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Migration Behaviour and Chemical Speciation of Np and Am under Nuclear Waste Repository Conditions

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The report deals with laboratory-scale experiments investigating the behaviour of neptunium and americium in soil material surrounding clay and rock salt formations. In the case of a glauconitic sand and under oxic conditions almost all the ^{237}Np activity leached out from the waste matrix was retained in the column. The speciation of neptunium and americium in groundwater was studied by several techniques.

Migration experiments of americium in brine indicated a saturation of the soil governed by a chromatographic movement.

Introduction

Schemes for management of nuclear wastes involve their conversion into vitrified forms and disposal in deep geological environments, such as hard rock, clay layers and salt formation [1].

Transuranic nuclides in these conditioned wastes represent a possible long-term risk after disposal. In the case of an accidental event, where the geological formation should fail, the waste matrix could come in contact with groundwater from surrounding aquifers. In our laboratories we have set up an experimental system reproducing this scenario in order to investigate the migration behaviour of selected radionuclides in the so-called 'far-field', the ultimate barrier before the biosphere.

Our working methodology is based on a sort of feed-back loop established between the simulation experiments, the determination of the physico-chemical forms and model development. This report gives some preliminary results on the behaviour of neptunium and americium in a natural clay material, surrounding typical clay formations and salt domes.

Experimental

Two kinds of soil were used in this study. In the first series of experiments a sand containing 25% of glauconite* taken from the aquifer overlaying the Boom clay formation in Belgium was used. The synthetic groundwater used in the migration studies had the composition of water in equilibrium with the soil (pH 8.35; total carbonate content $3.5 \cdot 10^{-3}$ *M*; ionic strength of about 10^{-2} *M*) [2]. In the second set of experiments a quartz sand containing small amounts of iron oxide and clay material was employed to investigate the behaviour of americium leached by 5.4 *M* NaCl solution at pH around 5. Borosilicate glasses doped with single tracers (^{237}Np or ^{241}Am) under inert atmosphere at 1200 °C were used as the source term [3]. After the leaching of the glass, the contaminated water passed through the soil from the bottom to the top of the column, where the effluent was continuously monitored using appropriate counting techniques (liquid or γ-scintillation). In the case of ^{237}Np experiments, at the end of the percolation the column was left undisturbed until the equilibrium with the daughter was reached and the γ activity of ^{233}Pa measured. The γ-profiles of ^{241}Am in the column were recorded with a hyper-pure Ge detector using a scanning device.

Ultrafiltration analyses of the leachate were performed employing Nuclepore filters of different pore sizes. Electromigration investigations were carried out with a technique described elsewhere [4]. Ion exchange resins obtained from Bio Rad were used (AGIx8 and AG50Wx8, both 200 – 400 mesh).

Results and Discussion

Clay Option

The curves reported in Fig. 1 give the contamination patterns of americium-241 and neptunium-237 retained in glauconitic sand columns as a function of column length. These experiments were carried out under oxic conditions, where the oxidation states

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*Magnesium–iron allumino–silicate of the illite type.

TABLE I. Analysis of the Leachate of a Glass Doped with ^{237}Np.

	ion-exchange[a]	electromigration[b]	ultrafiltration
% cationic	0.12	0.23	–
% anionic	76.4	10.7	–
% retained by a 30 nm filter	–	–	1.7

[a] The balance to 100% was determined to be a neutral fraction.

[b] Activity moving towards the poles after 60 min of electromigration at a constant current of about 0.5 mA.

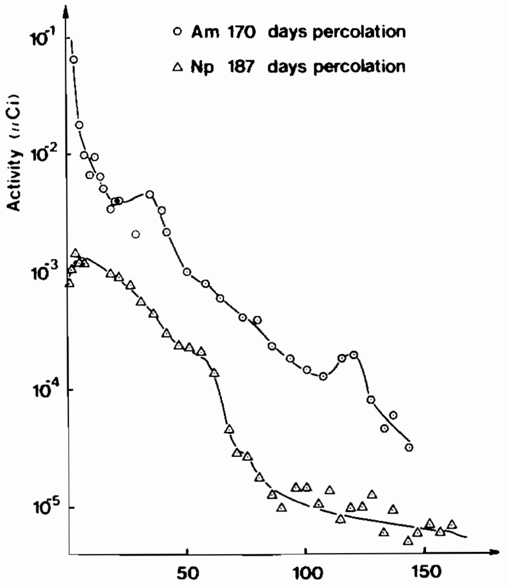

Fig. 1. Contamination profiles measured after slicing of the glauconitic sand columns. Total input activity: ^{241}Am 2.41 μCi, ^{237}Np $4.04 \cdot 10^{-2}$ μCi.

of the radionuclides are (V) for neptunium and (III) for americium.

In the case of neptunium, neptunyl(V) ions are currently considered the principal species governing the migration potential of this radionuclide. Our experiments with ^{237}Np were performed expressly in oxidizing environments. Such conditions simulate the worst situations likely to exist in the geological repository, and therefore give conservative estimates. The curve in Fig. 1 shows that the column effectively retained the leached activity. In order to account for the observed process, a direct investigation on neptunium species in groundwater was carried out. Table I gives the results of electromigration, ultrafiltration and ion-exchange analyses of the glass leachate. These data reveal the presence of soluble anionic species of neptunium(V).

The electromigration analysis of the leachate of a glass doped with ^{239}Np (γ-emitter) showed the existence of negatively charged species having a low mobility in the electric field. This behaviour may be explained by the presence of very small pseudocolloids due to the adsorption of neptunium(V) species on particular matter.

The high retention of Np(V) in the column should be even more enhanced in reducing environments, as Np(IV) is expected to be the major species. The total solubility of this radionuclide should in fact be drastically decreased, due to its high tendency of hydrolization [5].

As regards americium, most of the activity leached from the glass matrix was determined by ultrafiltration to be associated with colloidal fractions. The effluent of the column contained, however, only soluble anionic species and this is considered to be due to carbonate complexes of americium [6]. The total americium concentration at the inlet was 4×10^{-10} M, whereas the concentration of the actinide leaving the column was about 5×10^{-13} M. In the last portion of the column the americium concentration fixed by the soil was three orders of magnitude higher than in the effluent and once it reached the value of 2×10^{-10} M it remained constant with time. The retention of americium can therefore be explained by the very high filtering efficiency of the glauconitic sand in the first part of the column and a sorption saturation mechanism in the final portion [7].

The americium behaviour can be extrapolated to real ground-water conditions, since this radionuclide is expected to exist in the oxidation state (III) in both oxic and anoxic environments.

Rock Salt Option

Figure 2 reports the contamination profiles of americium in a column filled with a typical soil overlaying a rock salt formation. The progressive saturation of the retention capacity of the soil is observable as the percolation proceeds. The displacement of the solute front in a breakthrough curve was observed by monitoring the activity at the input and output of the column as a function of time. The results confirm a saturation effect.

Ultrafiltration experiments demonstrated that about 30% of the released activity present in the

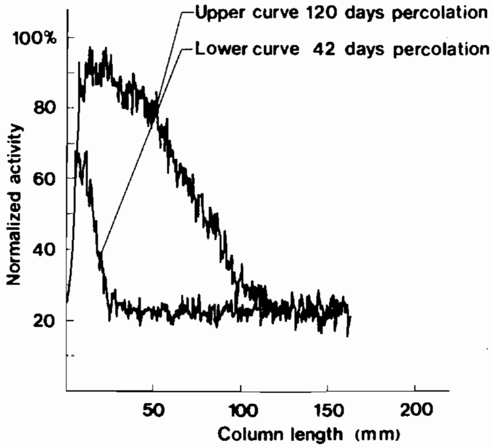

Fig. 2. Contamination profiles of americium measured by γ-scanning during the percolation steps.

leachate is in a colloidal form. The size distribution of Am colloids present in brine leachate differs markedly from the distribution observed in the fresh water leachate. The ultrafiltration experiments indicated that in the brine solution more than 50% of the radioactive colloids have dimensions smaller than 0.1 μm. By comparison in the case of fresh water, 50% of the americium colloids were found to be smaller than 1 μm [6].

A direct investigation of soluble chemical species of americium by electromigration and ion-exchange methods, already used in groundwaters in contact with the clay-sand, was not successful in the case of brine owing to the high ionic strength of the solution. In order to gain a better knowledge of the soluble species, an analysis based upon thermodynamic data was carried out. At the pH of brine the predominant soluble species appear to be some chloro-complexes of americium. The contamination profiles shown in Fig. 2 may therefore be the result of a chromatographic movement of cationic complexes of americium with chloride ions. This transport seems to be governed by a simple distribution coefficient. It should be noted however that there is a small colloidal fraction which may have been filtered in the first layers of the column [8].

Conclusions

The results of this study demonstrate how the geochemical environment and the radionuclide oxidation state affect the migration of transuranics.

In low ionic strength groundwater it is the filtering efficiency of the soil medium which governs the transport process of trivalent actinides.

Pentavalent neptunium appears to migrate through the soil column with the equilibrium being continuously displaced from an anionic carbonate complex to the slightly more adsorbable cationic species, NpO_2^+. The formation of pseudocolloids was also detected.

The observed saturation of active sites within the soil material is responsible for the low distribution of americium between the quartz sand and the brine solution used.

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