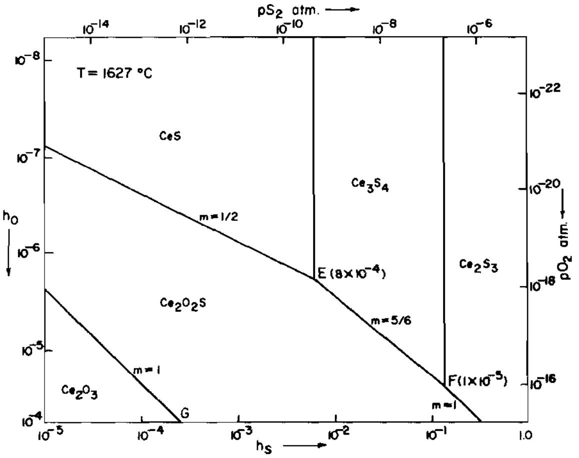

Fig. 4. The Ce–O–S phase stability diagram at 1672 °C for the control of sulfide inclusions in steel.

under which Ce_2O_3 may precipitate, *i.e.*, $h_o/h_s > 4.3$. This condition is easily met in the production of modern low sulfur steels.

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E11

Thermoelectric Properties of M^{4+}/M^{3+} and $MO_2{}^{2+}/MO_2{}^{+}$ Redox Couples of Neptunium and Plutonium in Aqueous $HClO_4$ and HNO_3 Media

P. BLANC and C. MADIC*

Institut de Recherche Technologique et de Développement Industriel, Division d'Etudes de Retraitement et des Déchets et de Chimie Appliquée, Départment de Génie Radioactif, Service des Etudes de Procédés, Section des Transuraniens, Centre d'Etudes Nucléaires de Fontenay-aux-Roses, B.P. No. 6, 92260 Fontenay-aux-Roses, France

The thermoelectric properties of redox couples of transuranium elements in acidic, slightly complexing media ($HClO_4$ and HNO_3) have been considered. For these elements the redox couples suitable for that study correspond to the reversible M^{4+}/M^{3+} and $MO_2{}^{2+}/MO_2{}^{+}$ systems. So only the couples of neptunium and plutonium have been studied with the following precautions. First, the use of an inert atmosphere (N_2) prevents the oxidation of Np^{3+} ion. Second, the selection of a pH close to 3.5 minimizes the disproportionation reaction of $PuO_2{}^{+}$ ion.

Theoretical considerations lead to the conclusion that the electromotive force between two inert electrodes in contact with an aqueous solution containing the reversible redox couple and subjected to two different temperatures is expressed according to:

$$\Delta V = \Delta T x \epsilon \qquad (1)$$

where ΔT is the gradient of temperature and ϵ the thermoelectric power of the redox couple which can be written as:

$$\epsilon = \epsilon_o + \frac{R}{nF} \log \frac{[Ox]}{[Red]} + \frac{R}{nF} \log \frac{\gamma_{Ox}}{\gamma_{Red}} \qquad (2)$$

Equation (2) is an approximation of the derived of the Nernst equation versus temperature, where the terms possess their usual signification and ϵ_o is the absolute thermoelectric power proportional to the difference in the standard entropies of the two ions of the redox couples:

$$\epsilon_o = \frac{\Delta S_o}{nF} \qquad (3)$$

For all M^{4+}/M^{3+} and $MO_2{}^{2+}/MO_2{}^{+}$ redox couples of the neptunium and plutonium elements a check of the validity of equation (1) and of the different terms of equation (2) has been made by studying first, the variation of ΔV versus the gradient of temperature ΔT for solutions with constant composition, second, the variations of the thermoelectric power ϵ for constant temperature gradient versus the ratio [Ox]/[Red] at constant ionic strength or verus the ionic strength for solutions of constant [Ox]/[Red] ratio.

Fig. 1 shows the good linear relations $\Delta V = f(\Delta T)$ obtained for all the couples studied in similar conditions. It can be noticed that the slopes of the straight lines (*i.e.* the thermoelectric power ϵ) are large in the case of the M^{4+}/M^{3+} couples and small for the $MO_2{}^{2+}/MO_2{}^{+}$ couples. For the M^{4+}/M^{3+} systems the results for both elements are very close, on the contrary a noticeable difference is observed between neptunium and plutonium for $MO_2{}^{2+}/MO_2{}^{+}$ couples.

For constant ΔT values the validity of the second term of equation (2) was verified accurately for all the systems with variations of [Ox]/[Red] ratio at least equal to two orders of magnitude. The proportionality factor of the equation $\epsilon = k x \log[Ox]/[Red]$ was found to be: 0.184 mV/K(Np^{4+}/Np^{3+}); 0.182 mV/K(Pu^{4+})/Pu^{3+}); 0.197 mV/K($NpO_2{}^{2+}/NpO_2{}^{+}$); 0.197 mV/K($PuO_2{}^{2+}/PuO_2{}^{+}$). These values are in excellent agreement with the theoretical calculated value equal to: 0.197 mV/K.

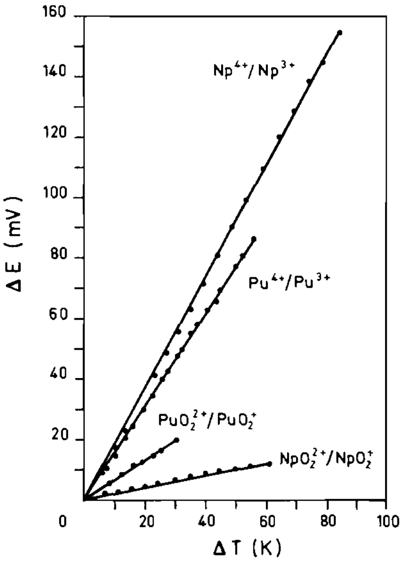

Fig. 1. Thermoelectric powers of neptunium and plutonium M^{4+}/M^{3+} and $MO_2{}^{2+}/MO_2{}^{+}$ redox couples.

Fig. 2 presents the variations of the thermoelectric power ϵ *versus* the ionic strength using constant [Ox]/[Red] ratio. For the $MO_2{}^{2+}/MO_2{}^{+}$ couples these variations are very close to those predicted by Debye and Hückel theory. The extrapolations to zero ionic strength give the following ϵ_0 values: +0.430 mV/K and +0.850 mV/K for neptunium and plutonium respectively. The M^{4+}/M^{3+} couples possess a quite different pattern: the decrease of ionic strength, obtained by a decrease of $HClO_4$ or HNO_3 acid concentrations, induces a diminution of ϵ for Pu^{4+}/Pu^{3+} couple and the appearance of a maximum in the case of Np^{4+}/Np^{3+}. These behaviors are different of those predicted by Debye and Hückel theory; the origin of the discrepancy is certainly the hydrolysis of the acidic cations: Np^{4+} and Pu^{4+}. Nevertheless extrapolations from data obtained for solutions with high acid concentration permit reasonable estimations of ϵ_0 for these couples: ϵ_0 were found in the range 2.0 to 2.25 mV/K for both elements.

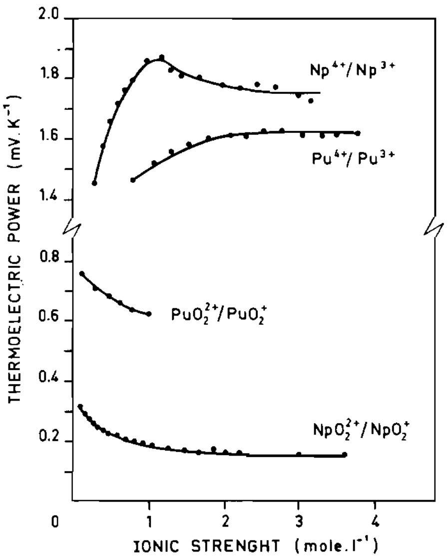

Fig. 2. Influence of ionic strength on the thermoelectric powers of neptunium and plutonium M^{4+}/M^{3+} and $MO_2{}^{2+}/MO_2{}^{+}$ redox couples.

For all the M^{4+}/M^{3+} and $MO_2{}^{2+}/MO_2{}^{+}$ systems studied non significant differences were found between the $HClO_4$ and HNO_3 media.

Couples	ΔS_0 J mol^{-1} K^{-1} (this work)	ΔS_0 J mol^{-1} K^{-1} Fuger & Oetteing [1]
Np^{4+}/Np^{3+}	205 ± 12	210 ± 27
Pu^{4+}/Pu^{3+}	205 ± 12	205 ± 27
$NpO_2{}^{2+}/NpO_2{}^{+}$	41	71 ± 16
$PuO_2{}^{2+}/PuO_2{}^{+}$	82	67 ± 16

The Table compares the ΔSo calculated with equation (3) and the experimental ϵ_0 with those published by FUGER and OETTING [1]. ΔSo estimated values for M^{4+}/M^{3+} couples are in fair agreement with those from the literature. The experimental and published ΔSo for $PuO_2{}^{2+}/PuO_2{}^{+}$ are reasonably close, but for $NpO_2{}^{2+}/NpO_2{}^{+}$ couple a large deviation is observed. No explanation is found for this result since these $MO_2{}^{2+}/MO_2{}^{+}$ couples are expected to present similar behaviors. So, this deviation, in terms of ΔS_0, means some unexpected difference in the structure of the $MO_2{}^{2+}$ or $MO_2{}^{+}$ aquo ions between neptunium and plutonium.

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E12

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

G. BIDOGLIO*, A. DE PLANO, A. AVOGADRO and
C. N. MURRAY

Commission of the European Communities, Joint Research Centre, 21020 Ispra (Va), Italy

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.

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.

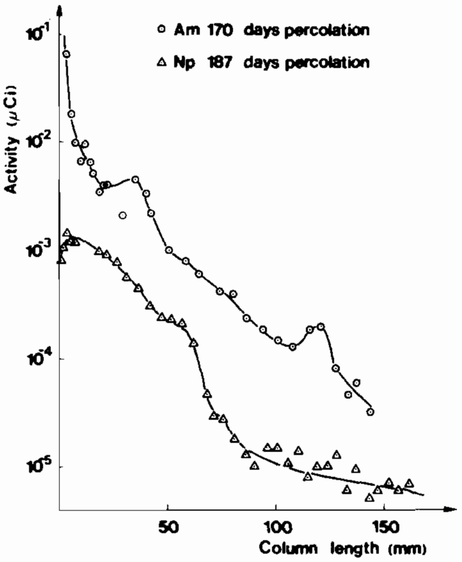

Fig. 1. Contamination profile measured after slicing of the glauconitic sand column. Total input activity: Am 2.41 μCi, Np 4.04×10^{-2} μCi.

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