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The investigation of the neptunium complexes formed upon interaction of high level waste glass and Boom Clay media

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Abstract

Since complexes formed between actinides released from high level waste glass and humic acids present in high concentration in Boom Clay porewater may control the actinide solubility in the clay formation, a research programme has been started to study the complexes formed between neptunium, the most critical actinide in the Belgian performance assessment studies, and Boom Clay porewater. The leaching experiments give a maximum solution concentration of Np in Boom Clay porewater of 10^{-6} M after 24 days. In the leachates, Np is mainly associated with colloidal particles of small sizes and is present as a mixture of two oxidation states, V and IV. The retention of Np in the glass increases with increasing SA/V (geometrical surface area on solution volume ratio). A high solution concentration is accompanied by a high retention of Np. The characterisation of the mobile Boom Clay organic matter (OM) gives a proton exchange capacity (PEC) equal to 2.9 meq g^{-1} OM at pH 8.5. Related to this value, the interaction constants (β) of the literature were reviewed and calculated according to their proton exchange capacity for the pH of interest. © 1998 Elsevier Science S.A.

Keywords: Neptunium; Glass leaching; Humic acid; Complexation

1. Introduction

The Boom Clay formation, which is the candidate host rock for the disposal of vitrified waste forms in Belgium, is characterised by a very high dissolved organic carbon concentration (DOC~200 mg l^{-1}) [1]. Complexation by humic substances may enhance the release of actinides from vitrified waste forms and their solubility. To validate the thermodynamic solubility calculations, the determination of a maximum and realistic solution concentration of actinides in Boom Clay porewater and the characterisation of the species formed are essential. Among the actinides released from the glass, Np-237 is the most critical one because of its long half life (2.14×10^{6} years) and its large abundance in nuclear waste. Neptunium will be essentially in the tetravalent oxidation state under reducing conditions expected for the Boom Clay repository. Therefore, it will strongly interact with humic substances.

Our research aims to study the influence of the humic substances on the Np release from the glass and its mobility in the Boom Clay porewater. The analyses focus on the determination of the mobile Np concentration by means of leaching experiments and the characterisation of the Np complexes using laser induced photoacoustic spectroscopy [2]. As a prerequisite for the experimental determination of the interaction constants of the Np(IV)–humate complexes, the characterisation of the Boom Clay OM is performed and the literature on Np(V) complexes are reviewed in terms of proton exchange capacity for pH close to the pH of Boom Clay water.

2. Experimental

The leaching test procedure and the characterisation of the Boom Clay OM are described.

2.1. Leaching tests

Experimental conditions for generating the Np complexes are taken from a study on Eu doped glass [3]. The PAMELA glass SM539, whose composition is given in [4], was used for the tests. Two Np concentrations (88 and 8.8

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kBq Np-237 per gram of glass) were incorporated into the glass to study their influence on the leached Np concentration. The leaching solutions were Boom Clay water sampled in the underground research facility whose composition is given in [4]. The influence of the humic acids (HA) was examined through the use of three concentrations, 50, 150 and 300 mg l^{-1}. Bubbling with Ar/0.4% CO_2 allowed us to obtain the pH of the Boom Clay porewater. To achieve high SA/*V* (geometrical surface area of the glass on solution volume) ratios, 1000 and 100 m^{-1}, powdered glass was used. The leach tests were done at 40 and 90°C for three test durations, 24, 90 and 180 days. The glass samples were added to the solutions in Teflon® containers in an anaerobic glove box purged with N_2.

To examine the presence of colloidal forms of Np and to determine the total Np concentration in solution, at the end of the leaching tests, the leachates were filtered through a filter of 0.45 μm and ultrafiltered over 10^5 MW cut-off membranes (Amicon YM100 membrane filtration systems). Some of the samples were also ultrafiltered over 3×10^4 MW cut-off membranes (Amicon YM30). The sorption behaviour of the membranes tested according to a procedure described by Nitsche [5], showed that it is not necessary to saturate the filter membranes. The activity of Np-237 in the different fractions was measured by total alpha counting (ZnS detector).

To check the oxidation state of Np in the leachates, a liquid–liquid extraction with TTA (thenoyltrifluoroacetone) [6] was performed on six of the leaching solutions. We assumed that the stability constant of the NpTTA complex is much greater than the interaction constant of the HA complex. The experimental procedure is given in [6].

2.2. Characterisation of the Boom Clay organic matter (OM)

Because of the dilute nature of the organic matter solutions, it was necessary to concentrate and isolate the humic substances by means of a diethylaminoethyl-cellulose (DEAE-cellulose) resin [7]. The concentrate was then purified and transformed to the proton form by the procedure of Dierckx [8]. The resulting colloidal suspension was freeze-dried. The mobile fraction of Boom Clay OM was, therefore, characterised by potentiometric titration using the Metrohm 716 DMS automatic Titrino with the Metrodata software. An aliquot of OM (300 mg l^{-1}) was brought into a closed titration vessel purged with N_2 to avoid CO_2 contamination. The humic acid was dissolved with 0.1 M $NaClO_4$ and pH adjusted to 10 with 0.1 M NaOH. The dynamic equivalence point titration protocol method was chosen using 0.1 M $HClO_4$ from pH 10 to pH 3.

3. Results and discussion

The first results of the leaching tests and the PEC for Boom Clay OM are presented.

3.1. Leaching experiments

The redox potential (SHE) and pH are measured before and after the leaching tests. Compared to a pH of 8.3 in the beginning of the tests, a maximum change of 0.78 pH unit is observed. A lower pH is observed for the higher HA concentration because of the higher H^+ concentration coming from the dissociation of HA. The redox potential ranges from −9 to +56 mV. During previous leaching tests [4], the valence state of Np was never measured. The glasses being produced in oxidising conditions, Np is probably in a pentavalent oxidation state. Under Boom Clay conditions, the presence of pyrite and OM associated with the clay minerals surfaces ensure reducing conditions, enough to reduce the leached oxidised Np. As we are using pure Boom Clay porewater, the concentration of redox species is very low and the redox measurement is not certain. The mobility of actinides can be determined by their valence which depends on pH and E_h as well as on the formation of secondary phases. At the working E_h and pH, the E_h–pH diagram for Np in carbonate free systems [9], if $Np(OH)_4$ is chosen as the dominant oxy solid, shows that $Np(OH)_5^-$ is the principal aqueous species. However, the log β of $Np(OH)_4$ aq. is highly uncertain and the boundary Np(V)/Np(IV) could also be shifted due to the presence of carbonate and humate complexes. The solvent extraction method shows the presence of both the oxidation states, V and IV.

According to recent measurements, the size limit for radionuclide mobility in Boom Clay is close to 10^5 MWU [4], which is the limit for the mobile HA molecules in Boom Clay. The mobile Np concentration in the leachates, presented in Table 1, is obtained by filtration over 10^5 and 3×10^4 MW cut-off membranes. Included in this size range, it is also important to examine colloids as they could increase the mobility of Np. The mobile concentrations vary between 10^{-6} and 10^{-7} M. These are higher than those calculated for $Np(OH)_4$ (10^{-9} M) as a solid phase but smaller than that found experimentally with NpO_2OH (10^{-4} M) [10].

To calculate the total amount of Np involved in the dissolution reaction, when the overall glass corrosion is known, we use the retention factor. The Np retention is calculated with respect to the amount of soluble boron, one of the network formers and the best corrosion tracer since it does not precipitate in secondary phases. The retention factor is therefore defined as $RF_{Np}=NL_B/NL_{Np}$ (normalised release of B divided by the normalised release of Np where NL_{Np} is determined from the total leached activity). As boron was not measured in the present experiments, we

Table 1
Np concentration in Boom Clay water after filtration over 0.45 μm, 10^5 and 3×10^4 MW cut-off membranes (mol/l) and % Np present in each fraction

	Exp. conditions			[Np] (μmole/l)			% Np	
% Np	T (°C)	SA/V (m^{-1})	[HA] (mg/l)	0.45 μm	5 nm	2 nm	<0.45 μm	<5 nm
0.034	40	100	300	1.12	0.82		26.5	73.5
0.34	40	100	150	0.68	0.52	0.32	24	76
0.34	40	100	300	0.63	0.5	0.18	21	79
0.34	90	100	50	1.55	0.53		66	34
0.34	90	100	150	1.4	1.15		18	82
0.34	90	100	300	1.0	0.74		26	74
0.034	90	1000	50	0.56	0.3		47	53
0.034	90	1000	150	0.78	0.47		40	60
0.034	90	1000	300	0.65	0.52		13	87
0.34	90	1000	50	3.6	1.7	1.68	53	47
0.34	90	1000	150	2.1	1.84	1.15	13	87
0.34	90	1000	300	2.4	1.86	1.4	25	75

obtain NL_B from previous inactive corrosion tests performed by Van Iseghem et al. [4]. A high solution concentration and consequently, a high Np retention are observed with increasing SA/V and increasing Np loading into the glass (Fig. 1). The retention appears to vary with SA/V when in fact the thickness of the surface layer of the glass should decrease with increasing SA/V. Neptunium is naturally retained when the solution concentration increases but the retention could also be due to adsorption of Np into the glass surface. At this stage, we do not have enough data to draw conclusions under the given conditions.

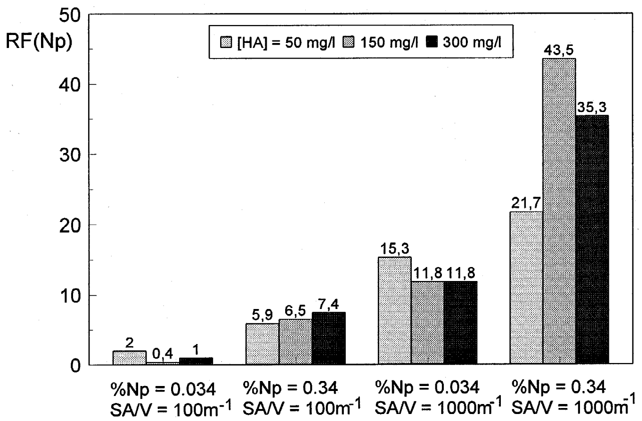

Fig. 1. Retention factor of Np as a function of SA/V and Np loading into the glass at 90°C.

By the use of ultrafiltration and laser induced photoacoustic spectroscopy, Bidoglio [11] demonstrated the association of Np with colloidal organic particles of low molecular sizes (a few nm). Results, given in Table 2, show that Np is mainly associated to small colloidal particles in the leachates. For a concentration of 300 mg l^{-1} HA, 76% (average value) of Np is bound to particles smaller than 5 nm. In the case of 150 mg l^{-1} HA, between 60 and 87% of Np is bound to particles smaller than 5 nm and for the lower HA concentration about 37% of Np is in

Table 2
Independent complexation constants (log β (lit)) and complexation constants (log β) calculated at pH relevant for Boom Clay porewater

Humic acid+PEC	Model	Log β (lit)[a]	pH	Log β (calc)	References
Gorbelen HA	LC[b]	3.66±0.02	8	2.71	Kim et al.
5.38 meq/g			9	3.1	[14]
Aldrich	2-site model	2.69±0.08	8.8	3.19	Moriyama et al.
5.3 meq/g			7.7	2.72	[16]
Aldrich	LC	3.66±0.05	8	2.84	Sakamoto et al.
5.1 meq/g			8.5	3.02	[17]
			9	3.19	
Aldrich	α	4.2± 0.15	8	4.97	Marquardt et al.
4.6 meq/g					[15]
Lake Bradford	α	2.50	7.5	2.48	Rao and Choppin
3.75 meq/g					[13]

[a] Log β (lit): pH-independent complexation constant for Np(V)–humate complex.
[b] LC: Loading capacity (mole fraction of the maximum available complexing sites of HA).

this fraction of particles. The majority of humic substances in Boom Clay are expected to be in this size range.

3.2. Characterisation of the Boom Clay organic matter

The complexation of Np(V) by HA was reported a few times in the literature [13–17], but no data are available for the Np(IV)–humate complexation, until now. The interaction constant of the Np–humate complex (β) can be expressed by:

$$\beta = [\mathrm{NpHA}]/[\mathrm{Np}]_{\mathrm{free}}[\mathrm{HA}]_{\mathrm{free}}$$

where [NpHA] is the concentration of complexed Np, $[\mathrm{Np}]_{\mathrm{free}}$ is the concentration of uncomplexed Np, and $[\mathrm{HA}]_{\mathrm{free}}$ the concentration of uncomplexed HA. $[\mathrm{HA}]_{\mathrm{free}}$ is obtained by substracting the [NpHA] from the total HA concentration, $[\mathrm{HA}]_{\mathrm{tot}}$. The total HA concentration is given by the PEC multiplied for a given amount of HA in solution in mg l^{-1}. Consequently, the proton exchange capacity obtained by acid–base titrations, is a prerequisite for the calculations of the β values of Np(IV)–humate complexes. To obtain PEC, the charge of the mobile Boom Clay OM due to the deprotonation of ionic groups was calculated according to the charge balance in the solution [12]. At pH 8.5 which corresponds to the pH of Boom Clay porewater, PEC is equal to 2.9 meq g^{-1} OM.

Constants from the literature were determined at different pH and ionic strength. In order to explain the pH dependence of the interaction constants and to eliminate this dependence, the authors introduced different concepts such as the loading capacity, the degree of ionization or the two-sites model. As we intend to use PEC to express the HA concentration and to work at pH around 8.5, only the interaction constants at relevant pH values were considered and recalculated, when it was necessary, by taking into account the PEC value. Table 2 reviews the independent interaction constants of Np(V)–humate complexes and gives the β values at pH from 7.5 to 9 calculated with the PEC. For different PEC, different site occupancy, the values can be used for our environmental conditions. Marquardt's value is somewhat different as it was determined with very low Np concentration. At this low Np concentration, Np will be preferentially bound to specific sites giving greater interaction constants. The reduction of Np(V) to Np(IV) by the environmental conditions will affect even more the complexation behaviour resulting in an increase of the stability constant.

4. Conclusions

A correct description of the chemical reactions around the glass is essential for the calculation of the quantity of mobilised Np. Humic substances constitute an important component in Boom Clay porewater which could increase the concentration of dissolved Np by complexation. The current state of the experiments gives a Np mobile concentration between 10^{-6} and 10^{-7} M after 24 days of leaching. The influence of the HA concentration on the leaching of Np is still not clear. More data are needed to clarify if the release is controlled by the kinetics of the glass matrix dissolution or the formation of secondary phases. The retention of Np increases with the increasing SA/*V* and increasing Np loading into the glass. Np is redox sensitive under conditions prevailing in situ in Boom Clay. As determined by ultrafiltration, the Np colloids are smaller than 5 nm which corresponds to the pore size in Boom Clay. Further characterisation and quantification of the Np–humate colloids have to be done.

The approach of this work is to consider PEC to calculate the HA concentration and the interaction constants at a pH around 8–9. Mobile Boom Clay OM has a PEC of about 2.9 meq g^{-1} OM. A reliable database for Np(IV) complexation is really needed for the safety assessment of the disposal of radioactive waste in Boom Clay.

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