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E12

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

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Transuranic nuclides present in conditioned waste represent a possible long-term risk after their disposal in geological repositories. In the case of an accident where the geological formation should fail, the waste matrix could come in contact with ground water 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 deals with laboratory-scale experiments investigating the behaviour of neptunium and americium in a natural clayey material surrounding typical clay formations and salt domes.

Clay Option. Figure 1 shows the retention profiles of americium and neptunium when a contaminated ground water passes through a column of glauconitic sand under oxic conditions. An interesting comparison can be made between the two curves. In spite of the existence of anionic carbonate complexes of americium [1] which are not easily adsorbed by the geological material, most of the leached activity is retained by the column. In such a dynamic system, there is a continuous equilibrium displacement towards the more adsorbed species. Moreover, the large amount of colloidal particles identified in the leachate was retained by the column. This behaviour can be extrapolated to real ground water conditions since americium is expected to exist in the oxidation state (III) in both oxic and anoxic environments.

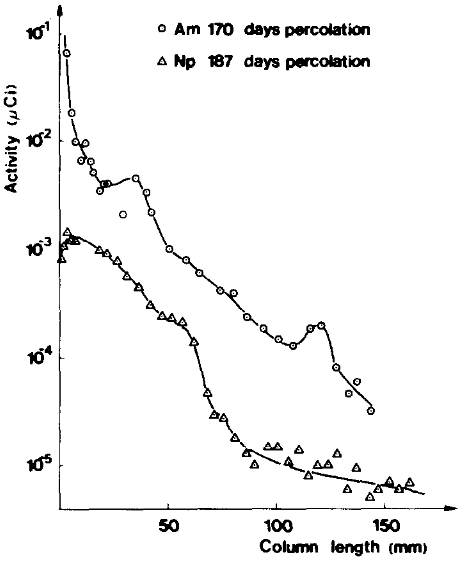

Fig. 1. Contamination profile measured after slicing of the glauconitic sand column. Total input activity: Am 2.41 μCi, Np 4.04×10^{-2} μCi.

In the case of neptunium, the existence of neptunyl ions is currently considered one of the principal species governing the migration potential of this radionuclide. The curve in Fig. 1 shows that about 98% of the activity is sorbed in a 20 cm column. Speciation studies have been performed in order to account for the observed behaviour. Application of electromigration techniques developed at the J.R.C. [2], to investigation of Np(V) in 3.5×10^{-3} *M* $NaHCO_3$, revealed the presence of soluble anionic species. This may be explained through complexation with carbonate ions. The phenomenon is at present under investigation in parallel experiments. Electromigration analysis of the leachate of a glass doped with ^{239}Np showed the existence of negatively charged species. Considering their very low mobility in an electric field, they are thought to be microcolloids. The high retention of Np(V) in the column can be explained either by the very high filtering efficiency of the geological media or through a non-specific adsorption of anionic species on the glauconitic sand.

Such behaviour of neptunium in oxic conditions 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 be in fact drastically decreased, due to its high tendency of hydrolyzation [3].

Salt-rock Option. Figure 2 reports the contamination profile of americium in a column filled with a typical soil overlying a salt rock formation.

In the laboratory simulation experiment, a brine saturated solution flows over a borosilicate glass containing the ^{241}Am nuclide and then through a column containing the soil porous formation. Ultrafiltration experiments demonstrated that more than 90% of the released activity present in the leachate is in a colloidal form. The size distribution of colloids present in brine leachate differs markedly from the

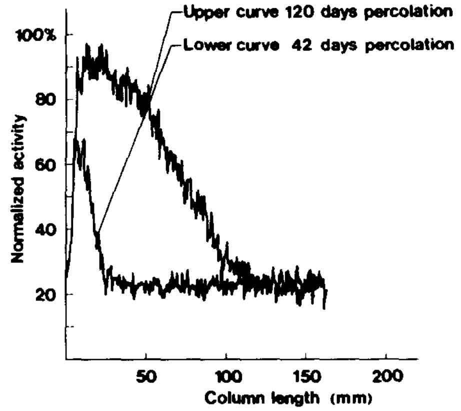

Fig. 2. Contamination profile of Am measured by γ-scanning during percolation step.

distribution observed in the fresh water leachate. The ultrafiltration experiments indicated that in the brine solution more than 50% of the radioactive colloids have dimension smaller than 0.1 μm. By comparison in the case of fresh water, 50% of the Am colloids were found to be smaller than 1 μm. The column contamination profile reported in Fig. 2 is therefore the result of two major mechanisms: colloidal filtration and the retention of soluble species. This second process however is hindered by the saturation of the active sites of the soil because of the extremely high ionic strength of the liquid phase.

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E13

Direct Spectrophotometric Determination of Cerium Sub-group Rare Earth Elements with m-Trifluoromethylchlorophosphonazo in the Presence of Yttrium Sub-group Elements in Nodular Cast Iron and Steel samples[+]

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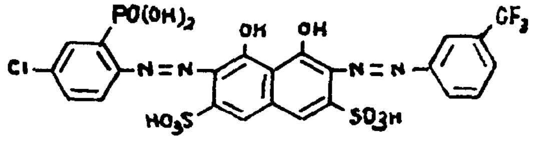
2,7-Bisazo derivatives of chromotropic acid have been used in the spectrophotometric determination of cerium sub-group rare earth elements, the most important being carboxynitrazo [1], due to their metallic complexes with high molar absorptivities. This reagent is applied to the analysis of ores with satisfactory results [2].

Recently, owing to the use of oxalic acid as masking reagent, selective spectrophotometric determination of cerium sub-group rare earth elements with CPAmN has been developed [3].

In the present work, the reaction of cerium sub-group rare earth elements with a new 2,7-bisazo derivative of chromotropic acid, the m-trifluoromethylchlorophosphonazo, is studied for its higher selectivity compared with the other reagents mentioned:



This paper describes the synthesis of the reagent and its use in the direct spectrophotometric determination of cerium sub-group rare earth elements in nodular cast iron and steel samples. The results obtained are favourable.

Reagents and Apparatus. Absorbance was measured on a Model UV-300 double-beam spectrophotometer and Model XG-125 spectrophotometer with 1-cm cells. The working standard solutions: 20 μg/ml.

Synthesis of m-Trifluoromethylchlorophosphonazo. 3-Trifluoromethylaniline was mixed with 20 ml of water and a solution of sodium nitrite (0.3 g in 8 ml of water), and then diazotized by adding 5 ml of 6 *M* hydrochloric acid by drops at 0–2 °C and stirring. The mixture is stirred 1 hr at 0–5 °C.

2 g Chlorophosphonazo I was dissolved in 30 ml of 5% lithium hydroxide solution and cooled to 0–2 °C. The diazotized solution prepared was added while stirring, the color of the solution changed from red to blue (the pH of the solution sometimes was adjusted to 9.5–10.5 with dilute lithium hydroxide solution or hydrochloric acid). After continuous stirring for 1 hr, the solution was allowed to stand overnight, acidified to pH 1–2 with hydrochloric acid, filtered and washed with 2 *M* hydrochloric acid 3 times.

The precipitate was dissolved in 80 ml of 5% lithium hydroxide solution and filtered. The solution was acidified to pH 1 with hydrochloric acid and then filtered and washed with 2 *M* hydrochloric acid 2–3 times. The product was dried at 50 °C, yielding 1.5 g of precipitate.

[+] Paper to be presented by Cheng Jai-kai, Laboratory of Analytical Chemistry, Dept. of Chemistry, Wuhan University, Wuhan, China.