Thoron Retention on Concrete, Mortar and Calcium Silicate Hydrated Phases (CSH) by µPIXE Analyses

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INTRODUCTION

Cement-based materials, like concrete and mortar, are widely used as barriers for radionuclide (RN) transport in radioactive waste repositories [1,2]. A deep characterization of these heterogeneous materials, and of their main minerals, is necessary to evaluate their capability of retaining critical radionuclides [3].

The ion beam technique micro-Particle Induced X-Ray Emission (µPIXE) is used to study thorium retention on the concrete and mortar, used in the Spanish low level waste repository, and on two calcium silicate hydrate (CSH) phases, formed upon cement hydration, with different Ca/Si ratio. A similar methodology was previously tested to quantify, at a mineral scale, Cs and I surface retention on solid concrete samples [4]. In the present study thorium was selected as representative of tetravalent actinides which is a heavy element well detectable by ion beam techniques. The complete characterization and retention study can be found in [5].

EXPERIMENTAL SET-UP

The concrete and mortar selected for this study are the materials respectively used as engineered barrier and as sealing material at the Spanish low-level radioactive waste repository of El Cabril (Cordoba, Spain). More details on these materials can be found in [6].

Calcium silicate hydrate (CSH) phases are amorphous minerals formed upon cement hydration with different chemistry xCaO·SiO₂·2H₂O, where x can be between 0.7 and 2. In this study, CSH phases were synthesized with Ca/Si ratio 1.7 and 0.9, following the methodology described in [3]. All samples were crushed for homogenization and were sieved <1 mm (ASTM 18).

For thorium sorption experiments, 0.5 grams of the four powder samples were contacted to 2 mL of thorium solution prepared in 0.1 M HCl, to a concentration of 10⁵ M. After 10 days of contact, samples were centrifuged and the solid phase was separated, slightly cleaned with deionised water and dried in an oven 90 ºC during two days. The final pHs of the suspensions were pH₅₀ = 12.28; pH₇ = 12.10; pH₉₀ = 9.76 and pH₁₇ = 11.76.

All powder samples were stacked to a carbon tape and covered with a graphite layer of 100 Å, to avoid charge effects during ion beam irradiation.

µPIXE measurements were carried out on 2x2 mm² areas at the nuclear microprobe facility at the Laboratori Nazionali di Legnaro (INFN, Italy). Samples were irradiated with 2 MeV protons with a beam size of around 4 µm² at perpendicular incidence. The typical beam currents were 1.5 nA, with a spatial resolution of 2 µm. A Canberra Ge detector with a polymer window of 0.4 µm thickness and maximum nominal resolution of 160 eV was used to enhance the sensitivity to heavy elements. All measurements were carried out with two Mylar filters of 4 µm thick and 48 µm thick with a hole in the centre that allows passing no more than 8% of the total signal.

For quantitative analyses, µPIXE images were processed with the Mappix code [7]. Individual PIXE spectra were obtained on selected areas, and quantitative analyses were performed with the windows version of the GUPIX code [8]. By µPIXE, the area composition (in elemental atomic %) and the tracer concentration retained can be obtained.

RESULTS

Figure 1 shows the elemental distribution maps (Ca, Si, Fe and Th) obtained by µPIXE on 2x2 mm² areas of the CSH samples traced with Th and the correspondent PIXE spectra: CSH 1.7 (figs 1a, 1b) and CSH 0.9 (figs 1c, 1d).

Only the Ca, Si, K and Fe maps are shown, but all elements with atomic number higher than Al can, in principle, be detected within our experimental conditions.

![Image of elemental distribution maps](image-url)

**Fig. 1.** Elemental distribution maps (Ca, Si, Fe and Th) obtained by µPIXE on 2x2 mm² areas of the CSH samples traced with Th and correspondent PIXE spectrum with the simulation: (a,b) CSH 1.7 + Th; (c,d) CSH 0.9 + Th.
Signals of Ca and Si are clearly visible and, in both samples, the μPIXE maps indicated that samples are rather homogeneous. In both samples (figures 1a and 1c), Fe impurities, not detected by EDX [5], are clearly visible in the PIXE spectra and in the maps. This detection is very relevant, since small Fe impurities can significantly affect actinide retention.

No Th is detected in μPIXE maps, in any of the analyzed areas. However, the analysis of the individual PIXE spectrum is required since in the distribution maps of elements at low concentration the background noise of other elements is overlapped and results can be misleading.

In figures 1b and 1d, the PIXE spectra of two areas analyzed on the CSH samples traced with Th are shown. The spectra fits, carried out with GUPIX code, for quantitative analyses are also presented in figures 1b and 2d. Peaks attributable to Si, Ca, major components of the CSH phases, can be perfectly detected. Cl peaks coming from the Th solution were also visible.

From the spectra fit, the Ca/Si ratio obtained were 1.64 ± 0.03 for the CSH 1.7 and 0.84 ± 0.03 for the CSH 0.9, similar values to those previously obtained by EDX [5]. In the spectra, the main X-ray lines of Fe were appreciated in both samples.

No Th clear peak is observed in any of the spectra carried out on CSH samples traced with Th. The Lα emission line of Th is at energy of 12.968 keV and within this energy region small peaks are overlapped by pile-up signal. Therefore, the Th identification and quantification depends on the fit goodness.

Spectra analyses indicated that Th is present, under detection limit, on the CSH sample with a Ca/Si ratio 0.9. However, the simulation admits the presence of Th in the CSH 1.7, as can be appreciated in the fit included in figure 2b. With the performed simulation the Th detected in the area is estimated to be around 5 ppm. We cannot ensure that Th is or not retained on the CSH surface since the values are close or under detection limit.

Figure 2 shows the elemental distribution maps (Si, Ca, Al, K, Fe and Th) obtained by μPIXE on 2x2 mm² areas on concrete and mortar traced with Th and correspondent PIXE spectrum with the simulation: (a, b) Mortar + Th; (c,d) Concrete + Th.

The main elements composing both materials are perfectly detected and visualized in the μPIXE maps. Since the samples are in powder conditions, the materials heterogeneity cannot be appreciated, as in preliminary analyses carried out on solid samples [7].

The quantitative analyses of the individual PIXE spectra, shown in figures 2b and 2d, were in agreement with the oxide composition of both materials [1,8]. No clear Th peak was observed in any of the spectra carried out on concrete or mortar phases traced with Th.

Next experiments will be carried out with higher Th concentration. Furthermore, as Th is an element of very low diffusion coefficient, the contact time will be increased.

The characterization of cement-based materials, and CSH phases, carried out by micro-Particle Induced X-Ray Emission (μPIXE) was very useful because it allowed evaluating material heterogeneity and quantified relevant trace elements, not detectable by other techniques (i.e. EDX) [5] potentially very relevant in actinide sorption.

The study of other RN, with X-Ray emission lines in areas not overlapped with the signals of main elements composing the materials is in principle possible by this methodology.

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