Radium behaviour during ferric oxi-hydroxides ageing

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Abstract. In uranium mill tailings, oxides and oxi-hydroxides are responsible of about 70% of the radium immobilization, half being associated to amorphous forms (mainly iron and manganese oxides/oxi-hydroxides). With time, crystallization of these amorphous forms can occur, inducing a redistribution of radium between solids and solution. If the amount of mobile radium increases, the impact of these tailings on the environment may become significant.

The aim of this study is to determine the amount of ^{226}Ra released in solution during the crystallization process of hydrous ferric oxi-hydroxide (HFO) containing ^{226}Ra. A reproducible co-precipitation procedure is developed. The transformation of Ra-HFO co-precipitate in crystallized forms (goethite, hematite, …) is studied by ageing amorphous solids at 40°C in different solutions.

After co-precipitation, about 20% of the initial ^{226}Ra present in solution is associated to amorphous HFO. At 40°C, whatever the solution composition (MES or $NaClO_4$), the solid evolution is very slow and, after 3-5 months, no significant amount of crystalline form is noticeable. Simultaneously, the amount of ^{226}Ra present in solution is constant in MES and $NaClO_4$ medium. In comparison, ^{226}Ra sorption shows off inclusion of ^{226}Ra in Ra-HFO precipitate.

1. INTRODUCTION

Two types of minerals are present in uranium mill tailings: clastic minerals representing the nature of the original hostrock and the ore paragenesis (quartz, Na- and K-feldspars, muscovite, biotite, smectites, calcite, pyrite, ...) and autigenic minerals which have crystallized after the deposition of the tailings (gypsum, barite, jarosite, iron and manganese oxi-hydroxides, hexavalent uranium minerals, lead and uranium silicates) [1]. After the deposit of tailings, different mechanisms occur (pyrite dissolution during system oxidation, precipitation of oxi-hydroxides as cement around clastic and authigenic minerals) and tailings are submitted to diagenesis for a long period of time (until to reach equilibria). These tailings contain still a large amount of radionuclides issuing from the uranium chains (^{238}U, ^{234}Th, ^{230}Th, ^{226}Ra, ^{210}Pb, …), present on the different solid phases.

Sequential extractions conducted on Ecarpiere tailings in Vendée [2] (acid treatment) and on Lengenfed tailings in Germany [3] (alkaline treatment) show that iron (and manganese in a lower part) oxi-hydroxides are responsible of about 70% of ^{226}Ra sorption, half being fixed on amorphous forms. The rest part of the ^{226}Ra is fixed on gypsum, barite and silicates phases (clays, feldspars, micas, quartz). With time, amorphous solids can evolve towards crystalline forms and the radionuclides behaviour can be modified.

Previous studies [4] have shown that, at 40°C, a crystallisation process of hydrous ferric oxi-hydroxides (HFO) occurs (formation of goethite) together with ^{226}Ra release in solution. But, the precipitation procedure used in theses studies led to some discrepancies in the data.

The aim of this study is to develop a reproducible co-precipitation procedure in order to obtain a sufficient amount of Ra-HFO to allow an ageing study on a single and homogeneous HFO sample. Elsewhere, different solid characterization methods have been used in order to point out the solid modifications during the ageing process. In order to increase the crystallization rate, a temperature of 40°C has been chosen for the ageing experiment. This temperature seems the best compromise between an increase of the evolution rate and the "in-situ" temperature. At least, in order to study the possible modifications of the properties of solid sorption sites, ^{226}Ra sorption onto amorphous and aged HFO is studied as a function of pH.

2. MATERIALS AND METHODS

2.1 Precipitation of ferrihydrite

80mL of 0.1M ferric solution ($FeCl_3$, $6H_2O$ Normapur PROLABO in 0.1M HNO_3), and 0.33 to 0.45mL of $RaCl_2$ AMERSHAM solution (43.95 kBq.mL^{-1} of ^{226}Ra in HCl 0.5M) is diluted in 220 to 280mL of deionised water. The final ^{226}Ra concentration is between 5.93 10^{-6} and 6.75 10^{-6}mM and the Fe(III) concentration was set at 22 to 26mM, the pH being closed to 2.

Coprecipitate of ^{226}Ra with Fe(III) was prepared by progressive addition of 1M low-CO_2 NaOH (NaOH Titrex) with a RADIOMETER automatic titration system (TIM900 titrator unit, ABU901 auto-burette with 20mL burette) to acidified ^{226}Ra solution [5]. Base was slowly added to this solution (over 1 to 3h) to an endpoint of pH 6. After about 15h, the pH of the slurry has slightly decreased and base was again added for adjustment to pH 6. About 20 to 30mL of NaOH was required to reach pH 6. The slurry was then centrifuged at 10000G during 15min (KR-22i JOUAN apparatus, AK500-11 rotor). All the experiments were conducted in NALGENE bottles (500mL). No sorption of ^{226}Ra on these vials was detected. In order to obtain sufficient amounts of solid, the solid fractions (ferrihydrite) of 3 precipitations were gathered and homogenised. For experiment A, the ferrihydrite was used without washing, while in experiment B, the ferrihydrite was washed 3 times with 300mL of deionised water before to be dried at ambient temperature.

2.2 Crystallisation experiments of ferrihydrite

Considering a previous study, 40°C was chosen for increasing reasonably the crystallisation rate. However, some ageing experiments have been conducted at 70°C in order to have a complete evolution of the solid.

The evolution experiment was realized through batch experiments using. About 2g of ferrihydrite was added to 900mL of solution (composition defined hereafter) in a 1000mL polyethylene bottle, which is introduced in a 1-D bath shaker (SBD50 HETO) at fixed temperature of 40°C. Two different solutions were used. Experiment A): the solution was a 0.1M solution of 2-(4-morpholino) ethane sulfonic acid (MES). MES was used to buffer the pH (pH = 6), and has a low trace element binding capacity and negligible impact on the rate of HFO transformation to crystalline product [6].

Experiment B): the solution was a 0.1M solution of $NaClO_4$ which pH was adjusted to 6. ClO_4^- ion didn't complex Fe (III) and Ra (II).

Periodic samplings of the suspension (maintained through agitation) were conducted with a 20mL pipette. In order to test the reproducibility of a such sampling procedure, 3 samples were realized each time, with solid/solution ratio between 0.2 and 5g.L^{-1} and centrifuged at 10000G during 15min (KR-22i JOUAN apparatus, AK 50-22 rotor). For experiment B, the solids obtained after centrifugation were washed 3 times with 20mL of deionised water, while for experiment A no washing occurs. For the 2 experiments, the solids were dried at ambient temperature before analysis.

2.3 ^{226}Ra sorption on ferrihydrite before and after evolution

In order to study the ^{226}Ra sorption onto solids, ferrihydrite was precipitated like previously described (^{226}Ra solution being replaced by the same volume of 0.5M HCl). After centrifugation and drying, a part of this precipitate was constituted the amorphous solid and stored. The other part of this precipitate was submitted to evolution in the same conditions than in 2.2), with a solid/solution ratio of about 2.5g.L^{-1} during 2 month. After centrifugation, the solid was dried at ambient temperature.

The ^{226}Ra sorption experiments were realized on these 2 solids following the same procedure. 0.1g of solid was put in contact with 20mL of solution containing the ^{226}Ra in NALGENE polyethylene tubes and shacked in a 3-D shaker (TURBULA). The ^{226}Ra solutions were prepared in 0.1M NaClO$_4$ (pH between 4 and 9) and in 0.1M MES (pH between 4 and 6). The temperature of the batch experiments was measured and varies from 24 to 30°C. For each initial pH, experiments were triplicate. After 24h of contact (previous studies have shown that this period was sufficient to reach equilibrium), the suspensions were centrifuged at 10000G during 15min and the solutions obtained were filtrated (0.22µm Millipore filter). Then, pH and ^{226}Ra measurements were realized. The amount of ^{226}Ra sorbed on HFO surface was deduced from the ^{226}Ra measure in solution, initially and after equilibrium.

2.4 Solution analysis

The pH was measured with a RADIOMETER automatic titration system (TIM900 titrator unit) by using a combined electrode (C2085, Red Rod electrode). ^{226}Ra was measured by gamma spectrometry (186.2 keV) with a EURISYS hyperpur germanium detector (40% of relative efficacity) on 15mL of solution with a counting time of 1h. The detection limit of ^{226}Ra is 4.7Bq.mL^{-1}. The Fe^{3+} concentration was measured with a VARIAN atomic absorption spectrometer (Spectra 220 FS) with a detection limit of 50µg.L^{-1} (9 10^{-7}M).

2.5 Solid analysis

X-ray diffraction were realised with a PHILIPS PW1729 X-ray diffractometer system. The specific surface area of the solids was measured with a COULTER SA3100 apparatus (using N$_2$ adsorption with a BET model). Preliminary studies have defined the degassing conditions of solids analysed (30°C during 15h). The microscopic observations have been realized with a S-3500N HITACHI secondary electron microscope (SEM).

3. EXPRESSION OF THE ^{226}RA RESULTS

$$\text{Percentage of radium sorbed } (\%) = (\frac{A_{initial} - A_{final}}{A_{initial}}).100 \qquad (1)$$

$$\text{Distribution coefficient of } ^{226}Ra \ K_d \ (L.kg^{-1}) = (\frac{A_{initial} - A_{final}}{A_{initial}}).\frac{V_{solution}}{M_{solid}} \qquad (2)$$

with $A_{initial}$: activity in blank solution (sorption) and in initial solution (crystallisation) (Bq)

A_{final} : ^{226}Ra activity in solution after contact with solid (Bq)

M_{solid} : mass of solid (g)

$V_{solution}$: volume of solution (L)

4. RESULTS AND DISCUSSION

4.1 Characterization of ferrihydrite (before and during evolution)

In order to follow the evolution with time of the solid, different characterization techniques have been used.

SEM observations allow to point out the beginning of crystallisation process (Figure 1). Freshly precipitated HFO (a) is constituted with smooth particles whereas, after 8 days at 70°C, nodules are observed on the surface.

This evolution of HFO is confirmed by X-ray diffraction patterns. Different steps of evolution are presented on Figure 2. For the freshly precipitated HFO, no peak appears and the baseline for small angles is very high, traducing the absence of crystalline forms in the analysed solid. With time, characteristics peaks of goethite and hematite minerals appear and baseline level diminishes. At 70°C and after 36 days, the most part of HFO is crystallized.
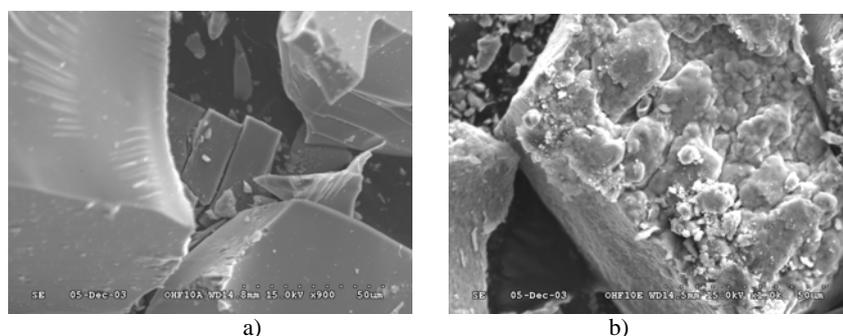

a)   b)

Figure 1. Photography of a) ferrihydrite before evolution (G = x900) and of b) ferrihydrite after 8 days of contact with 0.1M $NaClO_4$ at 70°C (G = x1000).
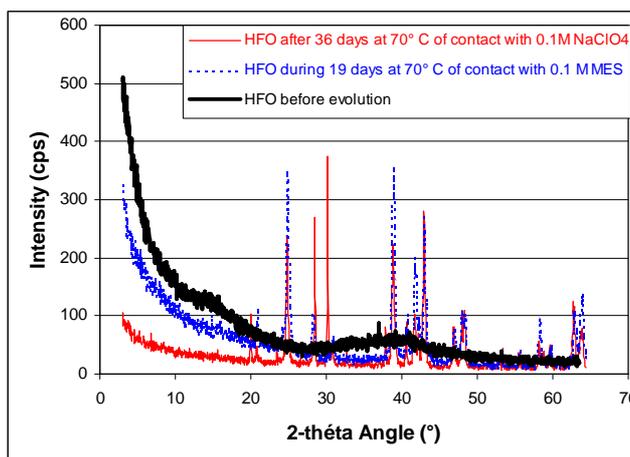

Figure 2. X-ray diffraction patterns of HFO at different evolution steps (t= 0-no evolution, 19 days, 36 days).

N_2 sorption/de-sorption curves allow the determination of specific surface area of solids according to BET model. Generally, specific surface area of amorphous solids is higher than those of crystallized ones. The specific surface areas of solids corresponding to different step of ageing are presented in Table 1.

Table 1. Specific surface area values (BET) measured on HFO in different conditions.

Evolution conditions	Specific surface area (BET) ($m^2.g^{-1}$)
No evolution	250.8 ± 12.5
Evolved in 0.1M MES at 70°C during 19 days	39.5 ± 2.0
Evolved in 0.1M NaClO$_4$ at 70°C during 36 days	16.3 ± 0.8

These data show that, with time, specific surface area decrease from $251 m^2.g^{-1}$ for freshly precipitated HFO to about $16 m^2.g^{-1}$ for an aged solid (70°C during 36 days in 0.1M NaClO$_4$). This decrease confirms a beginning of solid modification.

4.2 Radium behaviour during HFO ageing

After HFO precipitation, about 20% of [226]Ra is fixed to the solid, the iron concentration being lower than $100 \mu g.L^{-1}$ ($1.8\ 10^{-6}$M). Moreover, the washing step of co-precipitate removes 60 to 80% of the [226]Ra present on the solid. This amount corresponds to the solution still contained in the amorphous precipitate (strongly hydrated). Lefebvre [4] has reported a precipitation yield closed to 90% and no [226]Ra release during the washing step. It seems that our procedure, which allow the obtainment of a single sample for ageing experiment, has a limited precipitation rate for [226]Ra.

Anyway, the solid have been gently shacked at 40°C in MES and NaClO$_4$. The distribution coefficient of [226]Ra and the [226]Ra concentration in solution are plotted (Figure 3) as a function of time for 2 different solutions (MES, NaClO$_4$). In MES medium, [226]Ra concentration in solution remains constant and no peak is observed on XRD patterns of the solids sampled at different times. No crystallisation of HFO occurs in MES after 3 months of ageing at 40°C. During this period, MES solution ensures the buffering of the pH (between 5.7 and 6.2 for 3 months). In NaClO$_4$ medium, [226]Ra concentration present in solution doesn't vary with time. Simultaneously, the pH decreases from 6 to 3.7 after 5 months. Like for MES experiment, no peaks are observed on the DRX patterns of the different solids. It seems that, whatever the solution composition, after 3 months, no crystallization of the solids has occurred. For these two experiments, the [226]Ra distribution coefficient (K_d) varies between 250 and 410L.kg^{-1} in MES and between 100 and 220L.kg^{-1} in NaClO$_4$ medium.
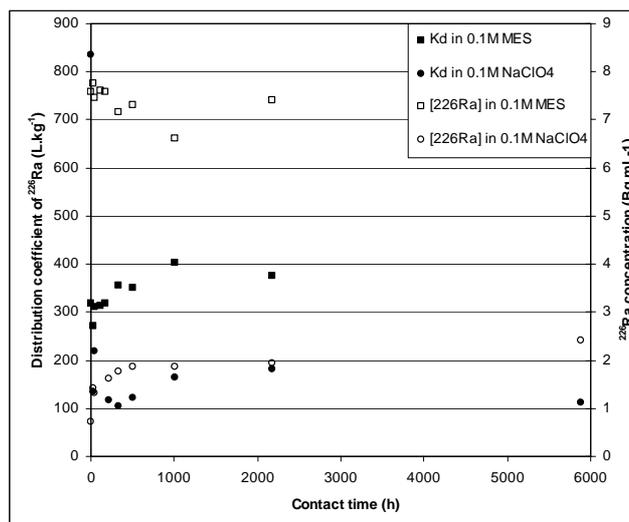

Figure 3. Evolution of distribution coefficient of [226]Ra and [226]Ra concentration in solution in function of time in 0.1M MES and in 0.1M NaClO$_4$.

N_2 sorption/de-sorption curves obtained for solids aged in MES medium are presented on Figure 4. These curves, obtained for freshly precipitated HFO and aged HFO (40°C in 0.1M MES during 20 weeks), present different shapes. No hysterisis is present for freshly precipitated HFO, while, for aged HFO, a hysterisis is present, traducing the presence of mesopores on the solid (pores size between 2 and 50nm). Amorphous HFO has begun to evolve (modification of the pores distribution) but no crystals were formed or formed in a too small quantity to be detected by XRD patterns.
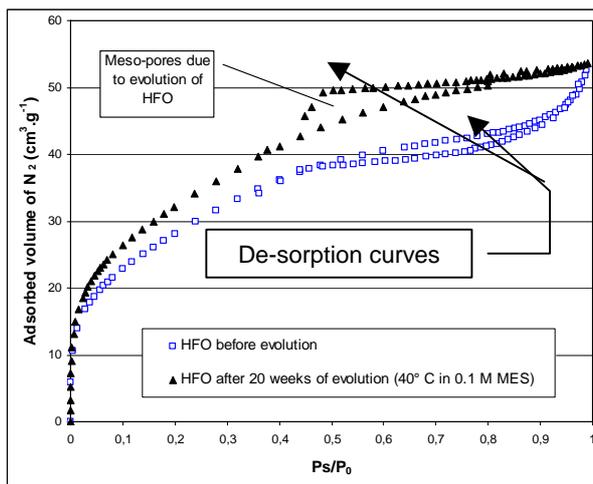

Figure 4. N_2 adsorption/desorption curves on HFO samples.

4.3 Radium sorption onto HFO

The [226]Ra sorption onto 2 solids, freshly precipitated HFO and 2 months aged, has been studied as a function of pH. The sorption curves are plotted on Figure 5. In both cases, the sorption increases with pH, low sorption for low pH and strong sorption for high pH. But, in the case of aged HFO, the sharp increase of sorption seems to appear for lower pH than for fresh HFO. The characteristics of the sorption sites (acidity constants, sorption constants) of HFO have been modified by the evolution of solid.
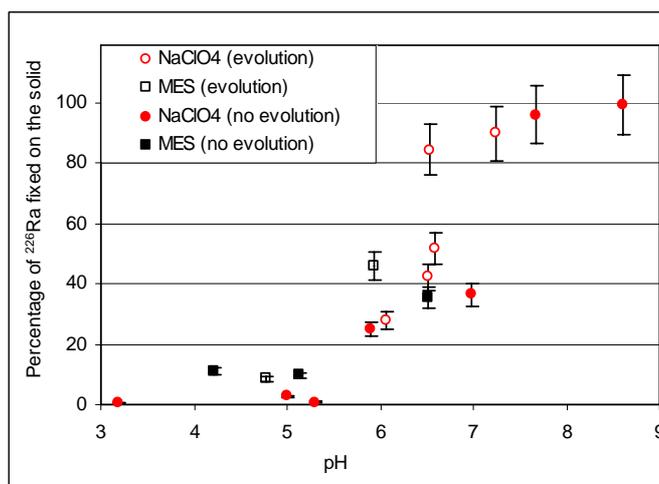

Figure 5. Evolution of percentage of [226]Ra fixed on HFO in function of pH.

In MES and NaClO$_4$, distribution coefficient of ^{226}Ra values determined for freshly precipitated HFO in these sorption experiments (respectively about 200 and 140L.kg^{-1} at pH 6) are lower than those determined in the evolution experiment. It can be due to the incorporation of all or part of ^{226}Ra in Ra-HFO precipitate.

5. CONCLUSION

This study has pointed out the importance of the precipitation procedure onto the nature of precipitate, the precipitation rate and on its evolution. No significant evolution of the solids (40°C for 3-5 months) was detectable by DRX measurements. But some modifications of organisation of the solid (porosity) can be pointed out through specific surface area measurements. Moreover, the ^{226}Ra sorption studies show that sorption properties of solid sites are modified during this ageing.

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