Complexation of Cu^{2+} , Ni^{2+} and UO_2^{2+} by Radiolytic Degradation Products of Bitumen

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Abstract

The influence of the radiolytic degradation products of bitumen on the speciation of radionuclides was studied under conditions which reflect those in the near field of a cementitious rad waste repository. The potential complexation capacity of the degradation products was studied and complexation experiments with Cu^{2+} , Ni^{2+} and UO_2^{2+} were performed. In general 1:1 complexes with $\log K$ values of between 5.7 and 6.0 for Cu^{2+} , 4.2 for Ni^{2+} and 6.1 for UO_2^{2+} were produced at an ionic strength of $\mu = 0.1$. The values are in good agreement with those found in the literature for oxalate complexes and suggest that oxalate determines the speciation of Cu^{2+} , Ni^{2+} and UO_2^{2+} in the bitumen water at $\text{pH} < 7$. However, under the high pH conditions typical of the near field of a cementitious repository, competition with OH-ligands will be large and oxalate, therefore, will not play a significant role in the speciation of radionuclides. The main conclusion of the study is that the degradation products of bitumen will have no influence on radionuclide speciation in a cementitious near-field and, as such, should not be considered in appropriate safety assessment models.

Introduction

For more than twenty years bitumen has been used world wide to solidify intermediate (ILW) and low-level (LLW) radioactive wastes. Currently, the spent fuel from Swiss nuclear power facilities are reprocessed outside Switzerland and the conditioned wastes will be returned for final disposal. A portion of this material (ca. 3400 t) from LLW and ILW will be bituminous [1]. A small amount (concentrates and ion exchange resins) also comes directly from the nuclear power plant in Gösgen (Switzerland).

A possible disadvantage of the use of bitumen could be its organic composition. It can be degraded by radiolytic and microbial processes [5, 15] and may form potential ligands for complexation with radionuclides. These ligands may influence the eventual fate of radionuclides, released from the solidified waste, in the near and far fields of a repository. Although the gaseous degradation products of bitumen have been well studied [2, 3, 4, 5], no information is available on the water soluble degradation products and their complexation potentials. The present work describes the radiolytic degradation of bitumen under near field conditions by external irradiation.

Materials and methods

Two types of bitumen were studied: distilled bitumen Mexphalt 80/100 and blown bitumen Mexphalt R 90/30. An aliquot of the bitumen was placed in a stainless steel container and approximately 1 liter of millipore-Q-water, pH adjusted to 12.5 with 1 M NaOH, was added to it. The container was placed in a Co-60 cell and irradiated until a total absorbed dose of about 5 MGy was reached (dose rate: 11 kGy/h). The applied dose (5.2 MGy) was estimated from the activity and composition of a bituminized waste product (WA-2) [6] (Fig. 1). Non-irradiated blanks were set up simultaneously with these tests. After irradiation, the water was collected and filtered through a $0.45 \mu\text{m}$ nominal pore size membrane filter and the solutions were stored in glass vials at 4°C .

Fig. 1. Total absorbed dose for a bituminized waste product (Cogema, Marcoule) with a specific activity of 7.4 GBq/L (β, γ) and 74 MBq/L (α) as a function of time [6].

The total organic carbon (TOC) in the solutions was measured by a combined UV-promoted persulphate oxidation method (Dohrmann DC-180). The inorganic carbon (carbonate) was analyzed by acid-base titration. The qualitative analysis of the degradation products (organic acids) in the irradiated water was carried out by GC-MS after esterification of the acids. Some of the carboxylic acids have been determined quantitatively by ion chromatography (Dionex 2010i).

For a 1:1 complex, the reaction between a metal M and a ligand L can be written as:

The titration behaviour can be derived from the stability constant:

$$K_{ML} = \frac{[ML]}{[M] \cdot [L]} \quad (2)$$

and the mass balance

$$C_M = [M] + [ML] \quad (3)$$

$$C_L = [L] + [ML] \quad (4)$$

as

$$C_M = \frac{[M] \cdot (1 + K \cdot C_L) + K[M]^2}{1 + K[M]} \quad (5)$$

where: C_M = total concentration of metal M in solution

C_L = total concentration of ligand L in solution

$[M]$ = concentration of uncomplexed metal in solution

$[L]$ = concentration of free ligand L in solution

$[ML]$ = concentration of complexed metal in solution

K_{ML} = stability constant of the ML complex.

25 cm³ of the bitumen water were placed in a 50 cm³ titration vessel. The pH of the solution was adjusted to 3.5 with concentrated HClO₄, after which the system was purged with prewetted nitrogen to remove CO₂. Finally, the pH was adjusted to the desired value with 1 M NaOH and the ionic strength was adjusted to $\mu = 0.1$ with 1 M NaClO₄. The solution was titrated with a 0.005 M Cu(NO₃)₂ solution. After each addition of Cu, the pH of the system was measured and kept constant automatically at the desired pH with 0.01 M NaOH and 0.01 M HClO₄. The uncomplexed Cu²⁺ in solution was measured by a Cu-ion sensitive electrode (Cristal membrane electrode, Metrohm) in combination with a Ag/AgCl reference electrode (Metrohm). All manipulations were performed at 25°C under a nitrogen atmosphere and were controlled by a titroprocessor (Titrprocessor 670, Metrohm).

Additionally, titrations with pure oxalate solutions (Na-oxalate, 5 ppm) were performed under the same experimental conditions.

Since no ion-sensitive electrodes are available for Ni²⁺ and UO₂²⁺, other methods had to be used for studying the complexation of these metals with organic ligands. Ion exchange is a method which has been applied successfully to the study of complex formation in solution. The technique was developed by Schubert *et al.* [7, 8, 9].

The working equation of the Schubert method can be expressed as:

$$\text{Log} \left(\frac{K_d^0}{K_d} - 1 \right) = \text{Log} K_{ML} + n \cdot \text{Log}[L] - \text{Log} A \quad (6)$$

where: K_d^0 = partition coefficient of M in the absence of ligand L

K_d = partition coefficient of M in the presence of ligand L

K_{ML} = stability constant of complex ML_n

$[L]$ = free ligand concentration

$A = 1 + K_{MB} \cdot [B]$
correction term when a buffer, B, with complexing properties has been used

n = number of ligands per metal atom.

Measuring the solid/liquid partition coefficient of the metal M in the presence (K_d) and absence (K_d^0) of different concentrations of the ligand L, and then

plotting $\text{Log} \left(\frac{K_d^0}{K_d} - 1 \right)$ against $\text{Log}(L)$ yields a straight

line. The slope of the line n represents the stoichiometry of the complex while $\text{Log} K_{ML}$ can be derived from the intercept with the y-axis after correction for $\text{Log} A$. The method only works when the complex formed is neutral or negatively charged and does not adsorb on the ion exchange resin.

10 g of a wet Dowex 50W X-4 cation exchange resin in the H⁺-form were converted to the Na⁺-form by washing the resin twice with 250 cm³ 0.1 M NaOH and equilibrating 3 times with 0.1 M NaClO₄. After equilibration, the resin was air dried and stored in a glass vial. About 100 mg of the Na-resin were transferred to 50 cm³ centrifuge tubes. 25 cm³ of a solution containing 0.12 M NaClO₄, 0.12 M NaOAc and different oxalate amounts were added. The volume was then adjusted to 30 cm³ with 5 cm³ of a $6 \cdot 10^{-6}$ M Ni²⁺ solution, spiked with ⁶³Ni, or a $8.4 \cdot 10^{-7}$ M UO₂²⁺ (²³³U) solution. The final compositions of the solutions were: 0.1 M NaClO₄, 0.01 M NaOAc and, in the case of Ni²⁺, 10^{-6} M Ni and 0, 2, 4, 8, 16 ppm oxalate. In the case of U, the concentration of UO₂²⁺ was $1.4 \cdot 10^{-7}$ M and oxalate varied between 0 and 2 ppm. The solutions were buffered at pH=5 by NaOAc to prevent hydrolysis as side reaction. The resin/solution mixtures were placed in an end-over-end shaker and equilibrated for 20 hours at room temperature. After equilibration, ⁶³Ni and ²³³U in solu-

tion were measured by liquid scintillation counting (Packard, Tricarb 2250 CA) using Instagel (Packard) as a scintillation cocktail. The partition coefficients of Ni and UO_2 were calculated from the difference in radioactivity in solution before and after equilibration.

Different amounts of bitumen water (10, 15 or 20 cm^3 in the case of UO_2^{2+} ; 35 or 70 cm^3 in the case of Ni^{2+}) were adjusted to $\text{pH}=3$ with concentrated HClO_4 to remove any carbonates. The pH was then adjusted to 5 and a NaOAc buffer and NaClO_4 added. The volume was finally made up to 100 cm^3 . The composition of these solutions was 0.012 M NaOAc and 0.12 M NaClO_4 . The oxalate concentration could be calculated from the dilution. With these mixtures, complexation experiments with Ni^{2+} and UO_2^{2+} were performed as described earlier for the pure oxalate solutions.

Results and discussion

Organic matrices are generally very susceptible to radiation and effects are strongly dose rate dependent. Short-term irradiations at high dose rates are often of

limited value for the evaluation of long-term irradiation effects. In reality, the irradiation will mainly come from internal sources and the bitumen matrix will be exposed to much lower dose rates than in the present work. Thus, the interpretation of the results obtained from tests on samples irradiated with high external dose rates must be treated with caution.

Most products found in the solution are fatty acids (Table 1). This is not surprising because fatty acids are abundant in bitumen [16]. Their concentration in solution, however, is very low. These fatty acids, in fact, cannot be considered as bitumen degradation products. Beside fatty acids, carbonate and four low molecular weight compounds are present: oxalic acid, phthalic acid, acetylacetic acid and the dibutylester of phthalic acid. The dibutylester of phthalic acid is often used as a softening agent in plastic and can be considered as a contaminant.

Oxalate is probably a reaction product of two $\cdot\text{COO}^-$ radicals formed by decarboxylation of fatty acids [17]. The concentration of oxalate in solution depends on the absorbed dose. Fig. 2 displays the relationship between the amount of oxalate produced per gram of bitumen and the total absorbed dose. The higher the dose, the higher the amount of oxalate produced. The saturation level will be reached at a dose larger than 6.0 MGy. The concentration of oxalate in the different bitumen waters is given in Table 2, together with the TOC and carbonate concentration. Again the dose dependence of the oxalate production can be observed. At a total applied dose of 0 MGy, no

Table 1. Organic compounds in water after external irradiation of bitumen-water mixtures (B1)

Name	Formula
Caprylic acid	$\text{CH}_3-(\text{CH}_2)_6-\text{COOH}$
Myristic acid	$\text{CH}_3-(\text{CH}_2)_{12}-\text{COOH}$
Palmitic acid	$\text{CH}_3-(\text{CH}_2)_{14}-\text{COOH}$
Stearic acid	$\text{CH}_3-(\text{CH}_2)_{16}-\text{COOH}$
Dimethylcaproic acid	$\text{CH}_3-(\text{CH}_2)_3-\text{C}(\text{CH}_3)_2-\text{COOH}$
Oxalic acid	COOH COOH
Acetylacetic acid	$\text{CH}_3-\text{C}(\text{O})=\text{CH}-\text{COOH}$
Phthalic acid
Dibutylester of Phthalic acid

Fig. 2. Amount of oxalate produced per gram of bitumen as a function of the absorbed dose. (Dose rate 11 kGy/h.)

Table 2. Concentration of oxalate, TOC and inorganic carbon in bitumen water with and without external irradiation (n.d. = no data)

Bitumen water	Oxalate mg/l	TOC mg/l	$\text{CO}_3^{2-} + \text{HCO}_3^-$ meq/l	pH_{eq}	Dose rate kGy/h	Dose MGy
B1 ^a	5.4	6.0	10.6	9.1	2.4	5.1
B2 ^b	3.3	4.5	n.d.	12.5	2.4	3.5
B3 ^a	7.6	10.1	20.6	10.7	11	6.0
U1 ^a	<0.1	0.9	1.7	12.7	0	0
U4 ^b	<0.1	1.6	2.0	12.7	0	0
B4 ^a	5.2	6.6	14	11.8	11	5.3

^a = Mexphalt 80/100.

^b = Mexphalt R 90/30.

Fig. 3. Titration of bitumen water (B2) with Cu^{2+} at $\text{pH}=6.00$, $\mu=0.1$ and $T=25^\circ\text{C}$.

Fig. 4. Titration of a pure oxalate solution (5 ppm) with Cu^{2+} at $\text{pH}=6.0$, $\mu=0.1$ and $T=25^\circ\text{C}$.

Table 3. Stability constants of complexes between Cu^{2+} and some mono- and dicarboxylic acids

Ligand	$\log K_1$ [18, 19] ($\mu=0.1$, $T=25^\circ\text{C}$)	$\log K_1$ [12] ($\mu=0.1$, $T=25^\circ\text{C}$)	$\log K_1$ [11] ($\mu=0.1$, $T=25^\circ\text{C}$)
Formate (m)	2.80	2.04 (30°C)	—
Acetate (m)	1.89; 1.80	2.05 (30°C); 2.38 (20°C)	1.83
Propionate (m)	—	2.06 (30°C)	—
Butyrate (m)	—	1.54 ($\mu=2.0$)	—
Caprylate (m)	<2(a)	—	—
Myristate (m)	<2(a)	—	—
Palmitate (m)	<2(a)	—	—
Stearate (m)	<2(a)	—	—
Acetylacetate (m)	<2(a)	—	—
Phthalate (d)	—	3.14	3.15
Oxalate (d)	6.30; 4.84	4.49 (20°C)	4.84
Malonate (d)	5.81; 5.0	5.04; 5.02	5.05
Succinate (d)	2.60	—	2.60
Glutarate (d)	2.40	—	—
Adipate (d)	2.30	—	—

(a) estimated values.

(m) monocarboxylic acids.

(d) dicarboxylic acids.

oxalate could be detected. As a result, oxalate can be considered as a real degradation product of bitumen. A large amount of carbonate is also present in solution, presumably because irradiation of bitumen produces CO_2 . The CO_2 so formed is scrubbed by the alkaline solutions and reacts to CO_3^{2-} . These reactions also cause a pH drop of the bitumen water (pH_{eq}). With ion chromatography, two additional low molecular weight products, acetate and formate, have been detected. These products, however, are irrelevant for the complexation studies because they form very weak complexes with radionuclides.

In order to provide an insight into the complexation behaviour of the degradation products, tests with Cu^{2+} have been used because the complexation capacity can easily be estimated by titration where the free, uncomplexed Cu^{2+} is monitored by a Cu-ion sensitive electrode. Fig. 3 displays the titration curve of the irradiated bitumen water (B2) and Fig. 4 a pure oxalate solution (5 ppm) with Cu^{2+} . The free Cu^{2+}

concentration (pCu) is given as a function of the total Cu concentration (pCu_{tot}). A straight line represents the case where no complexation occurs. The experimental data can be well described by equation (5) with $\text{Log } K = 5.85 - 6.00$ and $\text{Log } C_L = -4.45$ for the B2 solution (Mexphalt R 90/30) and $\text{Log } K = 5.65$ and $\text{Log } C_L = -4.10$ for the B3 solution (Mexphalt 80/100). This means that only one ligand in solution is important for the complexation of Cu^{2+} . The other ligands either form much weaker complexes with Cu^{2+} or their concentration is very low so that their contribution can be neglected. From the composition of the solution (Table 1) it is clear that only oxalate can contribute to the complexation of Cu^{2+} because it is the only compound that forms relatively stable complexes with Cu^{2+} and other elements (Table 3).

A direct comparison of the experimentally determined stability constant with the literature data for oxalate was not justifiable because of the large spread observed in the reported values [11, 12, 18, 19]. There-

Table 4. Overview of the $\log K$ and $\log L_T$ values derived from titrations of bitumen water (B2 and B3) and oxalate with Cu^{2+} at different pH values and $\mu=0.1$

	Bitumen water B2 Mexphalt 90/30		Bitumen water B3 Mexphalt 80/100		Oxalate 5 ppm	
	$\log K$	$\log L_T$	$\log K$	$\log L_T$	$\log K$	$\log L_T$
pH=6.0	5.85	-4.45	5.60	-4.10	6.00	-4.33
	5.85	-4.45	5.60	-4.10	6.00	-4.33
					5.65	-4.38
pH=5.0	5.60	-4.46	5.65	-4.10	5.70	-4.33
	6.00	-4.45	5.70	-4.10	5.75	-4.33
			5.70	-4.10		
	5.83 ± 0.17		5.63 ± 0.08		5.82 ± 0.17	

Table 5. Concentration of oxalate in bitumen water B2 and B3 determined by titration with Cu^{2+} and ion chromatography (IC)

	Bitumen water B2 Mexphalt 90/30	Bitumen water B3 Mexphalt 80/100	Oxalate 5 ppm
Titration	3.1 ppm	7.0 ppm	4.1 ppm
IC	3.3 ppm	7.6 ppm	5.0 ppm

Fig. 5. Titration of non-irradiated bitumen water (U4) with Cu^{2+} at pH=5, $\mu=0.1$ and $T=25^\circ\text{C}$.

fore, titrations with pure oxalate solutions were performed. The stability constant determined for the pure oxalate solutions under the same conditions ($\log K = 5.82 \pm 0.17$) is similar to that observed for the bitumen water B2 and B3 (Table 4). This confirms that Cu^{2+} is mainly complexed by oxalate in the bitumen water. The oxalate concentrations obtained by the titration with Cu^{2+} ($\log C_L$) are in good agreement with the values found by ion chromatography (Table 5).

Fig. 5 displays the titration of the non-irradiated bitumen water (U1) (contact time: 3 months) with Cu^{2+} . The titration yields a straight line indicating that no complexation of Cu^{2+} and degradation products can be observed. This is consistent with the analytical results in Table 2 (no oxalate present in solution in the non-irradiated solutions).

Fig. 6. Complexation of Ni^{2+} with oxalate and bitumen degradation products at pH=5.0 and $\mu=0.11$ (Schubert method). **Fig. 7.** Complexation of UO_2^{2+} with oxalate and bitumen degradation products at pH=5.0 and $\mu=0.11$ (Schubert method).

Fig. 6 and Fig. 7 show the results of the complexation study of Ni^{2+} and UO_2^{2+} with pure oxalate and with bitumen degradation products. The plot of $\log\left(\frac{K_d^0}{K_d} - 1\right)$ versus $\log[L]$ yields a straight line. The slope of the line (calculated by linear regression from the data for the pure oxalate solutions only) equals

Table 6. Comparison of experimental stability constants ($\log K$) of complexes of oxalate, with Ni^{2+} and UO_2^{2+} at pH=5 and $\mu=0.11$, with literature values

	Ni^{2+}	UO_2^{2+}
Oxalate	4.27 ± 0.05	6.10 ± 0.11
Bitumen water Mexphalt 80/100	4.38 ± 0.02	6.09 ± 0.11
Bitumen water Mexphalt 90/30	4.17 ± 0.02	6.13 ± 0.11
Literature	4.32 [11]* 5.3 [18, 19] 3.83 [12]	5.96 [11]* 6.36 [12]*

* Corrected to $\mu=0.1$ by the Davies equation [14].

one for both Ni^{2+} and UO_2^{2+} , indicating that a 1:1 complex has been formed:

For the bitumen degradation products it was assumed a priori that oxalate is the most important ligand present in solution. Fig. 6 and Fig. 7 show that the experimental points for the bitumen degradation products are close to the straight line, indicating that Ni^{2+} - and UO_2^{2+} -oxalate complexes have been formed. The stability constants of the complexes have been calculated by applying equation (6) to the individual experimental data, with $n=1$ and $\text{Log } A=0.03$ for Ni^{2+} and 0.55 for UO_2^{2+} . This procedure gives a more accurate value for $\text{Log } K$ than the extrapolation method (intercept with the y-axis) because the latter involves extrapolation to L concentrations which are 4 to 5 orders of magnitude higher than the L concentration range covered by the experimental measurements [10]. The values of the stability constants ($\text{Log } K$) have been summarized in Table 6, together with some data found in the literature. It is evident from Figs. 6 and 7 and the results in Table 6 that the data for the bitumen degradation products are completely consistent with those of pure oxalate. It can therefore be concluded that oxalate is the most important ligand present in the bitumen water. The non-irradiated samples, U1 and U4, display some degree of complexation of Ni^{2+} and UO_2^{2+} . The complexing capacity of these solutions was equivalent to a solution containing 0.1–0.3 ppm oxalate.

To get an idea of the influence of the bitumen degradation products on the behaviour of radionuclides released to the near field, a speciation calculation with the PHREEQE geochemical code has been performed [13]. A significant contribution of the degradation products to the speciation of radionuclides indicates that an effect of these compounds on the fate of radionuclides might be expected. A modified thermodynamic database has been used [14]. The data for the metal oxalate interactions were selected from the PSI-MINEQL database. The concentrations of Ni and U were set arbitrarily at 10^{-10} M

Table 7. Composition of the SPP [20] water used for the PHREEQE calculations

Parameter	Cement SPP
Temperature [$^{\circ}\text{C}$]	25
pH	13.2
Ionic strength [M]	0.23
E_h (mV)	+139
Na^+ [M]	6.52×10^{-2}
K^+ [M]	1.61×10^{-1}
Mg^{2+} [M]	1.00×10^{-5}
Ca^{2+} [M]	2.31×10^{-3}
Fe_{tot} [M]	1.00×10^{-5}
Al [M]	2.00×10^{-4}
C_{tot} [M]	4.72×10^{-5}
Alkalinity [N]	2.31×10^{-1}
SiO_2 [M]	2.00×10^{-4}
Saturated Solids	Calcite

Table 8. Speciation of Ni and U in a cement pore water in equilibrium with calcite at three different levels of oxalate ($\text{Ni}_t: 10^{-10}$ M, $\text{U}_t: 10^{-10}$ M)

Oxalate	10^{-9} M	10^{-6} M	10^{-3} M
Species	%	%	%
$\text{Ni}(\text{OH})_3^-$	72.0	72.1	72.1
$\text{Ni}(\text{OH})_2^0$	27.9	27.9	27.9
$\text{UO}_2(\text{OH})_2^0$	100	100	100
Ox^{2-}	70.7	70.7	73.2
CaOx	29.3	29.3	26.8

and the oxalate concentration was varied between 10^{-9} M and 10^{-3} M. A Swedish standard Portland cement pore water (SPP) was chosen as reference (Table 7) [20]. Such a water would be representative of that in the near field of a low and intermediate level waste repository for a period of a hundred of years after repository closure [14]. The results of the speciation calculation are summarized in Table 8 and show that the presence of CO_3^{2-} and oxalate in such a high alkaline water has no influence on the speciation of Ni and U. The speciation of both elements in this environment is completely determined by the OH^- ligands.

Conclusions

The bituminization of low- and intermediate-level radioactive wastes operates satisfactorily world-wide. However, the use of bitumen is still debatable because of the organic nature of the material, which could supply potential complexing agents to the near field of a repository. The main objective of the present work was to study the radiolytic degradation of bitumen under near field conditions of a cementitious repository and to collect information about the water soluble

degradation products and their complexation potentials.

Oxalate and CO_3^{2-} are the main radiolytic degradation products of bitumen and are the only compounds that form relatively stable complexes with heavy metals and radionuclides below $\text{pH}=7$. However, calculations with the PHREEQE geochemical code show that, under the high pH conditions in a cement pore water (representing near field conditions of a LLW/ILW repository), the degradation products do not influence the speciation of Ni and U (and other radionuclides) so that they need not be considered in the appropriate safety assessment models.

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