

# **Sorption/Desorption phenomena in uranium mill tailings : Study of the distribution of radionuclides on pure solid phases and application to the modelling of source term.**

Sylvain BASSOT and Denise STAMMOSE

Institut de Protection et de Sûreté Nucléaire, DPRE, SERGD, BP6 92265 Fontenay-aux-Roses, Cedex, France

## **Abstract**

The mining and milling of the uranium raw material are processes which leave substantial volumes of uranium mill tailings. These radioactive waste products may have an environmental impact in far future. The health hazards occur in a number of pathways via radioactive gas emanation, external exposure, radioactive dust and through contamination of surface and ground waters. For long term consequences, modelling has to be performed to predict future exposures. Of course, the necessity of using predictive models requires a basic understanding of the relevant physical, chemical and geochemical properties of the system components.

In a previous paper [1], we have reported data obtained on uranium tailings deposited in Lengenfeld (Germany) 20 years ago. The solid phases (determined by XRD) are mainly quartz, dolomite and kaolinite. The lack of data concerning the mechanisms responsible for the retention of radionuclides on these solids has led us to perform batch experiments on pure solid phases. In this paper, we present the influence of the solution composition (pH, ionic strength) on the sorption of radium onto a solid phase (kaolinite). The variations obtained have allowed to define the mechanisms controlling the sorption and to determine the associated constants. The introduction of these values in geochemical codes based on thermodynamic equilibrium will allow to predict the mobility of radium in presence of these phases.

## **Key words**

Uranium mill tailings, radium, distribution coefficient, kaolinite, ion exchange

## **Introduction**

Uranium mining and milling have left behind great amounts of tailings containing both radionuclides (radium and uranium) and toxic elements (As, Ni,...) which may be released in the geosphere. The control of the release rate of potential contaminants from the wastes is the most important objective of long term management of these residues. Therefore, the knowledge of the original ores, the milling and extraction processes and the chemical and mineralogical characteristics of the tailings are required in order to predict the migration of the contaminants throughout the tailings.

Among numerous mineralogical phases, clayous phases (smectite, kaolinite) are quite important because of their high sorption capacity. Few data concerning the radium sorption onto solids phases are available in literature [2] and in most of cases, the radium behaviour is assumed to be quite similar to those of divalent cations (strontium, barium...). This paper is devoted to the study of the sorption of radium onto kaolinite as a function of sodium concentration and pH in order to elucidate the mechanisms responsible of the radium sorption.

## **Experimental part**

The studied solid was kaolinite provided by Sigma. This solid was purified in order to saturate all the sorption sites by  $\text{Na}^+$  cations. The study of  $\text{Na}^+$  sorption on this kaolinite by L. GORGEON [3] has led to determine a Cation Exchange Capacity (CEC) of  $4.2 \times 10^{-2} \text{ meq.g}^{-1}$  whereas the cobalthexamine method has indicated a CEC value of  $2.8 \times 10^{-2} \text{ meq.g}^{-1}$ . This difference was due to the presence of two reactionnel sites as we could see in our results. The specific area of the purified kaolinite was estimated to  $13.2 \text{ m}^2.\text{g}^{-1} \pm 0.1 \text{ m}^2.\text{g}^{-1}$  and the exchangeable cation was sodium. The solution of radium was obtained by dilution of tracers in sodium chlorure ( $226 \times 10^3 \text{ Bq}$  of  $^{226}\text{Ra}$  solution provided by Amersham). All other chemicals were reagent grade.

All the sorption experiments were performed in batch at  $22^\circ\text{C}$ . No attempt to exclude air was made. The ratio volume of solution to mass of clay was fixed to  $20 \text{ ml.g}^{-1}$ . The solution containing radium was added to the solid and then the mixing was shaken (3-D shaking). After one day (result of kinetic study), the slurry was centrifuged (4900 rpm, 30 mn). The pH was then measured in the solution with a Sentron pH-meter and

the radium concentration in solution was determined by gamma spectrometry with a high resolution hyperpure germanium spectrometer.

Radium distribution coefficients  $D$  were calculated as the amount of radium sorbed on the solid divided by the amount of radium remaining in solution :

$$D_{(ml.g^{-1})} = ([Ra]_{solid}/[Ra]_{solution}) \times V/m \quad (1)$$

## Results and discussion

### Time dependence

For different sodium concentrations, the sorption has been studied as a function of time (Figure1).

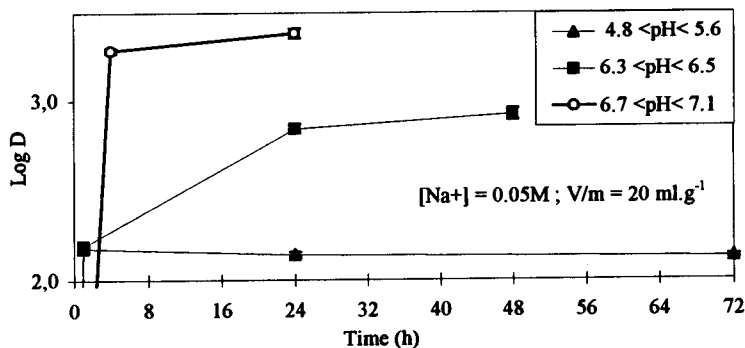


Figure 1 : Time influence on the radium sorption on kaolinite

A two steps kinetics is observed. The first step (rapid) is attributed to the sorption onto the surface, while the second often continuing for days is attributed to a diffusion process of the species through the first hydrated layers of the solid [4]. To avoid a possible alteration of clay for long settling time and considering the low variations of the amounts sorbed after 24 hours, all the experiments have been conducted with an equilibrium time of 24 hours.

### pH dependence

The variations of the amounts of sorbed radium as a function of pH for different sodium concentrations are presented on Figure 2.

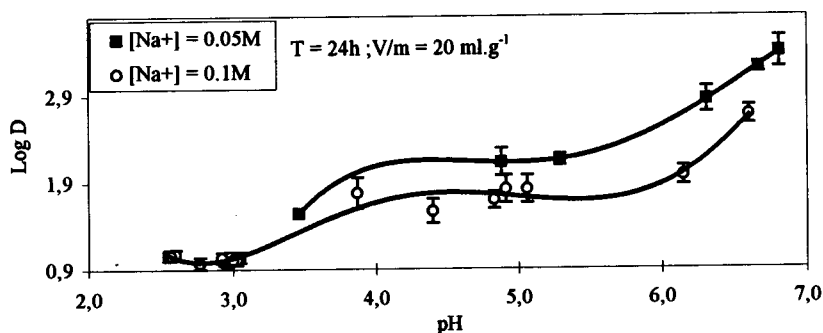


Figure 2 : pH influence on the radium sorption on kaolinite

For the two sodium concentrations, the distribution coefficient increases with pH excepted a plateau between pH 4 and 5.5 for which  $\log D$  is constant. A possible explanation of this shape is a competition between  $H^+$ ,  $Na^+$  and  $Ra^{2+}$  at low pH. For  $pH > 4$ , only competition between  $Na^+$  and  $Ra^{2+}$  occurs and the distribution coefficient remains constant with increasing pH. For  $pH > 6$ ,  $D$  increases sharply. A similar curve has already been mentioned elsewhere [3] and has been attributed to another kind of sorption sites on kaolinite.

### $[Na^+]$ concentration dependence

The ionic exchange mechanism between radium and sodium can be written:



$\{XNa^+\}$ ,  $\{(X)_2Ra^{2+}\}$  = sorbed species

$$\text{and } K_{Na/Ra} = \frac{[(X)_2Ra^{2+}][Na^+]^2}{[XNa^+]^2[Ra^{2+}]} \quad (3)$$

$K_{Na/Ra}$  = selectivity coefficient between sodium and radium for sorption on kaolinite

Combining (1), (2) and (3), we obtain the relation :

$$\log D_{Ra} = \log K_{Na/Ra} + 2\log CEC - 2\log[Na^+] = \text{Constant} - 2\log[Na^+] \quad (4)$$

This model predicts a linear variation of D with the electrolyte concentration. The sorption of radium as a function of sodium concentration has been studied in a pH range 8 to 9. At high pH value, the  $H^+$  concentration in solution is widely lower than  $Na^+$  concentration and the sorption sites are occupied by sodium. The data expressed as  $\log D = f(\log[Na^+])$  are plotted on Figure 3.

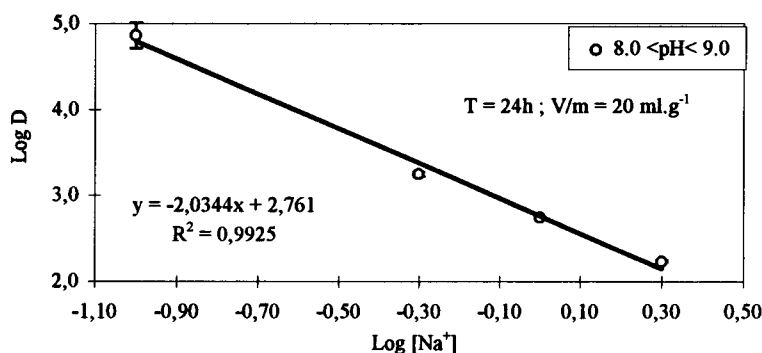


Figure 3 : Influence of  $Na^+$  concentration on the radium sorption on kaolinite

The straight line obtained has a slope of -2.0344 ( $R^2 = 0.9925$ ), which confirm the cation exchange mechanism between radium and sodium. The selectivity coefficient  $K_{Na/Ra}$  can be estimated by the intercept of the curve and the CEC value measured by L. GEORGON [3]. A very high value ( $3.2 \times 10^5 \text{ g.ml}^{-1}$ ) is obtained corresponding to a stronger affinity of radium than sodium for the sorption sites on kaolinite.

This study has allowed an estimation of the Na/Ra selectivity coefficient. Moreover, the strong influence of pH on the cation sorption onto kaolinite has been clearly observed, due to the competition between  $Na^+$ ,  $Ra^{2+}$  and  $H^+$  for sorption sites.

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# METHODOLOGY OF ENVIRONMENTAL IMPACT STUDY AND OPTIMIZATION OF RELEASES

Application to the Study Centre of CADARACHE

FRENCH ATOMIC ENERGY COMMISSION

by

JC CARIES (Health Physics Department)

## OBJECTIVES :

- Impact study.
- Optimization of releases.

## PRINCIPLES :

- Activities in the air and the water computed independently.
- The dose error contains more information than the dose itself ; it is representative of the knowledge evolution of the site.
- Computations of sensitivity and global error are essential in the modelling - experimentation interaction.
- Assessment of doses in the organs.
- Information feedback of the data-processing tools of a CEA subsidiary company (CISI) : modularity and flexible operation.

## PROCEDURE :

- Source term : Spectrum of the radionuclides.
- Impact study (per station).
  - \* computations of transfers to both food and man ; sensitivities and error computations,
  - \* main parameters with regard to the value : dose + error ( $d + \Delta d$ )
- Surveillance plan of the site.
  - \* computations of the number of stations to be studied for a fixed percentage of ( $d + \Delta d$ ),
  - \* reduced equation of transfers , mapping and meshing of the site,
  - \* exposures and food activities computations in every mesh, and filing.
- Optimization of releases (critical station)
  - \* determination of the boundary level of exposures,
  - \* successive iterations with the source term of the impact study and tests with different spectra of the source term.

**RESULTS :** Liquid transfers :  $\Delta d = (7 \text{ to } 10) \times d$  - Atmospheric transfers :  $\Delta d = (3 \text{ to } 7) \times d$

	AIR				WATER					
	<sup>85</sup> Kr	<sup>3</sup> H	<sup>131</sup> I	<sup>125</sup> Sb	<sup>3</sup> H	<sup>60</sup> Co	<sup>137</sup> Cs	<sup>90</sup> Sr+Y	<sup>241</sup> Am	<sup>239</sup> Pu
Authorized releases (1978) Bq/year (1)	555.E12		18,5.E9		1,85.E12		3,7.E9		0,37.E9	
If $d + \Delta d = 10 \mu\text{Sv/year}$ multiplying factor of (1)	(if 100% <sup>3</sup> H) 0,3		22		65		24		0,3	

Maximum exposure due to present releases from the Centre :  $d < 1 \mu\text{Sv/year}$  - Present tritium releases from the Centre: some per cent of the authorized releases

## OPTIMIZATION: $\alpha$ emitters

Objective: release  $\ll 0,3 \times$  authorization by:

- improving analyses to avoid adding up detection limits
- retaining the solid particles of the effluents in the installations.