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Study of the radium sorption/desorption on goethite

S. Bassot (1), D. Stammose (1), C. Mallet (1), J.-M. Ferreux (2), C. Lefebvre (1)
(1) Institut de Protection et de Sûreté Nucléaire, DPRE, SERGD, BP6 92265 Fontenay-aux-Roses Cedex, France
(2) Université de Franche-Comté, Laboratoire de Microanalyses Nucléaires, 25030 Besançon Cedex, France

ABSTRACT

The oxi-hydroxides, present at trace level in uranium mill tailings, are responsible of about 70% of the 226 radium sorption, half being fixed on crystallized forms. This radionuclide (half time = 1622y), present at high level (50 to 100kBq.kg^{-1}), can be released in groundwater, involving a possible contamination of the food chain (actual concentration limit = 0.37Bq.l^{-1}). So, it is very important to point out the mechanisms of the radium sorption/desorption on crystallized oxi-hydroxides as a function of chemical conditions of the system. The radium sorption on synthetic goethite α-FeOOH has been studied as a function of contact time, initial radium activity, pH, sodium and calcium concentrations. The results show that, after one hour of contact time (necessary to reach equilibrium), the radium sorption increases widely in a pH range 6-7. The increase of Na^+ concentration is without influence on the radium sorption, indicating the low interactions between sodium and surface sites. At the opposite, the presence of calcium in solution decreases widely the radium sorption, that indicates a competition between calcium and radium for the same kind of sorption sites of the oxi-hydroxide surface. The percentage of radium desorbed increases widely with time, from 1 to 120h and becomes constant at a time higher than 120h. This long equilibrium time for desorption in comparison with sorption one can be explain by a local evolution of the sorption sites of the solid, which become less accessible for the solution in contact.

INTRODUCTION

The main minerals contained in uranium mill tailings from acid treatment are clastic minerals corresponding to the nature of uranium rocks and to its paragenesis: quartz, sodic and potassic feldspars, muscovite, biotite, smectites, calcite. After deposit of the acid uranium mill tailings, different geochimical phenomena occur, linked to diagenetical evolution of the tailings. This evolution involve different mechanisms like mineral dissolution (pyrite dissolution during system oxidation), development of ferrous smectite or formation of authigenous minerals, which appear as cement or coating : gypsum, barytine, jarosite, Fe and Mn oxi-hydroxides, hexavalent uranium minerals (uranium phosphate, uranium vanadate, lead and uranium silicates) [1]. Sequential extractions realized on Ecarpiere tailings in Vendée [2] (acid treatment) show that Fe anf Mn oxi-hydroxides are responsible of about 70% of 226 radium sorption, half being fixed on crystallized forms. The rest of the 226 radium is fixed on gypsum, barytine and silicates phases (clays, feldspars, micas, quartz). In uranium mill tailings from acid treatment, the ferric oxi-hydroxides, although present at trace level, predominate in tailings in comparison with others metallic oxi-hydroxides because of ferric salts addition during acid treatment of the uranium ores. Objectives of these studies are to determine mechanisms of 226 radium sorption/desorption on goethite and the model to use for simulate this sorption and to evaluate the 226 radium behaviour in uranium mill tailings. Numerous studies have been realized on amorphous and cristallized ferric oxi-hydroxides, especially on uranium VI sorption [3, 4, 5, 6] and on heavy metal sorption [7, 8]. These studies describe the surface complexation site-binding model used to simulate uranium sorption on oxi-hydroxide and show the high influence of uranium complexation in solution on sorption capacity of oxi-hydroxides. Some studies have been realized on 226 radium sorption on manganese oxides [9, 10, 11], on different hydroxides (Fe, Ti, Zr, Mn) [12] and on different sediments [13]. But these data don’t allow to modelling radium behaviour in presence of oxides. In this paper, the radium sorption/desorption on synthetic goethite has been studied as a function of different parameters (contact time, equilibrium radium activities, pH, sodium and calcium concentrations).

EXPERIMENTAL

Materials and Apparatus

$FeCl_3$, $6H_2O$ Normapur Prolabo and HCl 37% Merck reagent grade were used to prepare Fe(III) solution. 1M NaOH Titrinorm Prolabo, 8M NaOH (NaOH Normapur Prolabo) and C_2H_5OH Ultrapur Prolabo were used to precipitate and clean the solids. $NaClO_4$,H_2O Merck and $RaCl_2$ (43,79kBq.g^{-1} of 226 radium in HCl 0,5M) Amersham were used after dilution in our experiments. N_2 gas was used to limit CO_2 dissolution. The pH of the solutions was measured with a Sentron pH-meter by using a combined electrode. NaOH addition in controled conditions has been realized with a Ismatec Instruments peristaltic pump. Batch experiments have been realized in polyethylene Nalgene tube of 20 ml in a 3-D Turbula shaker and the washing steps of the solid formed have been realized in a 1-D Comfort shaker. The solids were separated from solution by centrifugation using a KR-22i Jouan apparatus with AK 500-11 rotor (washing steps) and with AK 50-22 rotor (afer batch experiments). Before analysis, the centrifuged solution containing 226 radium has been filtred on 0.22µm filter Millipore. 226 radium in solution was analysed by gamma spectrometry with an Eurisys hyperpur germanium detector (40% of relative efficacity). The measures were realized on 15ml of solution volume in 60ml polyethylene bottle with a counting time of one hour. The detection limit of this method for 226 radium determinations is $4.7 Bq.ml^{-1}$ with a counting efficacity of 12,4% at 186,2keV. A Philips PW1729 X-ray diffractometer system is used to measure the cristallinity of the synthetized solids. The specific surface area of the solids was measured with a Coulter SA3100 apparatus in using N_2 adsorption with a BET model. The microscopic observations have been realized with a S-3500N Hitachi secondary electron microscope.

Procedure of synthesis

The iron oxi-hydroxide used as a sorbant in this study was prepared by reacting NaOH with $FeCl_3,6H_2O$ following the procedure of Nirdosh [12]. The solid was precipited by progressive addition ($3ml.min^{-1}$) of 1M and 8M NaOH in a solution composed with 380g of $FeCl_3,6H_2O$ in 500ml of 1M HCl. The solid precipitation begins at pH 1.7 but has been stopped between 12 and 12.5. The solid formed was mixed in 1-D shaker during 22h at 70°C in order to cristallise the amorphous precipitate. Then, the solid was centrifugated during 30min (40640G). The solid was washed 3 times with 500ml of acidified solution (pH 3) at 60°C and 3 times with C_2H_5OH at 60°C. Then, the solid was pound in agathe bottle and was kept in stock at 30°C.

Sorption/desorption experiments

The radium sorption was realized through batch experiments using a 3-D shaker. 0.1g of solid was put in contact with 20ml of solution containing the 226 radium. Before closing the tube, a N_2-bubbling in surface of the solution has been realized in order to limit CO_2 dissolution. ClO_4^- ion was chosen as counter ion because it does not build complexes with Fe(III) and Ra(II). The temperature of the batch experiments was measured and varies from 24 to 30°C. The percentage of radium sorbed on goethite surface has been calculated from the 226 radium measure in solution of a blank, which has been realized for all the series of experiments. For desorption experiments, solids containing 226 radium have been weighted in order to determine the volume of solution still in contact with solid after solid-liquid separation. Therefore, the residual 226 radium activity can be withdrawn and the amount of 226 radium desorbed can be determined precisely. The procedure of 226 radium desorption was the same that for the sorption, but with a solution without 226 radium.

EXPRESSION OF THE RESULTS AND PRECISION OF THE MEASURES

$$\text{Percentage of radium sorbed (\%)} = \left(\frac{A_b - A_s}{A_b}\right).100$$

$$\text{Percentage of radium desorbed (\%)} = \left(\frac{A_d - A_r}{A_b - A_s}\right).100$$

$$\text{Ra activity in solid (Bq.g}^{-1}\text{)} = (A_b - A_s)\frac{M_{solution}}{M_{solid}}$$

$$\text{Ra activity in solution (Bq.ml}^{-1}\text{)} = A_s\frac{M_{solution}}{V_{solution}}$$

$$\text{Coefficient distribution of radium Kd (l.kg}^{-1}\text{)} = \frac{(A_b - A_s)}{A_s}\frac{V_{solution}}{M_{solid}}$$

with A_b : radium activity in blank solution ($Bq.g^{-1}$)
A_s : radium activity in solution in contact with solid for sorption experiments ($Bq.g^{-1}$)
A_d : radium activity in solution in contact with solid for desorption experiments ($Bq.g^{-1}$)
A_r : residual radium activity from sorption experiments ($Bq.g^{-1}$)
M_{solid} : mass of solid (g)
$M_{solution}$: mass of solution (g)
$V_{solution}$: volume of solution (ml)

The incertitude measured on A_b is about 1% whereas those measured on A_s is between 5 and 10%. In consequence, we have estimated the precision of the measures on the percentage of the radium sorbed and desorbed at 10%.

RESULTS AND DISCUSSION

Solid studies

The solid formed has been chemically and mineralogically analyzed. The solid contains 99.2% of Fe_2O_3 essentially (95-99%) on the form of goethite (α-FeOOH). There is 0 to 5% of lepidocrocite (γ-FeOOH). The specific surface area value is $75.9 \pm 0.2 m^2.g^{-1}$. The microscopic observation shows an ellipsoïdal form of the particles with a length between 0.1 and 2µm and with a mean width of 0.1µm (Figure 1).

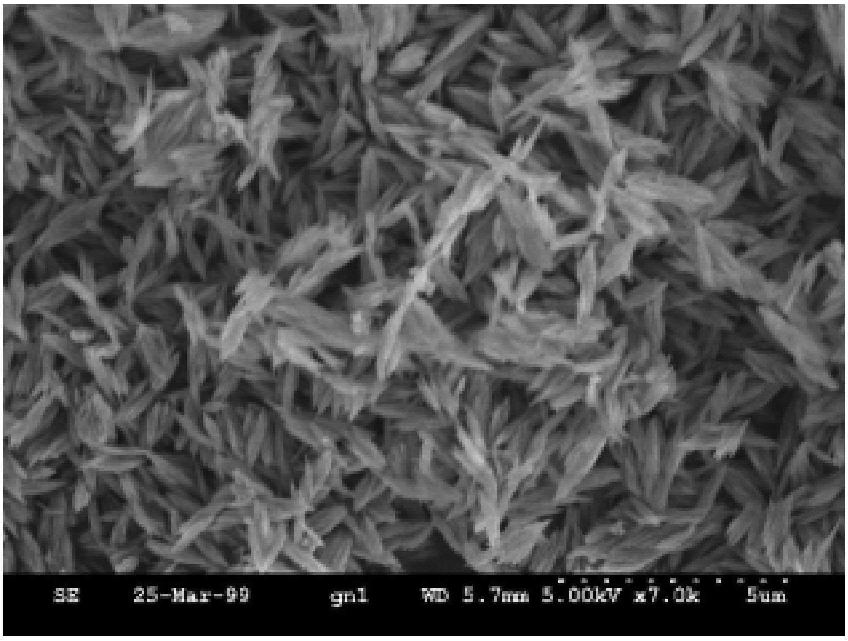


Figure 1 : Photography of microscopic observation of the goethite formed (Magnification = x7000)

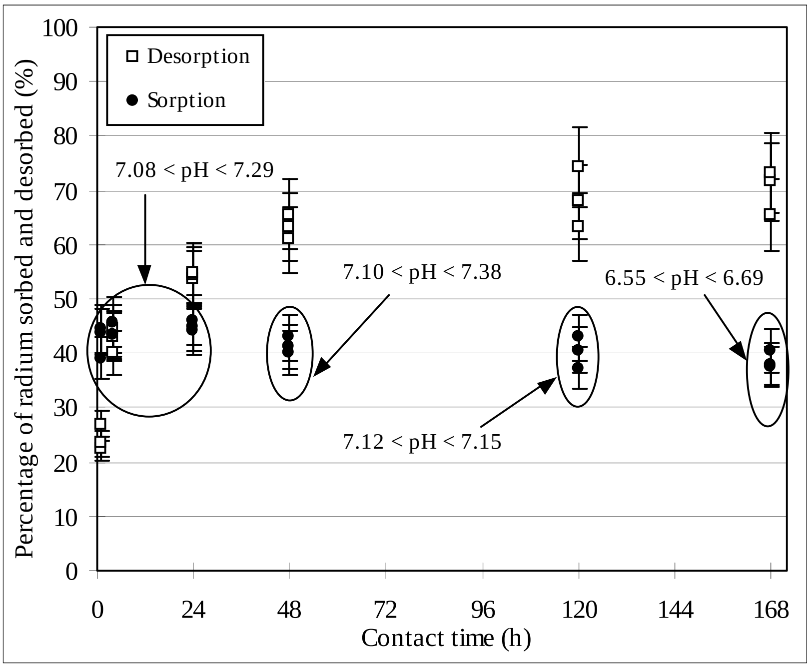
Solution studies

Radium speciation in solution

The radium speciation calculated with a geochemical code [14] using thermodynamical data of Langmuir [15] shows that $Ra(OH)^+$ species concentration is always weak, lower than 1% of the total radium in solution whatever the pH of the solution. In a system without calcium in solution and assuming a $pCO_2(g)$ equal to 3.4 10^{-5}atm, the simulation shows that $RaCO_3$ percentage increases from 0 to about 5% when the pH increases from 8 to 9.6. Even, at this low value of $pCO_2(g)$ (3.4 10^{-5}atm), the presence of calcium in solution involves precipitation of calcite by consummation of HCO_3^- and induces a decrease of $RaCO_3$ species concentration in solution. In this case, the simulation indicates that about 98% of the radium present in solution at pH 12 is on the Ra^{2+} form. Moreover, the simulation shows that precipitation of $Ra(OH)_2$ and $RaCO_3$ don't take place in our system whatever pH and carbonate concentration in solution may be.

Kintetics aspects of the radium sorption/desorption

The figure 2 shows the evolution of the radium sorption percentage as a function of contact time between solid and solution, for a pH closed to 7 and for an initial radium activity near 3200Bq (160 $Bq.ml^{-1}$). The radium sorbed percentage increases sharply in the first minutes of the contact and after one hour of contact time, there is no increasing of radium sorption, with a percentage of radium sorbed between 40 and 50%. The slight decrease observed between 24 and 168h is probably due to the decrease of the pH, from 7.38 to 6.55. One hour of contact time is sufficient to obtain sorption equilibrium and so, all the sorption experiments presented in this study have been realized with one hour of contact time. The radium desorption equilibrium (pH=5.6) seems to be obtain after 120h of contact time instead of 1h for sorption experiments. After 168h of contact time, about 30% of the radium still remains on the solid. This result can be explained by a local evolution of the sorption sites of the solide, which become less accessible for the solution in contact. Moreover, we must take into account that desorption experiments have been realized at lower pH than sorption experiments. Farther in this paper, we will see that increasing pH induces an increase of radium sorption and, so a decrease of radium desorption percentage. This involves an overestimation of the percentage of the radium desorbed in comparison with desorption results at pH closed to 7.



$[NaClO_4] = 0.1M$

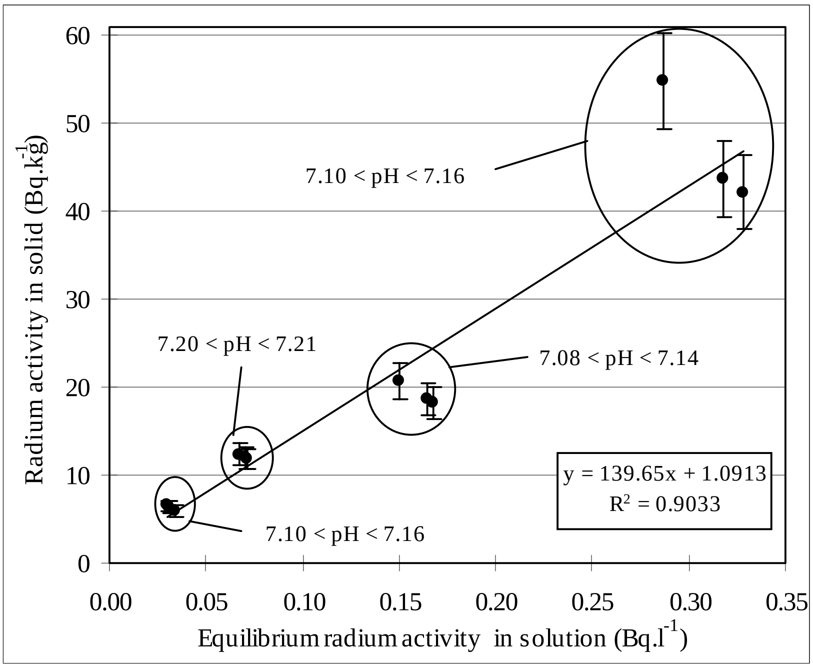
Sorption conditions :
$T_{mean} = 24.3°C$
$A_{Ra\ ini.} = 3252$ to 3264Bq

Desorption conditions :
$T_{mean} = 24.0°C$
pH ~ 5.6

Figure 2 : Kinetic of the radium sorption/desorption on goethite

Influence of the initial radium activity

The radium sorption isotherm on goethite is presented on figure 3 for pH closed to 7.



Sorption conditions :

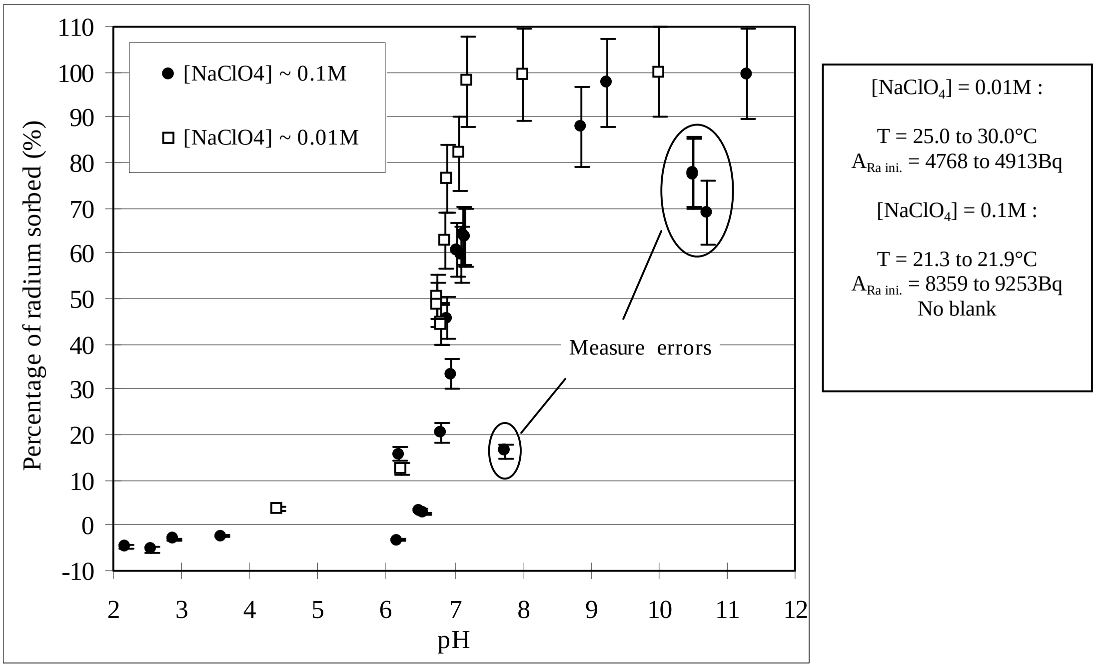
$T_{mean} = 21.8°C$
$[NaClO_4] = 0.1M$

Figure 3 : Radium sorption isotherm on goethite

The straight-line indicates that there is no saturation of the sorption sites of the solid by Ra^{2+} ions and there is no precipitation of the radium, whatever the initial radium in solution may be. For the experiments presented here, the initial radium activities are between 3000 and 9000Bq. The highest initial radium concentration is about 5.10^{-8}M (10^{-9}mol in 20ml), which is a very low value compared to the number of surfaces sites, near 10^{-4}mol.g^{-1} (10^{-5}mol in 0.1g of goethite). At this low radium level in solution, only a fraction of the total surface area is covered by Ra^{2+}.

Influence of pH

The figure 4 shows the evolution of the radium sorption percentage as a function of pH, for a contact time of one hour and for an initial radium activity between 4700 and 9300Bq.



$[NaClO_4] = 0.01M$:

T = 25.0 to 30.0°C
$A_{Ra\ ini.}$ = 4768 to 4913Bq

$[NaClO_4] = 0.1M$:

T = 21.3 to 21.9°C
$A_{Ra\ ini.}$ = 8359 to 9253Bq
No blank

Figure 4 : Influence of pH and sodium concentration in solution on the radium sorption on goethite

This figure shows a high increase of the percentage of radium sorbed when pH increases from 6 to 8, until a value of 100% of radium sorbed at pH 9-12. This result indicates that there is no influence of $RaCO_3$ species in solution at high pH. These results confirm those obtained by Nirdosh [12] on FeO(OH) at pH 10, with a percentage of radium removal from solution of about 100%. This high increase of the percentage of radium sorbed in a pH range between 6 and 7, lower than the zero point of surface charge of this goethite ($pH_{ZPC} \sim 8.5$), indicates the high affinity of Ra^{2+} for sorption sites of the goehtite surface. The explanation of the pH influence on radium sorption can be made according to the surface complexation site-binding model. The development of surface charge at the ferric oxi-hydroxide/water interface is due to amphoteric ionization reactions of surface functional groups (FeOH) through the uptake or release of H^+ and OH^- [4] :

$$-\mathrm{FeOH}_2^+ \Leftrightarrow -\mathrm{FeOH} + \mathrm{H}^+_{\mathrm{surface}} \qquad K^{\mathrm{int}}_{\mathrm{a1}} \qquad \text{(equation 1)}$$

$$-\mathrm{FeOH} \Leftrightarrow -\mathrm{FeO}^- + \mathrm{H}^+_{\mathrm{surface}} \qquad K^{\mathrm{int}}_{\mathrm{a2}} \qquad \text{(equation 2)}$$

where $-\mathrm{FeOH}_2^+$ and $-\mathrm{FeO}^-$: ionized surface species

$K^{\mathrm{int}}_{\mathrm{a1}}$ and $K^{\mathrm{int}}_{\mathrm{a2}}$: intrinsic acidity constants

Considering the data presented on the divalent cations sorption [16, 17] , we can assume that Ra^{2+}, located in the inner Helmholtz plane, form complexes with the surface groups :

$$2(-\mathrm{FeOH}) + \mathrm{Ra}^{2+} \Leftrightarrow \left[(-\mathrm{FeO}^-)_2\,\mathrm{Ra}^{2+}\right] + 2\mathrm{H}^+_{\mathrm{surface}} \qquad K^{\mathrm{int}}_{\mathrm{Ra1}} \qquad \text{(equation 3)}$$

$$-\mathrm{FeOH} + \mathrm{Ra}^{2+} \Leftrightarrow \left[(-\mathrm{FeO}^-)\mathrm{Ra}^{2+}\right]^+ + \mathrm{H}^+_{\mathrm{surface}} \qquad K^{\mathrm{int}}_{\mathrm{Ra2}} \qquad \text{(equation 4)}$$

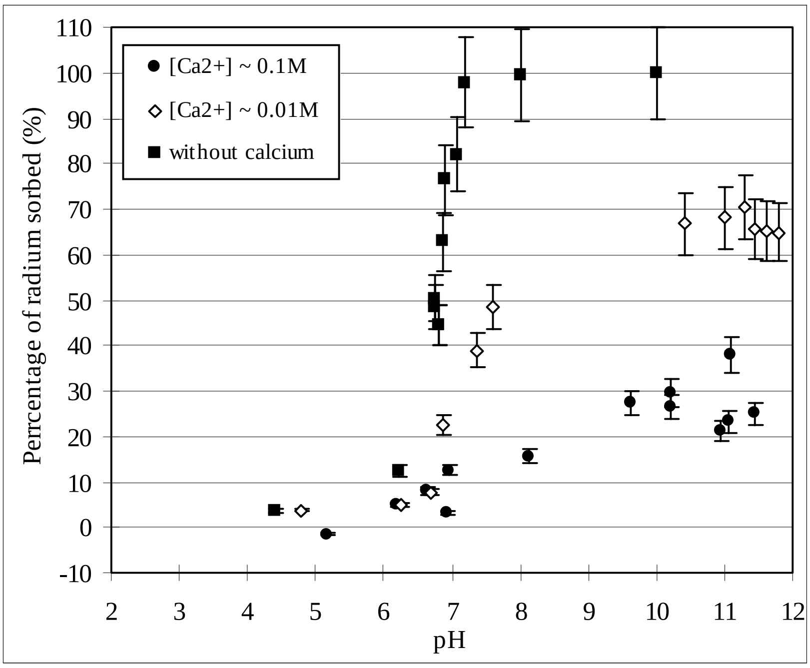
These relations permit to explain the high dependence of the radium sorption with pH of the solution.

Influence of electrolyte $NaClO_4$ concentration

The figure 4 shows that changes in background electrolyte concentration have relatively little effect on the position of the adsorption edge. This indicates that there is a slight competition effect between Na^+ and Ra^{2+} for the sorption sites of the goethite, with a very low decrease of the percentage of radium sorbed when the $NaClO_4$ concentration increases from 0.01 to 0.1M. This result is confirmed by Nirdosh [12] with $NaNO_3$ electrolyte and by Hayes [17]. This low competition is due to the specific characteristics of the Na^+ and Ra^{2+} ions. The Na^+ ion is a structurant ion unhydrolysable, which can penetrated easily in the ordonated layer of the solvant, up to the inner Helmholtz plane because this ion has tendancy to preserve the local order of this zone. Na^+ is adsorbed on the goethite surface by electrostatic effect and unspecific strength. On the opposite, as divalent cations Cd^{2+} and Pb^{2+}, the Ra^{2+} ion is sorbed by specific strength as an inner-sphere complex. This is confirmed by results of Hayes [17], which show that inner-sphere model is more appropriate for divalent cations than sorption models involving outer-sphere surface complexes. This complexation corresponds to an approach of the cation very near to the surface and so corresponds to a high interaction between the cation and the surface. The radium sorption takes place at the surface of the goethite, on the FeOH sites, as $\left[(FeO^{-}Ra^{2+})\right]^{+}$ and $\left[(FeO^{-})_2Ra^{2+}\right]$. The Ra^{2+} sorption is so more important that the Na^+ sorption on goethite, that explicate the low influence of the Na^+ concentration on the percentage of the radium sorbed.

Influence of calcium concentration

The figure 5 shows the evolution of the radium sorption percentage as a function of pH for different calcium concentrations.



Sorption conditions :

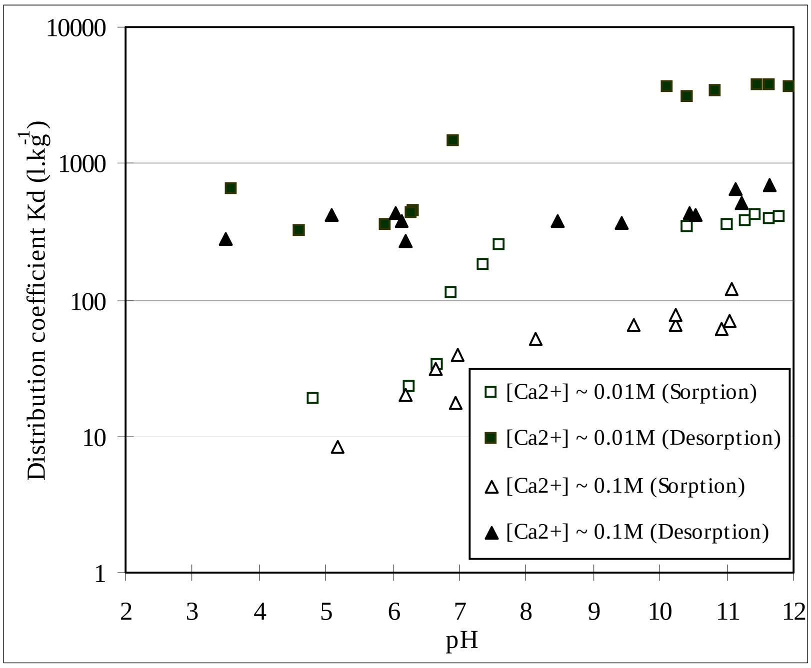
T = 25.0 to 30.0°C
$A_{Ra\ ini.}$ = 4742 to 4913Bq
$[NaClO_4]$ = 0.01M

Figure 5 : Influence of the calcium concentration in solution on the radium sorption on goethite

This figure shows that the radium sorption is highly influenced by Ca^{2+} concentration at pH value up to 7. At pH value lower than 7, the influence of Ca^{2+} concentration on radium sorption is negligible because the sorption sites are positively charged. At a pH value up to 8 and for a Ca^{2+} concentration of 0.01M, the radium sorption percentage is between 60 and 70% and for a Ca^{2+} concentration of 0.1M, it is between 20 and 30%. This indicates that there is a high competition effect between Ca^{2+} and Ra^{2+} for the sorption sites of the goethite surface, with a high decrease of the percentage of radium sorbed when the Ca^{2+} concentration increases from 0 to 0.1M. Speciation calculations indicate that calcite precipitation can take place higher than pH 8 for Ca^{2+} concentration higher than 10^{-2}M but the mineralogical analysis of the solid doesn't show off this phase. The possible removal of radium from solution with calcite precipitation seems to have little influence.

Reversibility of the radium sorption

The radium sorption/desorption expressed as Kd in presence of calcium is plotted on figure 6 as a function of pH. The result shows that, for sorption and desorption, at pH up to 7, Kd values are higher for Ca^{2+} 0.01M than for Ca^{2+} 0.1M, which confirm the competiton between Ca^{2+} and Ra^{2+} for the surface sites of the gœthite. Whatever the calcium concentration, the distribution coefficient Kd is much higher for desorption than for sorption (about one order of magnitude for Ca^{2+} 0.01M and about 0.5 order of magnitude for Ca^{2+} 0.1M). This traduces a partial irreversibility of the sorption mechanism. A possible local evolution of the sorption sites of the goethite, which become less accessible for the solution in contact can be an explanation.



$[NaClO_4]$ = 0.01M

Sorption conditions :
T_{mean} = 25 to 30°C
$A_{Ra\ ini.}$ = 4742 to 4913Bq

Desorption conditions :
T_{mean} = 25.0°C
Contact time = 48h

Figure 6 : Influence of pH and calcium concentration in solution on distribution coefficient Kd of radium sorption/desorption on goethite

CONCLUSION

The results of this study show that one hour of contact time is necessary to reach equilibrium for radium sorption experiments. The radium sorption increases widely in a pH range 6-7, lower than the zero point of surface charge of this goethite (pH_{ZPC} ~ 8.5), that indicates the high affinity of the radium for sorption sites of the goehtite surface. Below this pH range, the radium sorption is weak because of the positive surface charge of the solid (-$FeOH_2^+$). Above this pH range, the radium sorption is about 100% due to the neutral and negative surface charge (-FeOH and -FeO^-). The increase of Na^+ concentration from 10^{-2} to 10^{-1}M is without influence on the radium sorption. This traduces the low interactions between sodium and surface sites (electrostatic bounds). At the opposite, the presence of calcium in solution (up to 10^{-1}M of Ca^{2+}) decreases widely the radium sorption, that indicates a competition between calcium and radium for the same kind of sorption sites of the oxi-hydroxide surface. The radium desorption has been studied as a function of time. The percentage of radium desorbed increases widely with time, from 1 to 120h and becomes constant at a time up to 120h, with a desorption of 70% of the radium initially sorbed. This long equilibrium time for desorption in comparison with sorption one can be explain by a local evolution of the sorption sites of the solid, which become less accessible for the solution in contact. Moreover, in presence of calcium, the radium distribution coefficient Kd is higher for desorption than for sorption (about one order of magnitude for Ca^{2+} 0.01M), which confirms the local evolution of the solid surface.

This work will continue with a more precise characterization of the ferric oxi-hydroxide (number of surface sites, acidity intrinsic constants). Therefore, a determination of the sorption constants will be possible using the inner-sphere complex modelling. Using these constants, il will be possible to simulate radium release from ferric oxi-hydroxides present in uranium mill tailings.

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