm⁻³).

Sample	$\begin{array}{c} R_{d^{\star}}\\ (cm^{3} \cdot g^{-1} \cdot m^{-2})\end{array}$	R ²	Sorption model	Hysteresis
BG	3.8 ± 0.4	0.99	Q = 25C1.03	0.97
GA	4.9 ± 0.94	0.99	Q = 108C1.13	0.96

The decrease in desorption at higher concentrations of Ni bound suggests that some of the Ni is trapped in dead pore ends due to steric hindrances or desorption does not occur as supported by the high hysteresis values. From Equation (1), the relationship between the amount bound Q_b (mol·g⁻¹), the hysteresis H (dimensionless) and the amount desorbed Q_d (mol·g⁻¹) is given by Equation (3) (rearrangement of Equation (1)).

$$Q_{d} = Q_{b} \left(1 - H \right) \tag{4}$$

From Equation (3); when:

H approaches 1, desorption approaches zero and the system is said to be irreversible, this holds true for BG and GA.

As H approaches zero, desorption approaches to 100 percent and the system is said to be reversible.



Figure 4. Log-Log plot of Ni desorption profile for sorption processes taking place by the Freundlich model. Desorption experiments performed using DI water and a single wash involving BG and GA. Equilibration pH from ca. 7.5. Deviation from linearity is observed for at higher metal loading to the surface.

2.4. ⁶³Ni Desorption from Granitic Rocks and Minerals-Biotite and Muscovite Mica

Sorption to Biotite Mica (BM) and Muscovite Mica were best described by the linear model as shown in **Table 5**. Results obtained for the desorption experiments with DI water in a single wash process showed very low desorption for MM as compared to BM. Mean percentage desorption values for MM and BM were 0% and 36.1% respectively. Desorption followed a linear trend, however, there is deviation from linearity for MM (**Figure 5**). The reason for this can be due to the structure of the mineral. Mica is a sheet silicate containing iron, magnesium, aluminium, silicon, oxygen, and hydrogen form sheets that are weakly bound together by potassium ions. The weakly held K⁺ ions are easily replaced in solution leading to permanent negative charges on the mica particle surface. It is this permanent negative charge that is responsible for the high sorption observed through the formation of strong chemical binding between Ni and the solid surfaces in the process of chemisorption (Guohui, 2008).

There is a big difference between the H values for BM and MM. Micas have a layer charge of about 1 per half-cell formula unit and are both dioctahedral for the case of muscovite and trioctahedral for biotite (Sparks, 2011). These differences can be attributed to several of the factors mentioned in **Figure 1**, which include: Desorption starting under non-equilibrium conditions and Loss of sorbate mass in batch system.

3. Conclusion

From the results, one main observation pertained to the fact that desorption



Figure 5. Log-Log plot of Ni desorption profile. Desorption experiments performed using DI water and a single wash involving BG and GA. Equilibration pH from ca. 7.5. Deviation from linearity is observed for MM at higher metal loading to the surface.

 Table 5. Desorption parameters for Ni sorption-desorption with BM and MM in a single wash process showing difference in H.

	Mean $R_d \pm SD$ (cm ³ ·g ⁻¹)	$R_{d^{\star}} \pm SD$ $(cm^{3} \cdot g^{-1} \cdot m^{-2})$	Hysteresis
Muscovite Mica (MM)	8.5 ± 1.3	5.0 ± 0.7	0.95
Biotite Mica (BM)	7.2 ± 0.7	4.2 ± 0.4	0.72



Variation of hysteresis with R_{d*} for Ni sorption to selected granitic rocks and minerals

Figure 6. Variation of Hysteresis with measured R_{d^*} for different rocks and minerals, Single wash. Negative H value for RQ has not been included. R_{d^*} values are corrected for surface area.

decreased as sorption increased, although desorption was generally low and almost zero for MM, BG, GA, GrG, RG, and OF. To conclude it can be said that there is a relationship between the sorption and desorption processes. The more sorbing a mineral is, the more the hysteresis observed. The results also confirmed low sorption to quartz and high sorption to granitic rocks. However, there is a need to understand the processes leading to high values of hysteresis even though most of its causes were mentioned. There is need for spectroscopic analysis using techniques such as extended X-ray absorption spectroscopy to investigate the metal-solid interaction at the molecular level. The resistance of bound radionuclide to desorb is usually expressed mathematically using the concentration of metal bound and the concentration of metal free in solution at equilibrium. However, radionuclide retardation in the geosphere is mostly described using R_d is made rather than the concentration bound or desorbed. Thus, using the data obtained corrected for surface area, a mathematical relationship between the R_{d^*} and the hysteresis H of Ni desorption from a granitic sample can be approximated as:

$$H = 0.82 R_{d*}^{0.07}$$
(5)

Based on **Figure 6**, the expression is derived from Excel, with R² value of 0.87.

The above expression is valid for R_d values normalised for surface area per gram of sample for Ni sorption to granitic rocks and minerals. However, due to the lack of data from published work, it is not possible to compare data obtained from previous work.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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