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Radium uptake by recrystallized gypsum: an incorporation study

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Abstract

Batch experiments of 226Ra uptake by recrystallized gypsum CaSO4.2H2O(s), monitored over 200 days, have shown that the published value for the distribution coefficient of 226Ra between gypsum and an aqueous phase, 0.03 (Gnanapragasam and Lewis, 1995), is an upper limit. This suggests that this value needs to be confirmed. A solid solution between gypsum and radium sulfate (Ca,Ra)SO4.2H2O(s) cannot be considered per se, which is not surprising considering gypsum’s high solubility product (lg Ks = -4.58) and the ionic radius of VIIIRa (1.48 Å), when compared to that of VIIICa (1.12 Å).

Keywords: gypsum; radium; solid solution; distribution coefficient.

1. Introduction

According to its half period, 1620 y, and its mobility, 226Ra is one of the main contaminants of concern (COC) present within the Uranium ore processing wastes. Indeed, 226Ra, a decay product of the 238U decay chain, is naturally present in the ore, and is not targeted by the ore treatment. Its abundance in mining environments is so low that no proper mineral phase has ever been found. Its mobility can then only be lowered by interactions with surrounding mineral phases present in its environment, such as surface interactions and/or formation of a solid solution. 226Ra uptake by sulfate, clays and ferrous oxides, is actually known [1-3]. Gypsum (CaSO4.2H2O(s)) and barite (BaSO4(s)) are the two main sulfate found in

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226Ra’s environment. Even though interactions between 226Ra and barite are well studied and are still exploited to reduce 226Ra water concentration [4], interactions between 226Ra and gypsum are less known. Interactions between 226Ra and gypsum are usually described by the distribution coefficient D according to:

\[ D = \left( \frac{[226Ra]/[Ca]}{[226Ra]/[Ca]} \right)_{\text{solid}} / \left( \frac{[226Ra]/[Ca]}{[226Ra]/[Ca]} \right)_{\text{solution}} \]  

Where \( \left( \frac{[226Ra]/[Ca]}{[226Ra]/[Ca]} \right)_{\text{solid}} \) and \( \left( \frac{[226Ra]/[Ca]}{[226Ra]/[Ca]} \right)_{\text{solution}} \) represent respectively the molar ratio in the solid and in the solution between 226Ra and Ca, the major element substituted. Even though the difference in ionic radii between Ca and Ra is too high (~ 30 %) to allow any substitution, two different values of D have been previously determined, both via coprecipitation experiments of 226Ra in gypsum. One is estimated to be about 0.03, determined by Gnanapragasam and Lewis in 1995 [5]; the other study, by Yoshida et al. in 2009 [6], estimates a considerably higher value of about 0.3.

The management of the COC during and after the ore exploitation represents a major issue in the minimization of the environmental footprint of such activities. The prediction and the modeling of their behavior with time are essential to ensure a durable rehabilitation of former mining sites. Though, available literature values of the distribution coefficient D of 226Ra between gypsum and the aqueous phase differ too much to allow a satisfactory model of 226Ra’s behavior with time.

The purpose of this study is to re-examine the distribution coefficient of 226Ra between aqueous solutions and gypsum, conducting an incorporation experiment of 226Ra into gypsum under equilibrium conditions.

2. Material and Methods

The incorporation experiment of 226Ra in gypsum under equilibrium conditions consists of following the evolution of 226Ra activity over time in the aqueous solution in contact with gypsum. The trace element is incorporated in crystal lattice sites usually occupied by Ca, major element of the solid, through the dissolution/recrystallization process characteristic of the dynamic equilibrium stated between the solid and the solution. As the trace element incorporation in the solid phase depends on the dissolution/recrystallization rate, a kinetic monitoring of such processes is achieved by following the 45Ca (half-life: 163 d) uptake through its corrected activity decrease with time. The incorporation of 45Ca into the mineral up to isotopic equilibrium can be described by the following exponential law [3]:

\[ A(t)/A_0(t) = \exp \left( -\frac{(S/L) \cdot \Omega \cdot \sigma \cdot t}{[Ca]_{\text{saturation}}} \right) \]  

Where A(t) et A_0(t) represent respectively the activity of 45Ca in the solution and the initial activity remaining in solution at the sampling time t, \( S/L \) represents the solid to liquid ratio (g.L\(^{-1}\)), \( \Omega \) is the dissolution/recrystallization rate (mol.m\(^{-2}\).day\(^{-1}\)), \( \sigma \) is the solid’s specific surface (m\(^2\).g\(^{-1}\)), [Ca]_{saturation} is the Ca content of a water saturated with gypsum and t is the interaction time (d). The \( S/L \) and [Ca]_{saturation} parameters are assumed to be constant during the experiment; \( \sigma \) is also assumed constant with time even though it has not been measured yet because of analytical difficulties. The recrystallization rate is then obtained by fitting the 45Ca activity data.

This incorporation experiment has been run with synthetic gypsum obtained from a supersaturated solution. After several days in a stove heated at 40 °C, the nature of the dried solid is checked by powder XRD. Two sets of ten batches have been prepared: one spiked with 226Ra tracer, the other one with 45Ca tracer. The slurries were then mounted on rotating end-over-end shakers to provide a continuous mixing. At regular time intervals, the batches were centrifuged during 1h at 20 000 rpm. After filtration, 226Ra was analyzed by gamma spectrometry, using the 186 keV peak for direct counting, 45Ca was measured by liquid scintillation. For each set, 3 standards have been prepared with only the solution in equilibrium with gypsum and spiked in the same way as the suspensions.
3. Results and discussion

In spite of a significant decrease in $^{45}$Ca activity in the solution with time, showing the ongoing dissolution/recrystallization processes occurring in the solid (Fig. 1a), $^{226}$Ra activity in the solution ($A^{226}$Ra) shows no evolution with time considering the uncertainty of the measure (Fig. 2). $A(t)/A_0(t)$ ratio plotted against time shows the presence of two successive rates, with a transition happening approximately 10 days after the spikes (Fig. 1a). The fit of the experimental results according to Eq. 2 leads to the estimation of a first dissolution/recrystallization rate of $1.14 \times 10^{-5}$ mol.m$^{-2}$.d$^{-1}$ between 1 and 10 days and a second one of $3.92 \times 10^{-6}$ mol.m$^{-2}$.d$^{-1}$ between 10 and 200 days of experiment.

These values have been obtained considering a constant solid to liquid ratio ($S/L$) of 31.4 g.L$^{-1}$, a specific surface of 0.5 m$^2$.g$^{-1}$ and a [Ca] saturation of $1.5 \times 10^{-2}$ M. The SEM image of the initial solid (Fig. 1b) reveals signs of dehydration with the presence of numerous desiccation figures at the solid surface, which are less pronounced after 3 days of immersion in the solution (Fig. 1c). These observations lead to the conclusion that the prolonged journey of the solid in the stove has conducted to its dehydration, so that the rapid rate corresponds to a first step of rehydration of the solid, and the second rate characterizes the dissolution/recrystallization processes occurring in the solid under equilibrium conditions.

The amount of newly formed solid (recrystallized) [Ca]solid in moles during the experiment can be estimated as follows:

$$[\text{Ca}]_{\text{solid}} = \Omega \sigma m t$$  \hspace{1cm} (3)

Where $m$ represents the mass of solid introduced in solution (g). Over 200 days of experiment, about $2.10^{-2}$ g of gypsum have been recrystallized (7 % of the initial solid). The amount of $^{226}$Ra incorporated by the recrystallized solid is then obtained transforming Eq. 1:

$$[\text{Ra}]_{\text{solid}} = D[\text{Ra}]_{\text{solution}} [\text{Ca}]_{\text{solide}} /[\text{Ca}]_{\text{solution}}$$  \hspace{1cm} (4)

The experimental results reported on a diagram showing the evolution of $^{226}$Ra solution activity with time (black dots) indicate no decrease of this activity over 200 days (Fig. 2). Considering the two existing values of $D$, 0.03 [5] and 0.3 [6] and 10 % of uncertainty on the measures, two envelopes of the theoretical evolution of $^{226}$Ra solution activity with time have been calculated (Fig. 2). The results are close to those expected for a $D$ of 0.03, indicating that the distribution coefficient of $^{226}$Ra between gypsum and the aqueous phase is more likely to be low, probably even lower than the 0.03 value. Other sorption/desorption and coprecipitation experimental results have shown no evolution of $^{226}$Ra’s activity.
neither in the solution nor in the solid with time, suggesting that these two other mechanisms are not more efficient than incorporation in reducing Ra’s mobility by interactions with gypsum. Several arguments can be proposed to explain this lack of interactions between $^{226}$Ra and gypsum: the two main criteria governing element substitution are the ion charge and the ionic radius. Whereas calcium and radium have the same ion charge (+2), the difference between their ionic radii in eight-coordination (Ca’s coordination number in gypsum) is significantly high: 1.12 Å for Ca and 1.48 Å for $^{226}$Ra. $^{226}$Ra appears to be too big to enter Ca’s site in gypsum. Furthermore, gypsum has a high solubility product ($\lg K_s = -4.58$) compared to barite’s ($\lg K_s = -9.97$), which is probably another factor inhibiting the incorporation of $^{226}$Ra in gypsum by substitution of Ca.

![Fig. 2. Evolution of $^{226}$Ra solution activity with time.](image)

4. Conclusion

This study shows that $^{226}$Ra is poorly incorporated into gypsum, so that a solid solution between gypsum and radium sulfate (Ca,Ra)$_2$SO$_4$.2H$_2$O(s) cannot be considered per se. Other sulfate phases, with intermediate solubility product between gypsum’s and barite’s, such as celestite and anglesite, could be more favorable to incorporation of $^{226}$Ra.

References