

Sorption Kinetics of ^{152}Eu to Different Granitic Materials in Carbonate Systems

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Abstract

Granitic rocks are being considered as burial sites for high- and medium-level radioactive wastes by many countries. These rocks have predominantly three mineral phases, which include mica, quartz and feldspars. The rate of inorganic ion sorption on mineral surfaces is not well understood, partly because of the complex processes occurring at mineral-water interfaces. Estimation of the kinetic functions and appropriate sorption constants from batch experiments can provide an insight into the sorption processes. This work aims at determining rate constants and reaction orders. Sorption kinetic experiments were conducted using granitic rock and component minerals to understand how different carbonated systems will affect the rate constants and to determine the rate constant and see which sorption mechanisms are dominant. The granitic rocks and minerals were first reduced in size. 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 EuCl_3 solution, giving a solid-liquid ratio of 1:200. Experiments with ^{152}Eu were analysed using the Cobra(II) Auto Gamma counting between 100 to 1500 keV at 2 sigma. $1 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ solutions of EuCl_3 were prepared. Different amounts of carbonate were added into the solution to give carbonate concentrations of 1×10^{-2} and $1 \times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$ for high carbonate (HC) and low carbonate (LC) systems, respectively. The results for BG showed that data fitted best to the Langmuir model with saturation of sorption sites. This is evident from the Langmuir linearised isotherm. R^2 values for CF, LC and HC systems were close to one. Calculated R_d values showed the effect of carbonate for sorption in the three systems. Mean R_d values were calculated as $97 \text{ cm}^3\cdot\text{g}^{-1}$ for CF, $81 \text{ cm}^3\cdot\text{g}^{-1}$ for LC and $21 \text{ cm}^3\cdot\text{g}^{-1}$ for HC systems. Thus, the R_d decreased as the concentration of carbonate increased in solution. Using the linearised Lang-

muir isotherms, the maximum concentrations of Eu bound after 520 hours were calculated as 7.8×10^{-6} , 7.7×10^{-6} , and $6.9 \times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$ for CF, LC and HC systems, respectively. Sorption was fast initially, and reached saturation at longer equilibration times (desorption observed for Eu sorption to MM in CF system above 42 h equilibration). The presence of carbonate in solution altered the overall speciation of the metal in solution, which can affect sorption rates. Results showed that sorption to mica was not strongly dependent on intraparticle diffusion. Pseudo-second order rate constants were calculated for samples and for mica, the constants for CF, LC and HC systems were -980 , -7.3 and $-3.7 \text{ (mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1})$, respectively. Overall, the study was able to determine first- and second-order rate constants, which can be used in geochemical models to understand sorption mechanisms for granitic rocks and minerals.

Keywords

Sorption Kinetics, First Order, Second Order, Intraparticle Diffusion

1. Background

Granitic rocks are being considered as the host deep geological burial site for high- and medium-level radioactive wastes by many countries. These rocks have predominantly three mineral phases, which include mica, quartz and feldspars. Work done by Ebong and Nick (Ebong & Nick, 2012) threw light on the component additivity concept (the R_d of the granitic rock is the sum of the R_d of the component minerals). This work without making such comparisons seeks to understand how Eu sorption to rock samples will vary with that of its component minerals. The sorption is characterised not solely by the distribution coefficient but by the rate of sorption and the different mechanisms by which solute is removed from solution by the rock samples and their mineral phases. Work by Ebong et al. (2026) using Energy dispersive X-ray, microanalysis has already shown that Eu is taken up by granitic rocks, especially on the mica phases.

The rate of inorganic ion sorption on mineral surfaces is not well understood, partly because of the complex processes occurring at mineral-water interfaces (Štamberg et al., 2003). Estimation of the kinetic functions and appropriate sorption constants from batch experiments can provide an insight into the sorption processes not affected by flow phenomena, which can dominate in real porous systems (Baik et al., 2003). Sorption kinetics can significantly affect the migration of radionuclides in soils or rocks under certain natural conditions, such as during the rapid flow of groundwater in rock fractures. Knowledge of the rate can be important not only in modelling the migration but also for the elucidation of the mechanism of interaction, since it can characterise the process governing the interaction (so called control processes) (Kato et al., 1998). Different mechanisms can result in different kinetics of radionuclide uptake. Very limited information on the kinetics of Eu sorption and desorption on minerals and natural solids exists in the literature (Baik et al., 2003).

1.1. Carbonate and Eu Migration

The nature of the counter-ions, destined to stabilise heavy metals in the cationic form, can also influence their sorption by sorbent materials. Some anions such as the CO_3^{2-} have an affinity towards the metal, so that they form a complex such as $\text{EuOHCO}_{3(\text{aq})}$, which influences the sorption kinetics (Fourest, 1993). Previous studies have shown that the mineralogical composition in granitic rock fractures is very different from that of the rock matrix (Baik et al., 2009). Groundwater flowing through fractures usually contains calcites as secondary minerals resulting from fractured and weathered rocks. Calcite (a stable polymorph of CaCO_3) is thus a major constituent in the groundwater of many potential host rocks currently under consideration for the disposal of radioactive wastes (Baik et al., 2009). Even in the chemically disturbed zone formed around a cementitious repository, calcite remains largely unaffected by the hyper-alkaline waters migrating out of the near field. Thus, due to its abundance and geochemical stability, CaCO_3 could play an important role in the retardation of radionuclides released from a repository for nuclear wastes (Tits et al., 2005). Carbonate complexation as well as hydrolysis of actinide ions is one of the most important chemical reactions in neutral and alkaline solutions under environmental conditions (Hoffman & Choppin, 1986).

The main objectives of this study include: 1) To investigate the effect of different concentrations of carbonate on the sorption capacity of Eu on different granitic materials with Eu, acting as an analogue for trivalent actinides, between solution and surface phases. 2) To investigate the effect of carbonate on the rate constants and control processes for the immobilisation/retardation at constant pH and constant ionic strength.

With regards to the adsorption/desorption processes, thermodynamic data obtained from studies of equilibria provide only information on the final state of the system, but kinetics deals with changes in chemical properties with time. The growth in adsorption kinetics is of interest in the risk assessment exercise for a radioactive waste repository, as it may be of importance to evaluate how fast the radionuclides are retarded in an aquatic environment, such as that which could be found in the far field of the repository. However, the rate of retardation is also dependent on other factors present in the groundwater environment. As groundwater flows through geologic media, there is a possibility of contact with calcium carbonate-rich rock types and other related substances, such as colloids, which can change the chemical potential of the underground aquatic environment. The changes that result may also affect the sorption rates and the overall sorption process. In this work, the effect of carbonate on the sorption of Eu has been investigated both in high carbonate and low carbonate systems, with sorption in a carbonate-free system acting as a control.

Groundwater analysis as reported by Allard et al. (Allard et al., 1980), showed groundwater to contain as high as $123 \text{ mg}\cdot\text{g}^{-1}$ of HCO_3^- , much higher levels than for both sulphates and chlorides (Allard et al., 1980). The presence of carbonate as a major component of groundwater has been highlighted by Arcos (Arcos, 2008)

and Hoffman and Choppin (Hoffman & Choppin, 1986). The effect of NaHCO_3 on Eu sorption was also investigated by Koeppenkastrup and De Carlo (Koeppenkastrup & De Carlo, 1993) based on observations from sorption kinetics. They observed that carbonate complexation slowed the rate of uptake of Eu by manganese and iron oxides. Also, work by other workers showed that HREE (Heavy rare earth elements) sorption was strongly suppressed in the presence of strong carbonate complexation (Farquhar et al., 1997). The solution chemistry of some rare earth elements is well understood; however, the surface chemistry is not well understood (Farquhar et al., 1997). The effects of carbonate on the sorption of Eu on geological materials will be important in understanding the effect of Eu sorption in elevated carbonate systems.

1.2. Modelling the Kinetics of Eu Sorption

Different approaches to the treatment of kinetic data from batch sorption experiments were used by different investigators, such as Ho et al. (Ho et al., 1995), who took into consideration pseudo-second order kinetics, and Juang and Chen (Juang & Chen, 1997), who applied the Elovich model to chemisorption to treat sorption data.

1.2.1. First Order Reactions

The first of the approaches is to assume that the sorption process takes place as a first-order process, in which the time-dependent equation is given by Aksoyoglu (Aksoyoglu, 1989).

$$R_{st} = R_{s\infty} (1 - e^{-Kt}) \quad (1)$$

where: R_{st} —Sorption coefficient at time t ($\text{cm}^3 \cdot \text{g}^{-1}$), $R_{s\infty}$ —Sorption coefficient at steady-state ($\text{cm}^3 \cdot \text{g}^{-1}$), t —Time (s), K —Rate constant (s^{-1}).

The linearised form of the equation is: $\ln \left[1 - \frac{R_{st}}{R_{s\infty}} \right] = -Kt$.

A plot of $\ln \left[1 - \frac{R_{st}}{R_{s\infty}} \right]$ as a function of time (t) should be linear for a first-order

reaction. Applying the least square method, the points should lie on a straight line, otherwise the first-order assumption is not applicable (Aksoyoglu, 1989). The second interpretation proposed by Aksoyoglu (Aksoyoglu, 1989) makes the following assumptions: the particles are porous, of spherical shape, of a single size and that the radionuclide diffuses into these micropores. The adsorption of solutes from solution by porous adsorption involves three steps:

- 1) Bulk transport of solute in the solution is usually rapid because of mixing.
- 2) Film transport involves diffusion of solute through a hypothetical film boundary layer.
- 3) Except for a small amount of adsorption that occurs on the exterior of the adsorbent, the solute then diffuses within the pore volumes of the adsorbent and/or along pore-wall surfaces to an active adsorption site (intra-particle transport). The

actual adsorption of solute on interior surface sites is generally considered to be very rapid and hence makes an insignificant contribution to the overall adsorption rate. Film and intra-particles transport are thus the major factors controlling rates of adsorption from solution by porous adsorbent. The slower of the two steps is the rate-limiting. At low concentrations and for the reactions controlled by film diffusion, the rate reaction increases linearly with concentration, provided other conditions are unchanged (Ho et al., 1995).

When film and intra-particle diffusion are involved in determining the rate, the relationship is no longer linear. At high concentrations, the rate reaches a maximum where intra-particle diffusion is the rate-determining step, and the rate is independent of concentration.

1.2.2. Pseudo-First Order Reaction

Due to the many Eu species present, it can be extremely difficult and complex to model the sorption kinetics of individual species. One way around that is proposed in this work, i.e., to sum all the different species as a single entity, as shown in Equation (2). The rate of the sorption process can be modelled based on the overall decrease of the sum of all the Eu species present in solution, as shown by Equation (2). Above pH 5, the total concentration of Eu present in solution is a combination of all the species of Eu^{3+} present in solution (van der Lee, 2003) as calculated from the JChess speciation code in Figures 3-5. Eu sorption may thus involve all species which are thermodynamically or kinetically stable.

$$Eu_{tot} = \sum_i^n Eu \quad (2)$$

where Eu_i is the total Eu in solution from Eu species i to n , both being integers. The Eu sorption process can be expressed based on the surface complexation reactions shown below. $\equiv SOH + Eu_{tot} \rightleftharpoons SO \sum_i^n Eu + xH^+$ This non-stoichiometric equation depicts the sorption process. Assuming the concentration of $\equiv SOH$ to be far greater than that of Eu_i , i.e., saturation of sites doesn't occur, the rate equation can be written as: $\frac{dEu_{tot}}{dt} = -K_1 \sum_i^n Eu$ resulting to $Eu_{tot} = Eu_{t0} e^{-kt}$.

A plot of $\text{Log} [Eu_{tot}]$ as a function of t will be a straight line with a rate constant k . For sorption process in which a steady state is attained between the forward and the reverse processes, the kinetics could be modelled taking into consideration both processes.

1.2.3. Pseudo-Second Order Reaction

Ho et al. (Ho et al., 1995) proposed a pseudo-second order model expressed in the form:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (3)$$

where $h = k_2 q_e^2$ and can be described as the initial rate constant as t approaches zero. q_t is the amount of metal ion on the mineral surface ($\text{mol} \cdot \text{g}^{-1}$) at any time t . q_e is the

amount of metal ion sorbed at equilibrium ($\text{mol}\cdot\text{g}^{-1}$); k is the pseudo-second order rate constant ($\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$). If the pseudo-second order kinetics is applicable, t/q_t vs. t will give a linear plot, which allows the computation of q_e , k_2 and h without having to know any parameters beforehand. According to Ho et al. (Ho et al., 1995), if the plot is linear, then the sorption process may be described as chemisorption. Thus, the sorption process involves the formation of strong chemical bonds between Eu and the solid surface, as opposed to other sorption processes such as cation exchange.

1.2.4. Modelling Intra-Particle Diffusion

The immobilisation of radionuclides by rocks and minerals is expected to occur by electrostatic interactions between the sorption sites and charged metal ion species in solution. However, intra-particle diffusion plays an important part in the bulk removal of species in solution. Theoretical treatments of intra-particle diffusion yield rather complex mathematical relationships which differ in form as functions of the geometry of the sorbent particles (Ho et al., 1995). The intra-particle model is expressed by Srivastava and colleagues (Srivastava et al., 1989) and by Weber and Morris (Weber & Morris, 1963) as:

$$q_t = K_i t_a \quad (4)$$

A linearised form of the equation is written as: $\ln(q_t) = \ln(K_i) + a \ln(t)$.

Where “ a ” is the gradient of the linear plots, depicting the mechanism of the adsorption process. A functional relationship common to most treatments of intra-particle diffusion is that uptake varies almost proportionately with the half-power of time ($t^{0.5}$) (Ho et al., 1995). A linear variation between the quantities bound with $t^{0.5}$ predicts that a large initial fraction of the reaction is controlled by intra-particle diffusion. Good linearisation of the data is observed if intra-particle diffusion is the rate-limiting step rather than sorption due to bonding with sorption sites. $q_t = k_i t^{0.5}$. Where k_i is the intraparticle diffusion rate constant $\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-0.5}$. Higher values of k_i illustrate an enhancement in the rate of adsorption and adsorption mechanism, which is related to stronger bonding between metal ions and adsorbent particles (Demirbas et al., 2004).

1.3. Eu Speciation Carbonate-Free System

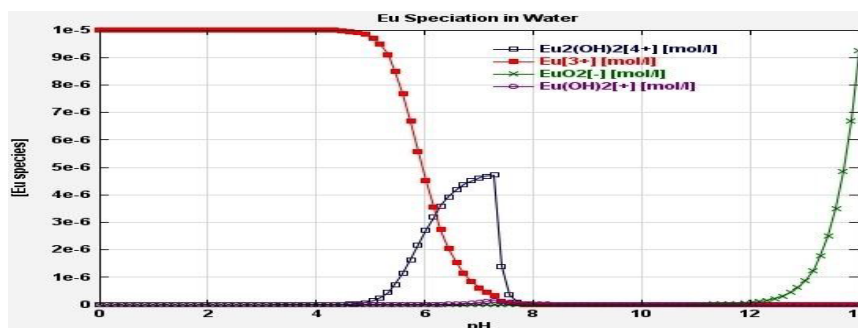


Figure 1. Eu speciation in DI water as calculated using JChess, geochemical code using the default JChess database, taking a cut off concentration of $1 \times 10^{-14} \text{ mol}\cdot\text{dm}^{-3}$ for species to be considered (van der Lee, 2003).

JChess geochemical code (speciation programme) by Ecole de Mines de Paris France, was used to study the variation of Eu species in solution in the absence of any complexing agents such as carbonate. **Figure 1** shows the main species in solution between pH of 7 and 9. The pH range 7 to 9 was selected because the measured equilibration pH of rocks in solution is in this range, as shown in **Table 1**, showing the equilibration pHs for different rocks and minerals.

1.4. Eu Speciation in Low-Carbonate System

Eu speciation in the presence of very low concentrations of NaHCO_3 gave 18 different species of Eu, with some of the species appearing as carbonate complexes of Eu, as shown in **Figure 2**. Taking a cut-off concentration point at $1 \times 10^{-14} \text{ mol}\cdot\text{dm}^{-3}$ for the sake of clarity, removed from the speciation plots those species with aqueous concentrations below $1 \times 10^{-14} \text{ mol}\cdot\text{dm}^{-3}$.

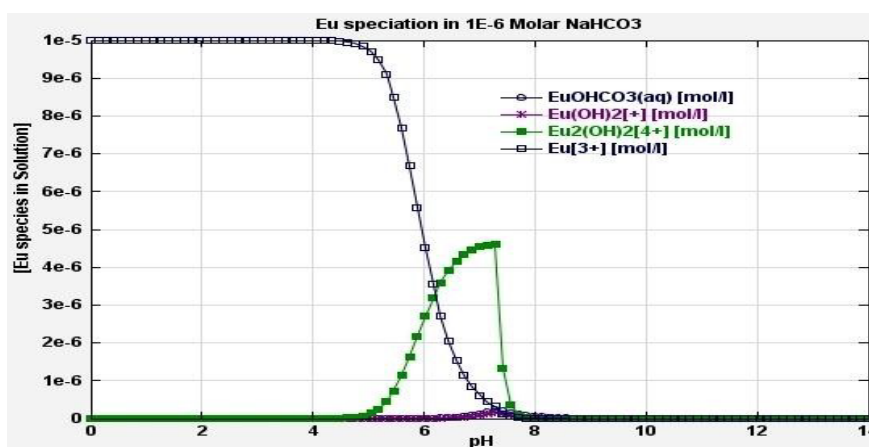


Figure 2. Eu speciation in low carbonate system as calculated using JChess, geochemical code, taking a cut-off concentration of $1 \times 10^{-14} \text{ mol}\cdot\text{dm}^{-3}$ for species to be considered (van der Lee, 2003).

1.5. Eu Speciation in High-Carbonate System

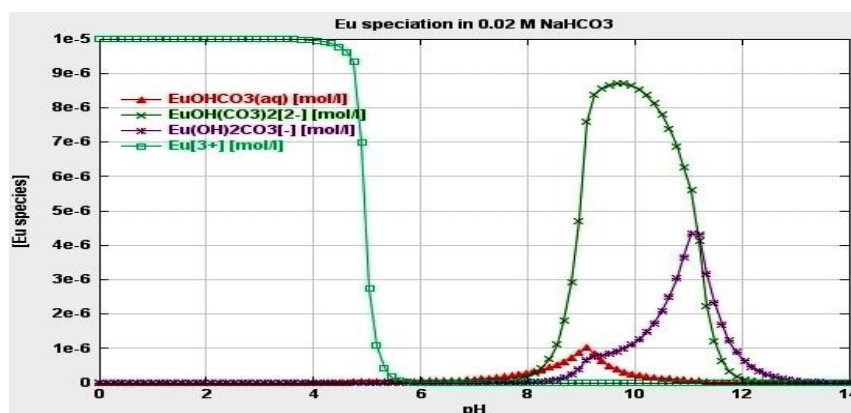


Figure 3. Eu speciation in high carbonate system as calculated using JChess, geochemical code. Taking a cut-off concentration of $1 \times 10^{-14} \text{ mol}\cdot\text{dm}^{-3}$ for species to be considered (van der Lee, 2003).

At high concentrations of carbonate in the system, the speciation was much different from speciation in no and low concentration of carbonate. **Figure 3** shows the different major species after a cut-off point of $1 \times 10^{-14} \text{ mol}\cdot\text{dm}^{-3}$. Within pH range 8 to 12, major species such as $\text{EuOH}(\text{CO}_2)_2^{2-}_{(\text{aq})}$ and $\text{Eu}(\text{OH})_2\text{CO}_3^{-}_{(\text{aq})}$ were dominant as compared to low and carbonate-free solutions.

Table 1. Equilibration pH measurements in different carbonate systems.

Sample	Carbonate free	Low carbonate $1.0 \times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$	High carbonate $2.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$
Biotite Granite (BG)	8.2	8.7	9.5
Grey Granite (GrG)	8.4	8.5	9.5
Rapakivi Granite (RG)	8.1	8.3	9.5
Rose Quartz (RQ)	6.0	8.3	9.5
Orthoclase Feldspar (OF)	7.5	9.5	9.5
Muscovite Mica (MM)	7.7	8.8	9.5

The difference between carbonate-free and low-carbonate system is highlighted by the speciation of Eu in solution, at pH > 12.

pH values were measured during the sorption process to observe any changes in pH that could affect the sorption process, as sorption is pH dependent. From observations in **Table 1**, it can be seen that the observed pH was in the range 7 to 10. This was within the pH range considered in the speciation of Eu in all three systems.

2. Experimental Set-Up

The main constituents of silica-rich rock types such as granite are quartz, feldspars, and biotite (Allard et al., 1980). The sorption properties of the intact rock will obviously depend on the constituents of the different individual components of the rock. Biotite Granite (BG), Muscovite Mica (MM), Orthoclase Feldspar (OF) and Rose Quartz (RQ) were used. The adsorbents were first reduced in size. The size reduction was necessary for the performance of batch equilibrium experiments because 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 (Aksoyoglu, 1989). In addition, the kinetics of processes controlled by diffusion in porous particles is directly related to particle size. Smaller adsorbents will therefore require shorter equilibration times if any porosity was present (Aksoyoglu, 1989; Murali & Mathur, 2002). All rock and mineral samples were supplied by UK Geologist Equipment as intact samples. Results of quantitative powder XRD analyses from the British Geological Survey indicated that the

granites had approximately similar mineralogies and were predominantly composed of quartz (mean *ca.*33%), plagioclase feldspar (mean *ca.*31%) and K-feldspar (mean *ca.*31%). 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 EuCl_3 solution (Aldrich), giving a solid-liquid ratio of 1:200. Experiments with ^{152}Eu were analysed using the Cobra(II) Auto Gamma counting between 100 to 1500 keV at 2 sigma. $1 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ solutions of EuCl_3 were prepared. Analysing the samples using gamma counting was made possible by spiking the solution with 0.1 cm^3 of ^{152}Eu and equilibrating. Due to the small volume of the spike, the overall concentration of the EuCl_3 solution is assumed not to be negligible. Different amounts of carbonate were added into the solution to give carbonate concentrations of 1×10^{-2} and $1 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ for high carbonate (HC) and low carbonate (LC) systems, respectively. These two sets of solutions were referred to as “high and low carbonate” solutions in this work. In one set of experiments, no carbonate was added, and this is described as the “no carbonate” solution. Different reactor vials were prepared for each sampling time. Three replicates of each sampling time were prepared. After equilibrating for the required time, two cm^3 of the supernatant were removed. Blank samples with no solids were also prepared. Due to the comparative nature of the study, it was important to make sure the equilibration, sample separation procedures and pH of the samples remained the same. Measurements before and after equilibration did not show any significant difference. For every set of experiments, the main difference was ionic strength, which did not change for a particular level of carbonate concentration. Experiments were carried out at room temperature.

3. Results and Discussion

To understand the effect of carbonate, sorption data have been modelled using the Langmuir isotherm (Fitting data to the Langmuir, Freundlich and Linear model showed that the Linearised Langmuir model gave the best fit as shown by the root mean square value) to determine the sorption capacity for the three systems. First and second order rate constants were calculated and comparisons made between the three systems.

Static batch sorption experiments were designed to study the rate and sorption capacity of Eu to Biotite Granite (BG) in the presence of different amounts of NaHCO_3 , to understand the effect of carbonate both on the sorption of Eu to granitic rocks and minerals, and also to study how carbonate can affect the rate of removal of radionuclides present in the system. Both pseudo-first and second-order adsorption models were used to describe the data. In both models, all the steps of adsorption, such as external diffusion, internal diffusion, and adsorption, are combined together, and the overall adsorption rate is proportional to either the driving force (as in the pseudo-first-order equation) or the square of the driving force (as in the pseudo-second-order equation) (Pang & Gong, 2008).

3.1. Eu Sorption to Biotite Granite (BG)

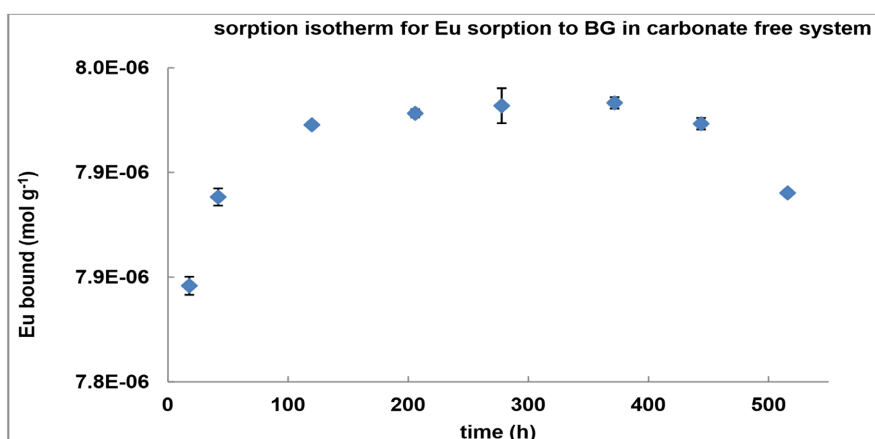


Figure 4. Kinetic sorption isotherm for Eu sorption to BG in carbonate free solution.

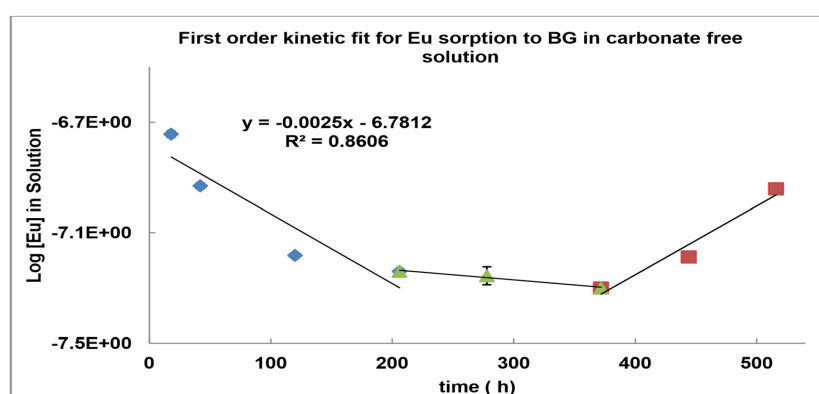


Figure 5. PFO fit for Eu sorption to BG in carbonate-free system. Equilibration pH of system 7 to 8, mass of solid = 0.2 g, solution volume = 40 cm³. Data obtained by fitting data to Equation (3).

The first part of this section concerns the application of empirical models to sorption data. Results for BG showed that data fitted best to the Langmuir model with saturation of sorption sites. This is evident from the Langmuir linearised isotherm. R^2 values for CF, LC and HC systems were close to one. Calculated R_d values showed the effect of carbonate for sorption in the three systems. Mean R_d values were calculated as 97 cm³·g⁻¹ for CF, 81 cm³·g⁻¹ for LC and 21 cm³·g⁻¹ for HC systems. Thus, the R_d decreased as the concentration of carbonate increased in solution. Using the linearised Langmuir isotherms, the maximum concentrations of Eu bound after 520 hours were calculated as 7.8×10^{-6} , 7.7×10^{-6} , and 6.9×10^{-6} mol·dm⁻³ for CF, LC and HC systems, respectively. Thus, results show a decrease in the sorption capacity as the concentration of carbonate increased.

Using the first and second order kinetic models, data were analysed to obtain first and second order rate constants. The rate constants were then compared for the three systems to understand the effect of carbonate on the sorption rate and to determine which sorption model best described the sorption data. **Figure 4**

shows the variation of sorption with time. The figure shows sorption is time-dependent. However, above 370 hours, sorption/desorption mechanisms become apparent, as shown by the positive slope of the plot after 370 hours of equilibration. **Figure 5** shows that the PFO kinetic model partially fits to the data. A negative slope for first-order kinetics shows that the concentration of Eu bound is increasing with time, while that in solution is decreasing.

There was no difference between CF and LC systems in terms of the sorption kinetics, as supported by Eu speciation in both systems (**Figure 6** and **Figure 7**).

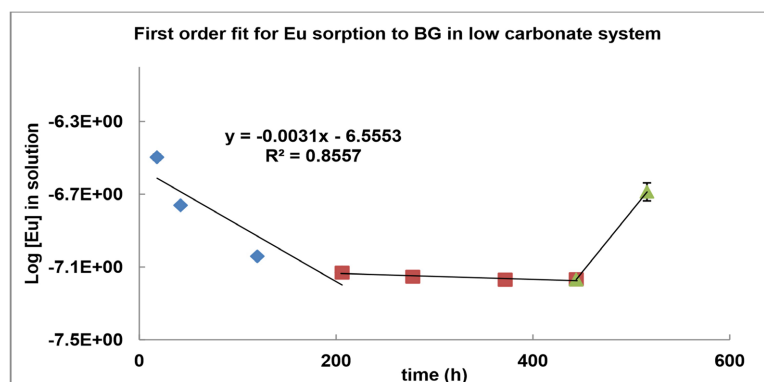


Figure 6. PFO fit for Eu sorption to BG in low carbonate system, at equilibration pH of *ca.*7.5.

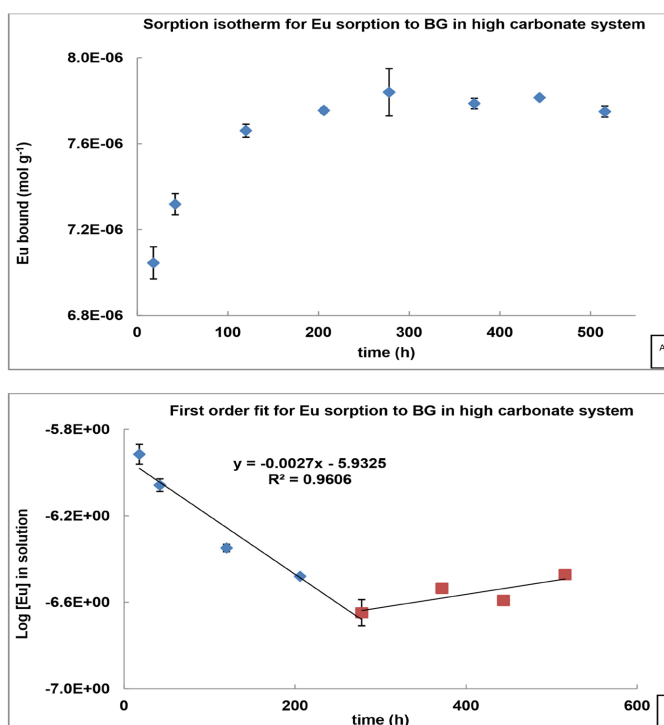


Figure 7. Kinetic sorption isotherms for Eu sorption to BG in high carbonate system. BPFO fit for Eu sorption to BG in high carbonate system, at equilibration pH of *ca.*9.5. Graph shows discontinuity (B) above 200 hours of equilibration as a result of change of sorption mechanism.

Eu sorption in 0.02 mol dm^{-3} carbonate solution (HC) showed sorption increased with time. Saturation of sorption sites was attained after 200 h, with no apparent desorption observed, as was the case with the CF and LC systems.

Data fitted to a first-order kinetic model for Eu sorption to BG in the presence of different amounts of carbonate. From the results, it can be seen that the rate constant changes from negative to positive as equilibration time increases. Initially, sorption fits a PFO model, in which the rate of sorption is dependent on the concentration of Eu in solution. However, at longer equilibration times, the rate constant changes as indicated by the positive gradient. This indicates that the sorption process has changed, due to attainment of steady state, in which the metal ions are equally distributed between available sorption sites and the solution. Initial sorption kinetics can be very fast, resulting in a pseudo-equilibrium system (non-attainment of a steady state system), however, with longer equilibration times, there is redistribution of Eu between the solid and solution phases of the system, resulting in a decrease in rate of sorption and change in sorption process. The decrease in sorption can be attributed to a decrease in the amount of metal present in solution, and also to occupation of sorption sites as sorption nears monolayer coverage (Chiou & Li, 2002) showed the linearised Langmuir isotherms with $R^2 = 0.99$ for CF, LC and HC systems. Although the sorption is seen to be rapid initially, the effect of carbonate is very obvious in the system with $0.02 \text{ mol} \cdot \text{dm}^{-3}$ carbonate. The time taken to attain saturation increased from low carbonate system to high carbonate system. It took about 280 h of equilibration for HC system while for LC and carbonate-free systems, it took about 120 h. The initial high sorption rate is reduced as compared to sorption on low or no carbonate systems due to the complexation reactions between Eu and carbonate. In high concentration of carbonate, negatively charged, higher molecular weight complexes are formed, such as $\text{EuOH}(\text{CO}_3)_2^{2-}$ and $\text{Eu}(\text{OH})_2\text{CO}_3^-$ (Figures 1-3), which affect the free Eu metal. Thus, the rate of Eu uptake is reduced.

Despite the observation above, the sorption process and mechanisms cannot be explained solely from a first-order perspective, in many cases, the PFO kinetic model is limited in explaining sorption kinetics for the whole range of contact times, and is generally applicable only for the initial stage of the sorption process (Horsfall & Spiff, 2005). There is a need to apply other models that may explain sorption kinetics based on the species present in solution.

Using kinetic sorption models, the data obtained were fitted to the first and second order models. The data did not fit to the first-order kinetic model for the entire equilibration period studied (the PFO kinetic model usually applies only at the initial stages of the sorption process) (Horsfall & Spiff, 2005). Therefore, the sorption process is dependent on only the concentration of sorption sites or the concentration of Eu species present in solution, i.e., it is not dependent on either the sum of the Eu species, or the concentration of the sorption sites. However, fitting the data to the PSO showed that the process depended on both the concentration of Eu species and that of the sorption sites.

In terms of sorption rates, the rate constants for sorption to BG were negative (-3.1×10^{-3} and $-2.7 \times 10^{-3} \text{ h}^{-1}$ for low and high carbonate systems after 280 h of equilibration respectively), signifying that the total concentration of Eu in solution decreases with time. The PFO kinetic sorption parameters are shown in **Table 2**. The values show that the rate constant for first-order kinetics in the region for which the data fitted, increased from LC to HC (-3.1×10^{-3} and $-2.7 \times 10^{-3} \text{ h}^{-1}$ for LC and HC systems, respectively, the negative sign indicating the direction of the sorption process). Based on the extent (R^2) to which the sorption data for the three systems fitted to the PFO model, it can be concluded that the sorption process will be first order as the concentration of carbonate increases in solution. The reason could be due to the difference in speciation between LC and HC systems. **Table 3** shows the major species in the three systems. The first-order rate constant was calculated as $-2.5 \times 10^{-3} \text{ h}^{-1}$ (CF). From the calculated rate constants, the rate of Eu uptake in the three systems is the same; however, the root mean square value is closer to unity for HC system.

Table 2. Kinetic fit parameters for Eu sorption to Biotite Granite in carbonate-free, low- and high-carbonate systems. k is the rate constant obtained from the gradient of the linearised first-order equation. Rate constant for RQ changes from negative to positive (low carbonate = $1 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$, high carbonate = $0.02 \text{ mol} \cdot \text{dm}^{-3}$).

	Carbonate free		Low carbonate		High carbonate	
Sample	$k \text{ (h}^{-1}\text{)}$	R^2	$k \text{ (h}^{-1}\text{)}$	R^2	$k \text{ (h}^{-1}\text{)}$	R^2
Biotite Granite	-2.5×10^{-3}	0.86	-3.1×10^{-3}	0.85	-2.7×10^{-3}	0.96
Grey Granite	-2.7×10^{-3}	0.88	-1.9×10^{-3}	0.93	-1.4×10^{-3}	0.93
Rapakivi Granite	-3.2×10^{-3}	0.92	-4.4×10^{-3}	0.94	-2.1×10^{-3}	0.95
Rose Quartz	2×10^{-5}	0.49	1.4×10^{-3}	0.82	-1.1×10^{-3}	0.96
Orthoclase Feldspar	-2.7×10^{-3}	0.96	-2×10^{-3}	0.94	-2.1×10^{-3}	0.95
Muscovite Mica	-1.4×10^{-2}	0.84	-2.9×10^{-3}	0.96	-1.1×10^{-3}	0.97

Table 3. Major Eu species in different carbonate solutions, showing species present at different pH ranges. Speciation calculated using JChess Code, taking a concentration cut-off point of $10^{-14} \text{ mol} \cdot \text{dm}^{-3}$, precipitation and dissolution disabled.

Carbonate-free system pH < 8	Low-carbonate system pH < 8	High-carbonate system 12 < pH < 8
Eu^{3+}	Eu^{3+}	EuOHCO_3
$\text{Eu}(\text{OH})_2^{4+}$	$\text{Eu}(\text{OH})_2^{4+}$	$\text{EuOH}(\text{CO}_3)^{2-}$
	EuOHCO_3	$\text{Eu}(\text{OH})_2\text{CO}_3^-$

Figure 8 shows the PSO kinetic model for Eu sorption to BG in all three systems. A good fit ($R^2 = 0.99$) was obtained Equation (3) for the entire equilibration period. However, this was not the case as seen with the first-order kinetic model. This implies that the data could be described using the PSO model proposed. The

conclusions to be drawn here include the fact that the sorption process is dependent on the concentration of Eu species and on the total number of sorption sites present in the system, and that the PSO kinetic model fits better to the data for the entire equilibration period, as shown by the R^2 value.

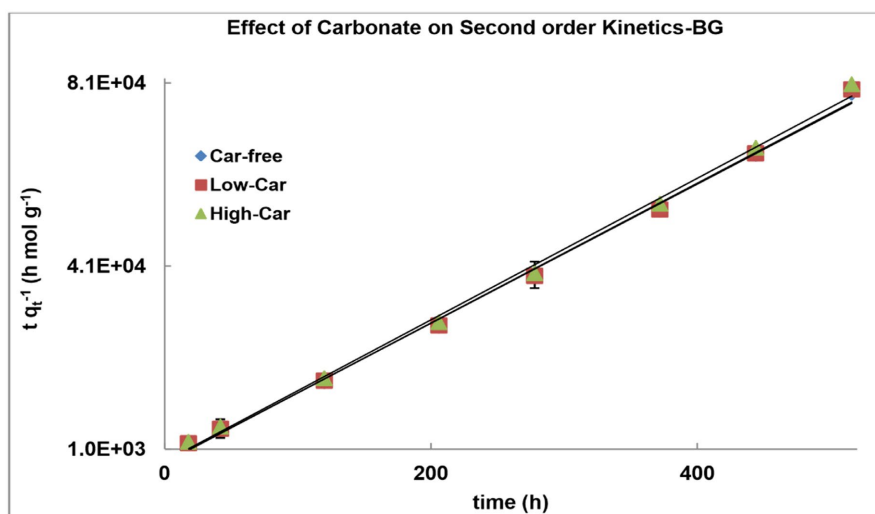


Figure 8. PSO isotherms for Eu sorption to Biotite Granite, in carbonate-free, low-carbonate and high-carbonate systems, at constant metal concentration. Data obtained by fitting experimental data to Equation (3).

Table 4 shows the PSO sorption parameters, determined by fitting experimental data to the PSO kinetic model (Equation (3)). It can be seen that in all three systems (carbonate-free, low-carbonate, and high-carbonate), the PSO rate constants are identical. The rate constants calculated are -12.25 (CF), -11.70 (LC) and -14.13 (HC) $\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$.

The similarity shown in the rate constants suggests that the presence of carbonate in groundwater may not affect the sorption of Eu to Biotite Granite. The adsorption process on a porous adsorbent generally involves three stages:

- 1) External diffusion;
- 2) Internal diffusion (or intra-particle diffusion);
- 3) Actual adsorption (Chang et al., 2003).

The adsorption step is usually very fast for the adsorption on porous adsorbents compared to the external or internal diffusion step and it is known that the adsorption equilibrium is reached within several minutes in the absence of internal diffusion for porous adsorbents (Chang et al., 2003). Thus, the long adsorption equilibrium time in experiments suggests that the internal diffusion may dominate the overall adsorption kinetics. As seen above, concerning the similarities of the PSO rate constants, this can be justified by the fact that sorption is not solely dependent on electrostatic interactions of the metal-solid complex. Negatively charged Eu species such as $\text{EuOH}(\text{CO}_3)_2^{2-}(\text{aq})$ and $\text{Eu}(\text{OH})_2\text{CO}_3^{-}(\text{aq})$ (present in HC system, as shown in Table 3) could be removed from solution by intraparticle dif-

fusion. Theoretical treatments of intraparticle diffusion yield rather complex mathematical relationships which differ in form as functions of the geometry of the sorbent particles (Ho et al., 1995). The intra-particle model is expressed by Srivastava and colleagues (Srivastava et al., 1989) and by Weber and Morris (Weber & Morris, 1963), as shown by 4. Sorption data from the different granitic samples were modelled by using intraparticle model and results are shown in Table 6. Intraparticle diffusion rate constants were obtained as -7×10^{-5} (CF), 6×10^{-5} (LC) and -3×10^{-5} (HC) $\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-0.5}$, implying that intraparticle occurred two times more in carbonate-free system than for high-carbonate system, probably due to the high molecular weight Eu-carbonate species present in the HC systems.

3.2. Kinetics of Eu Sorption to Grey Granite (GrG)

Results obtained for Grey Granite were fitted to the first and second order kinetic models, as was the case for BG. Eu sorption to GrG in the high carbonate system increased to a maximum amount (reaches a system of steady state) after about 200 h (as was the case with BG); however, for CF and LC systems, sorption was very fast initially and decreased with time. At the measured equilibration pH values (Table 1 in the experimental section), the major species in solution have been determined using JChess as $\text{EuOHCO}_3(\text{aq})$, $\text{EuOH}(\text{CO}_3)_2^{2-}(\text{aq})$, and $\text{Eu}(\text{OH})_2\text{CO}_3^{+}(\text{aq})$ for HC environment. For LC system, the major species at the equilibration pH of 8.5 are $\text{Eu}(\text{OH})_2^{2+}(\text{aq})$ and $\text{EuOHCO}_3(\text{aq})$, while for NC, the major species is $\text{Eu}(\text{OH})_2^{+}(\text{aq})$ at an equilibration pH of 8.3. The difference in speciation may be responsible for the difference in the sorption profile between HC and CF/LC. Despite the major differences in speciation, it can be said that the speciation of Eu in all three systems did not affect the net sorption capacity at the end of the equilibration period (ca. 520 h). As was observed for sorption to BG, the first model fitted to the sorption data partially (below 200 hours of equilibration time). Thus, rate constants are defined equilibration time < 200 hours. Table 2 shows sorption parameters for different granitic materials studied. From Table 2, the PFO rate is the following order: $-7 \times 10^{-5} \text{ h}^{-1}$ (CF) > $6 \times 10^{-5} \text{ h}^{-1}$ (LC) > $3 \times 10^{-5} \text{ h}^{-1}$ (HC), the negative on the rates indicating the direction of movement.

Second Order Kinetic for Grey Granite (GrG)

Eu sorption to GrG was similar to that of BG, in that sorption occurred by the Langmuir model. Earlier work by Ebong and Nick (Ebong & Nick, 2012) dealt on the application non-electrostatic sorption models to sorption data to obtain sorption parameters for isotherms such as the Langmuir, Linear K_d and Freundlich. The maximum concentration of Eu bound was determined from the linearised Langmuir isotherm. Mean R_d values were calculated, for the entire equilibration period as 55, 40 and 8 $\text{cm}^3 \cdot \text{g}^{-1}$ for carbonate-free, low-carbonate and high-carbonate systems, respectively. From the linearised isotherms, the maximum concentration of Eu bound was 7.6×10^{-6} , 7.4×10^{-6} , and 5.8×10^{-6} for carbonate-free, low-carbonate and high-carbonate systems, respectively. As with Eu sorption to BG, Eu sorption to GrG decreases as the concentration of carbonate in solution increases.

This is evident from both the R_d and the maximum concentration of Eu bound after 520 hours of equilibration.

Fitting sorption data obtained for BG to the first and second order models showed that the PSO model described the sorption process best. The comparison was done using R^2 values from the linearised first and second order model; results showed that the data fitted to the second order model for CF, LC and HC systems. Sorption parameters obtained are shown in **Table 4**. The effect of carbonate is shown by the PSO rate constant for the three systems. For the CF system, a high-rate constant ($-838.3 \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) was obtained compared to -13.1 for LC, and $27.62 \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for HC systems. The similarity between the PSO rate constant for LC and HC systems can be attributed to the presence of carbonate in the systems.

Comparing PFO kinetics and PSO kinetics, it was observed that discontinuities exist in the PFO model, when the entire equilibration period is considered; however, for the PSO model, no such discontinuities were observed. Discontinuities are due to a change in the sorption mechanism or the presence of a second sorption mechanism in the system. The presence of a second mechanism is evident from the change in the slope of the PFO isotherm above equilibration time of 200 h, as shown in **Figure 9**. The change from negative to positive values confirms that desorption is taking place in the system at equilibration times > 200 h. The rate constant in terms of the decrease of Eu in solution (sorption) is negative. A positive sign will thus indicate that Eu is desorbing. Thus, the whole process is dependent on the aqueous concentration of Eu in solution and the concentration of the sorption sites. A good linear fit ($R^2 = 0.99$) for all three systems was found.

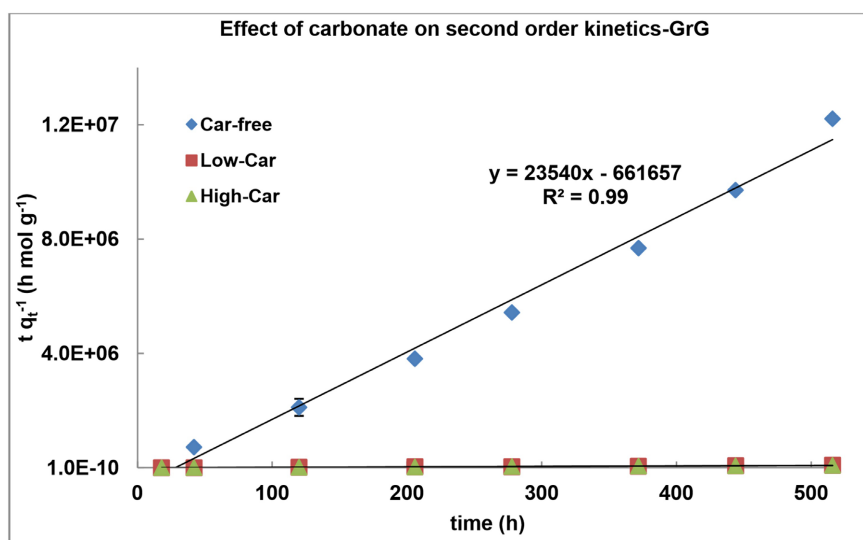


Figure 9. Comparing data for PSO kinetics for Eu sorption to GrG in carbonate-free, low- and high-carbonate systems. Figure shows that the slope for LC and HC systems is negligible compared to that of carbonate-free system, with LC and HC showing similar behaviour.

As noted above, sorption kinetics are a combination of several other processes,

such as external diffusion, internal diffusion (or intra-particle diffusion) and actual adsorption (Chang et al., 2003) at the solution-solid phase. Equation (4) was applied to study the intra-particle diffusion mechanism. The results are shown in Table 6. The rate constants for intraparticle diffusion were calculated as: -6.0×10^{-5} $R^2 = 0.93$ for CF, -6.0×10^{-5} $R^2 = 0.93$ for LC and 7.0×10^{-5} $R^2 = 0.98$ for HC system. The good fits to the intraparticle diffusion model are an indication that there might be other sorption mechanisms, such as IPD, apart from sorption due to electrostatic interactions between charged Eu species in solution.

3.3. Summary: Kinetics of Eu Sorption to Granitic Rocks

- The results showed similarity in the sorption pattern (sorption increased and levels off at steady state) for all three granitic rocks studied. This similarity is probably reflected in the similarity of the composite minerals;
- Results showed discontinuities in the linearised first-order kinetic models, taking into consideration the entire equilibration time;
- PFO kinetics was applicable only for a section of the sorption process. With desorption taking place after longer equilibration periods;
- For PSO kinetics, the rate constants shift from negative to positive values when the concentration of carbonate in solution increases from NC to LC and HC environments.
- Application of empirical sorption models showed that the R_d and maximum concentration of Eu bound decreased as the concentration of carbonate increased.
- Results also showed that sorption data were best described by the Langmuir model.

3.4. Kinetics of ^{152}Eu Sorption to Rose Quartz (RQ)

Sorption results for granitic rocks showed that the sorption capacity was suppressed in the presence of carbonate in the system. Results for RQ, however, showed the contrary. Sorption in the presence of carbonate was enhanced, as evident from the sorption isotherms (Figure 10). Sorption was best described by the Langmuir isotherm, as was the case with granitic rocks, linearised Langmuir sorption isotherms. Mean R_d values were calculated as 0.2, 1.7 and $19 \text{ cm}^3 \cdot \text{g}^{-1}$ for carbonate free, low carbonate and high carbonate systems, respectively. The increase in R_d with increase in carbonate concentration is highlighted by the maximum concentration of Eu bound. From the linearised Langmuir isotherms, the maximum concentration bound was $2.0 \times 10^{-8} \text{ mol} \cdot \text{dm}^{-3}$, for carbonate-free system, $2.4 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ and $5.42 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$.

Among the non-equilibrium processes influencing sorption, is the possible division of sorption sites into two types. The two-site sorption concept presumes that sorption can be classified into two fractions: Type 1, where sorption is assumed to be instantaneous, and Type 2, where sorption is considered time-dependent (Nkedi-Kizza et al., 2006). The two-type sorption site concept has been applied to describe the sorption kinetics of granitic minerals due to their non-heterogeneous phases, as opposed to the granitic rocks.

Kinetic studies with Rose Quartz (RQ) showed that the presence of carbonate in the system affected the rate of the sorption process, and the sorption sites are considered to be Type 2. **Figure 10** shows Eu sorption isotherms for Eu sorption in different aqueous carbonate concentrations. It can be seen that sorption increased with equilibration time before the system attained a steady state for the LC and HC systems. Sorption in the HC system can be said to be Type 1 (fast) and sorption in the LC system is said to be Type 2 (time dependent). Eu sorption in the carbonate-free system showed characteristically low levels of sorption to quartz. Eu sorption in CF system is time independent, with low sorption levels compared to the HC and LC systems (**Figure 10**). From **Figure 10**, it is evident that the presence of carbonate affected both the rate and the amount of sorption at the end of the equilibration process.

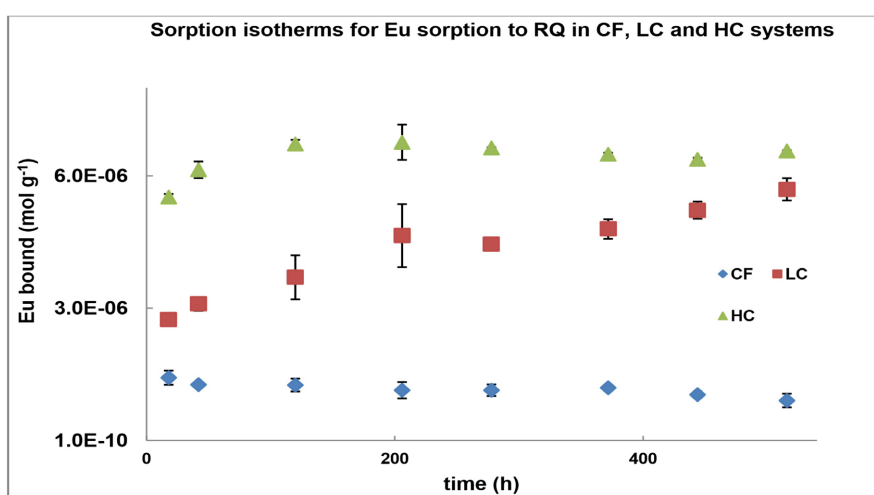


Figure 10. Kinetic sorption isotherms for Eu sorption to Rose Quartz in carbonate-free, low- and high-carbonate systems. Figure shows low sorption capacity for Eu in carbonate-free system.

One major difference between the sorption kinetics of Eu to RQ as compared to that of granitic rock samples is that the sorption capacity defined by the amount bound at the end of the experiment is different in each of the three systems studied. Looking at **Table 2**, it can be seen that the PFO rate constant is positive, 5×10^{-5} and $1.4 \times 10^{-3} \text{ h}^{-1}$ for CF and LC systems, respectively, and is negative ($-1.1 \times 10^{-3} \text{ h}^{-1}$) in high HC. The three systems fitted to PFO kinetics in the following order: HC system ($R^2 = 0.95$) > LC system ($R^2 = 0.82$) > CF system ($R^2 = 0.49$). This change can be attributed to change in the sorption mechanism, due to the presence of carbonate.

Kinetic data for RQ were fitted to the PSO model to compare with the PFO. It can be seen in **Table 2** that the kinetic data fitted to the PFO as the concentration of carbonate increased in solution. PSO kinetic fit parameters are shown in **Table 4**. Results show that the sorption data fitted to the PSO model in all three systems considered ($R^2 = 0.94$ for CF system, 0.99 for LC system, and 0.97 for HC system). The PSO rate constants varied in the order: -3837 for CF system > -198 for LC

system $> 3.5 \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for HC system.

3.5. Kinetics of Eu Sorption to Orthoclase Feldspar (OF)

Eu sorption capacity decreased as the concentration of carbonate increased, as was seen with the granitic rocks. Sorption data could be described using the Langmuir model. A study of the kinetics of Eu sorption to OF showed that sorption was Type 2 (Time dependent (Fourest, 1993) below 200 h of equilibration). Above 200 h of equilibration, Eu sorption becomes independent of time, due to saturation of sorption sites as shown by the Langmuir-type sorption isotherms. Fitting the data to PFO and PSO kinetics showed that both models could be used to describe the sorption data, especially prior to attainment of steady state (>200 h equilibration). Above 200 h equilibration, discontinuities in the linearised PFO were observed. However, the PSO kinetic model described the sorption better for the entire equilibration period. Sorption parameters are shown in Table 2, Table 4 and Table 5 for PFO, PSO and Eu sorption, respectively.

3.6. Kinetics of Eu Sorption to Muscovite Mica (MM)

Layered silicates such as Muscovite Mica contain two types of surface adsorption sites: those with a permanent charge, formed as a result of isomorphic substitution in the crystal structure, and with a pH-dependent charge appearing because of protonation or deprotonation of hydroxyl groups on the basal or edge surfaces of the tetrahedral or octahedral layers (Maslova et al., 2004). As is known, ion-exchange reactions usually take place on the basal surface, where sites with an unbalanced structural charge are located. For mica, this charge is negative, and the sorption of cations on these sites only slightly depends on the pH value of the solution (Maslova et al., 2004). Kinetic data for the sorption of Eu to Muscovite Mica showed that sorption was rapid (Type 1 independent of time) (Fourest, 1993) at shorter equilibration times of <42 h. This rapid sorption is due to the permanent negative charge present in the mica lattice. Eu(III) species on BSG grains are predominant as the ion exchange ($\equiv\text{X}_3\text{Eu}^0$) and the inner sphere complexes of $\equiv\text{S}_w\text{O}^-\text{Eu}(\text{OH})_{2,0}$, $\equiv\text{S}_s\text{O}^-\text{Eu}(\text{OH})_{2,0}$, $\equiv\text{S}_s\text{O}^-\text{Eu}_{2+}$, and $\equiv\text{S}_w\text{O}^-\text{Eu}_{2+}$ (Li et al. 2019). Langmuirian type isotherms for Eu sorption to MM in the LC and HC systems. Eu sorption in the carbonate-free system was also shown to be fast initially. However, after about 42 hours of equilibration, sorption decreased gradually due to non-attainment of steady state in the system. Data fitted to the PFO kinetic model for equilibration period of <42 h. Table 4 shows the different sorption rate parameters for PSO reaction models for all samples studied. It can be seen that the data fitted best to the second-order kinetic model. Fitting the data for MM to the intra-particle rate model gave a root mean square value of 0.76, confirming that sorption was not dependent only on electrostatic interaction.

An overview of the change in reaction mechanism from first order to second order is shown in Table 6. Thus, Eu sorption is dependent on the concentration of the sorption sites and the total Eu speciation in the reaction vessel. As the car-

bonate concentration increased, the rate constants remained negative for PFO reactions, while for PSO, the rate constants changed from negative to positive values (Table 6). R^2 values decreased as: HC > LC > CF system, as shown in Table 6 for PFO, while for PSO, there was no difference in the three systems. For the PSO model, the initial rate constant $^*h = k_2 q_e^2$ (rate constant as t approaches zero) changes from negative to positive as the concentration of carbonate increases in the CF, LC and HC systems. The effect of carbonate on the order of reaction is visible from the observations in Table 6. For carbonate-rich systems, sorption is influenced by $\text{EuOH}(\text{CO}_3)_{2(\text{aq})}^-$, $\text{Eu}(\text{OH})_2\text{CO}_{3(\text{aq})}^-$, and $\text{EuOHCO}_{3(\text{aq})}$. However, the net negative charge on the Eu species can reduce the rate of the sorption process. In the study of radionuclide retardation, where the metal is complexed with anionic species, the net sorption rate can be influenced by intra-particle diffusion.

Table 4. Fit parameters for second-order kinetics for Eu sorption to granitic rocks and minerals in different carbonate solutions. Table shows initial rate constant $^*h = k_2 q_e^2$ (rate constant as t approaches 0) changes from negative to positive as the concentration of carbonate increases from CF, LC and HC systems. Values derived from linearised isotherms. Data collected at the respective equilibration pH and room temperature at constant metal concentration.

	Carbonate free				Low carbonate				High carbonate			
	k_2 ($\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	*h ($\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) ($^*h = k_2 q_e^2$)	q_e ($\text{mol}\cdot\text{g}^{-1}$)	R^2	k_2 ($\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	*h ($\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) ($^*h = k_2 q_e^2$)	q_e ($\text{mol}\cdot\text{g}^{-1}$)	R^2	k_2 ($\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	*h ($\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) ($^*h = k_2 q_e^2$)	q_e ($\text{mol}\cdot\text{g}^{-1}$)	R^2
Biotite Granite	-12.25	-5.3×10^{-4}	6.6×10^{-3}	0.99	-11.7	-5.0×10^{-4}	6.5×10^{-3}	0.99	14.1	4.2×10^{-4}	6.5×10^{-3}	0.99
Grey Granite	-838.8	-1.5×10^{-6}	4.4×10^{-5}	0.99	-13.1	-5.6×10^{-4}	6.5×10^{-3}	0.99	27.6	1.1×10^{-3}	6.3×10^{-3}	0.99
Rapakivi Granite	-860.3	-1.5×10^{-6}	4.2×10^{-5}	0.99	-11.1	-4.6×10^{-4}	6.4×10^{-3}	0.99	70.4	3.0×10^{-3}	6.5×10^{-3}	0.99
Rose Quartz	-3837	-1.4×10^{-7}	6.1×10^{-6}	0.94	-198	-8.3×10^{-3}	6.5×10^{-3}	0.99	3.5	1.2×10^{-4}	5.8×10^{-3}	0.97
Orthoclase Feldspar	-1387	-2.4×10^{-6}	4.2×10^{-5}	0.99	-16.8	-6.7×10^{-4}	6.4×10^{-3}	0.99	3.4	1.7×10^{-4}	6.6×10^{-3}	0.98
Muscovite Mica	-980	-1.7×10^{-6}	4.2×10^{-5}	0.99	-7.3	-2.9×10^{-3}	2.0×10^{-2}	0.99	3.7	1.4×10^{-4}	6.1×10^{-3}	0.99

Note: k_2 is pseudo-second order rate constant, ($\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$). *h is the rate constant as t approaches zero. q_e is the amount bound at equilibrium ($\text{mol}\cdot\text{g}^{-1}$); where $^*h = k_2 q_e^2$ can be described as the initial rate constant as t approaches zero. q_t is the amount of metal ion on the mineral surface ($\text{mol}\cdot\text{g}^{-1}$) at any time t .

Table 5. Rate constants for intra-particle diffusion for Eu sorption to granitic materials in CF, LC and HC systems. Table shows the extent to which sorption data fitted to the IPD model. MM shows the least fit to IPD model. Data derived from linearised plots of the model (Equation (3)), the rate K_{id} measured in $\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-0.5}$.

	BG	GrG	RG	RQ	OF	MM
Carbonate Free	-7×10^{-5} $R^2 = 0.98$	-6×10^{-5} $R^2 = 0.93$	-6×10^{-5} $R^2 = 0.89$	-2×10^{-5} $R^2 = 0.80$	-4×10^{-5} $R^2 = 0.77$	1×10^{-5} $R^2 = 0.45$
Low Carbonate	-6×10^{-5} $R^2 = 0.93$	-5×10^{-5} $R^2 = 0.88$	6×10^{-5} $R^2 = 0.99$	1×10^{-3} $R^2 = 0.87$	2×10^{-4} $R^2 = 0.95$	1×10^{-4} $R^2 = 0.76$
High Carbonate	-3×10^{-5} $R^2 = 0.93$	7×10^{-5} $R^2 = 0.98$	1×10^{-4} $R^2 = 0.97$	1×10^{-3} $R^2 = 0.87$	-3×10^{-5} $R^2 = 0.55$	1×10^{-3} $R^2 = 0.76$

3.7. Effect of Carbonate on Kinetics

The effect of carbonate on the sorption kinetics is summarised in **Table 6** in terms of the sign (positive or negative) of the rate constant, the initial rate (h in the table) and the fit to the model. The table demonstrates the effect of carbonate on the sorption rates.

Table 6. Table relating PFO and PSO kinetics to different carbonate systems, showing the relative trends of the different sorption parameters obtained from kinetic data. The signs (–) and (+) indicate the extent to which the model describes the data, which is also highlighted by the root mean square value.

	CF	LC	HC
PFO	–	–	–
PSO	–	+	+++
Initial Rate	–	–	+
PFO Fit	Low	High	Very High
PSO Fit	Very High	Very High	Very High

Note: Increasing carbonate concentration.

4. Conclusion

Taking into consideration the complexity of the speciation of Eu in different carbonate concentrations, it can be concluded that carbonate in the groundwater might affect the sorption mechanisms by which granitic rocks will retard sorption. Generally, high carbonate concentrations are seen to affect the initial rates. From the results of the kinetic experiments, the following conclusions can be made. Using empirical models, it has been shown for all the systems that the presence of carbonate affected not only the rate but also the sorption capacity. Except for RQ, where the presence of carbonate enhanced both the R_d and the maximum concentration bound, carbonate decreased the R_d and maximum concentration of Eu bound for the granitic rocks, OF and MM. From the results, it can be seen that:

- 1) Sorption was fast initially, and reached saturation at longer equilibration times (desorption observed for Eu sorption to MM in CF system above 42 h equilibration).
- 2) The presence of carbonate in solution can alter the overall speciation of the metal in solution, which can affect sorption rates.
- 3) Sorption data fitted to the PFO kinetic model, partially for most cases, fewer than 200 h of equilibration. Data fitted to the PFO model as the concentration of carbonate increased in solution.
- 4) Sorption data fitted to the PSO model when the entire equilibration period is considered.

The effect of intra-particle diffusion is shown, with MM showing the least dependence on IPD.

Conflicts of Interest

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

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