Adsorption of actinides on cement compounds

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Abstract

The sorption of thorium, uranium, neptunium, plutonium and americium on hydrotalcite, tobermorite, ettringite and calcium silicate hydrate gel were investigated in water, saturated NaCl solution and Q-brine at 25, 55 and 85 °C. Speciation was also studied.

The data obtained will fulfil Freundlich's isotherm if the ion constituent is taken as a parameter but even Langmuir's isotherm will be valid if the ionic concentration of the various ionic species is taken into account.

A theoretical parameter was found which permits the solution capability of the various cementitious materials to be compared with respect to the relevant ionic species present.

1. Introduction

Within the framework of the tricoordinated research programme, dealing with the impact of additives and waste stream constituents on the immobilization potential of cementitious materials and performed by the University of Aberdeen (UK), AEA Windscale (UK) and Freie Universität Berlin (Germany) the present authors had to investigate the sorption of various actinides on cement components in media of practical importance, to obtain data for modelling the migration of these substances under the aspect of safeguards for waste repositories.

The relevant actinides to be taken into consideration were thorium, uranium, neptunium, americium, partially represented by europium labelled with ^{152}Eu, and plutonium, the adsorbents hydrotalcite, ettringite and calcium silicate hydrate (CSH) gel. The adsorbents are

C-S-H-Gel

Composition:
Calciumhydroxide (Ca(OH)$_2$), Silicagel (SiO$_2$ * n H$_2$O) and Al(OH)$_3$
C-S-H-Gel : relation Ca /Si = 1.2

Fig. 1. The structure of CSH gel.

well-known corrosion products of cement; the structure of CSH gel can be seen in Fig. 1.

The media chosen for practical reasons were water, saturated NaCl solution and Q-brine and the temperatures 25, 55 and 85 °C.

Criteria had to be found in order to compare the various cement components with respect to their sorption capabilities for the various actinides of interest under practical conditions.
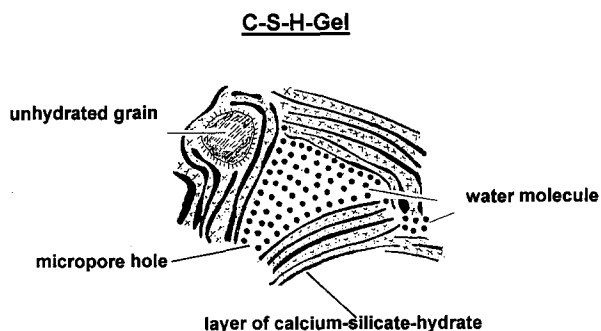
2. Experimental details

2.1. Preparation of solution

For all the systems under investigation the blank and stock solutions were prepared in the same way. The blank solutions were prepared by adding 1 g of each of the four selected cementitious materials to 300 ml of each of the media mentioned above. To prepare the different stock solutions, 0.5 g of each of the four different cement components were added to 150 ml of each of the three media, plus an amount of the substance under investigation sufficient for saturation. All the solutions were filtered with filters of 450 nm pore size.

2.2. Batch experiments

For the batch experiments the specific filtered stock solutions were diluted with the relevant filtered blank solution in the blank solution: stock solution ratios of 0:1, $1:10^{1/2}$, 1:10, $1:10^{3/2}$ and 1:100. 10 mg of each of the four different selected cementitious materials were added to 10 ml of each of the aforementioned mixtures. After obtaining equilibrium the concentrations of the elements under investigation were determined.

2.3. Determination of concentrations

To obtain equilibrium the various solid–liquid mixtures were shaken with a special device for 4 weeks. The ^{152}Eu content was determined by γ spectroscopy measuring the 122 keV γ-rays by use of an intrinsic germanium detector.

The natural thorium used for the experiments was labelled with ^{228}Th, the α-rays of which were measured with a liquid scintillation counter (LSC). The advantage of the tracer is its high specific activity and its short-lived decay products; its disadvantage is the long period of time (approximately 4 weeks), necessary before taking samples for radiochemical measurements in order to guarantee radiochemical equilibrium due to ^{222}Rn.

The relevant uranium concentrations were measured by the use of time-resolved laser-induced fluorescence spectroscopy after preparation with an activated silica gel micro column and by inductively coupled plasma mass spectroscopy.

Higher Np concentrations were determined by potentiometry, and lower concentrations by α spectroscopy.

3. Results

3.1. Criteria for comparing adsorption

All the adsorption data obtained obey Freundlich's [1] isotherm (see Fig. 2 as an example)

$$a_{\mathrm{ads}} = K_{\mathrm{F}} C_{\mathrm{eq}}^{N} \tag{1}$$

Here a_{ads} stands for the concentration of the sorbate in moles of adsorbate per gram adsorbent and c for the concentration of the sorbate in the solution at equilibrium in moles per cubic decimetre. K_{F} and N are constants.

However, Freundlich's isotherm is only empirical, since its constants have no specific physical meaning
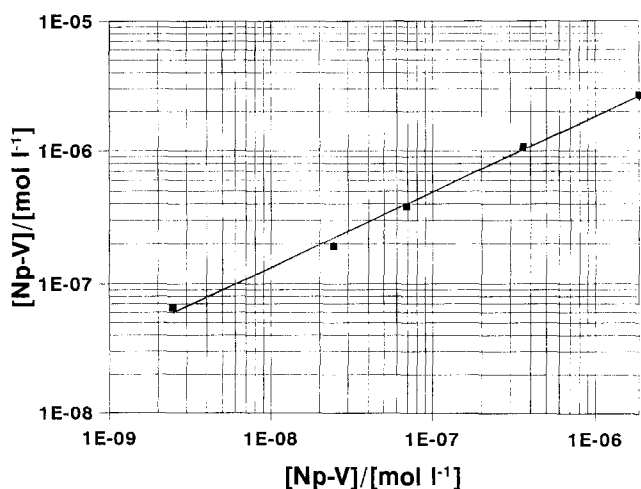

Fig. 2. Adsorption of neptunium(V) on hydrotalcite in saturated NaCl solution (Freundlich).

at all. So we wanted to apply Langmuir's isotherm to our data, because this isotherm can be derived not only kinetically but also thermodynamically [2].

Langmuir's isotherm will be fulfilled by our data if a_{ads} is listed vs. the concentration of the relevant ionic species present in the solution and not vs. the concentration of the ion constituents which equals the analytical concentration; Langmuir's isotherm is

$$a_{\mathrm{ads}} = \sum_{j=1}^{n} a_{\mathrm{max}j} \frac{b_j c_j}{1 + b_j c_j} \tag{2}$$

where b_j is proportional to $\bar{b}_j$, which is the equilibrium constant for the adsorption–desorption process. The constant $\bar{b}_j$ is related to the well-known free Gibbs adsorption energy $\Delta G_{\mathrm{ad}}^{\circ}$:

$$b_j \alpha \bar{b}_j = \exp\left(\frac{-\Delta G_{\mathrm{ad}}^{\circ}}{RT}\right) \tag{3}$$

Therefore it can be used for comparing adsorption capabilities.

3.2. Speciation

To obtain b_j the speciation of the substance under investigation must be known for the relevant media. Speciation can be studied by applying a set of equations (Table 1). The speciation of uranium in saturated NaCl solution and for neptunium in the same medium (Figs. 3 and 4) is given as an example (Table 2). At lower pH, $\mathrm{NpO_2}^+$ is the leading species; at higher pH $\mathrm{NpO_2(OH_2)}^-$ dominates in saturated NaCl solution at 25 °C.

$\mathrm{UO_2Cl_2}$ plays the leading part at low pH, substituted by $\mathrm{UO_2Cl(OH)_2}^-$ ions at higher pH values, the curve crossing at pH 4.3. At this pH, $\mathrm{UO_2Cl_2OH}^-$ reaches its maximum. When adding OH^- ions on the contrary which might happen if any cement is present, the ionic distribution differs greatly (see Fig. 3). At lower pH values, $\mathrm{UO_2Cl_2}$ is also the dominating species in the system. $\mathrm{UO_2Cl(OH)_2}^-$ plays a leading part but already competes with $(\mathrm{UO_2})_3(\mathrm{OH})_2^{2+}$. Even $(\mathrm{UO_2})_2(\mathrm{OH})_2^{2+}$ must be taken into account to a smaller extent.

TABLE 1. Equations for speciation

$$C_{\mathrm{M}j} = [M^n]_j + \sum_{j=1}^{s} p\beta_{\mathrm{pqz}} \frac{[M^n]_j^p [L^m]_j^z}{[H]_j^q}$$

$$C_{\mathrm{L}j} = [L^m]_j + \sum_{j=1}^{s} z\beta_{\mathrm{pqz}} \frac{[M^n]_j^p [L^m]_j^z}{[H]_j^q}$$

$$C_{\mathrm{H}j} = [H]_j + \sum_{j=1}^{s} q\beta_{\mathrm{pqz}} \frac{[M^n]_j^p [L^m]_j^z}{[H]_j^q} - \frac{K_w}{[H]_j^q}$$

$$K_{\mathrm{pqz}} = [M^n]_j^p [L^m]_j^z [OH]_j^q$$
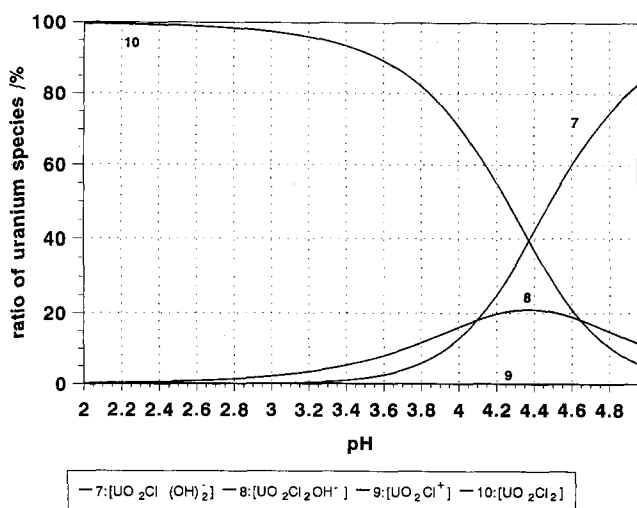
Fig. 3. Speciation of uranium(VI) in saturated NaCl solution (dilution).

$-7:[UO_2Cl\ (OH)_2^-]\quad-8:[UO_2Cl_2OH^-]\quad-9:[UO_2Cl^+]\quad-10:[UO_2Cl_2]$

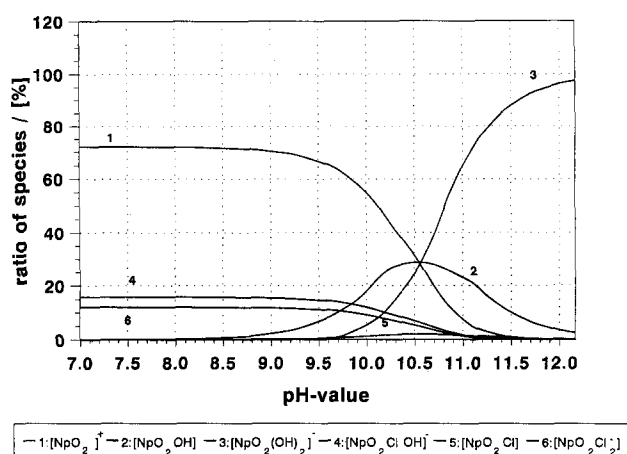$-1:[NpO_2^+]\quad-2:[NpO_2OH]\quad-3:[NpO_2(OH)_2^-]\quad-4:[NpO_2Cl\ OH]^-\quad-5:[NpO_2Cl]\quad-6:[NpO_2Cl_2^-]$

Fig. 4. Distribution of neptunium(V) in saturated NaCl solution.

TABLE 2. Ionic species and their relevant formation constants

Species	$\log \beta$
UO_2Cl_2	0.797
$UO_2Cl(OH)_2^-$	-8.01
$UO_2Cl_2(OH)^-$	-8.44
$(UO_2)_3(OH)_2^{2+}$	-6.15
$(UO_2)_2(OH)_2^{2+}$	-2.52
$NpO_2(OH)_2^-$	-21.60

3.3. The importance of the b_j values

As an example the b_j values for the neptunium and uranium systems are listed in Table 3. From the theoretical point of view the species with the highest b value should be preferentially adsorbed, but also the concentration of the specific species in solution must be taken into account, both factors influencing the competition for adsorption. If a high b_j value of a

TABLE 3. Parameter of adsorption of neptunium(V) in saturated NaCl solution at pH 10

Species	b_j (l mol^{-1})		
	Hydrotalcite	Ettringite	Tobermorite
NpO_2^+	1.0×10^6	2.6×10^6	2.5×10^7
NpO_2OH	2.6×10^8	3.2×10^8	(2.5×10^5)
$NpO_2(OH)_2^+$	(5.5×10^8)	1.1×10^9	(2.5×10^6)
NpO_2ClOH^-	8.8×10^6	1.2×10^7	(7.1×10)
NpO_2Cl	3.3	5.7×10	(2.9×10^{-1})
$NpO_2Cl_2^-$	1.1×10^6	2.6×10^7	2.9×10^9
a_{max} (mol g^{-1})	5.3×10^{-6}	1.4×10^{-6}	3.7×10^{-6}

species coincides with a high concentration ratio, this species will be adsorbed the most.

4. Discussion

A theoretical based handling of the data obtained from the adsorption experiments of the actinides Th, U, Np, Pu and Am on the cementitious materials mentioned above will be successful if speciation is taken into account, but also any change in the structure of the adsorbents must not be overlooked.

In the NaCl solution and in water at 55 °C, CSH gel started to change its structure after an exposure time of 4 weeks. In Q-brine at 55 °C, gypsum was formed. In general, ettringite is stable in the investigated systems except for NaCl solution at 55 °C after four weeks time. The same is true for hydrotalcite.

Tobermorite is rather stable in the selected systems except for Q-brine at 55 °C, in which gypsum is formed. The data obtained may also be considered under the aspect of cement, being especially suitable for the vitrification of real waste.

References

1 H. Freundlich, *Z. Phys. Chem.*, 57 (1906) 385.
2 K. Schwabe, *Physikalische Chemie*, 3. bearbeitete und erweiterte Aufl. 1. Bd., Akademie, Berlin, 1986.