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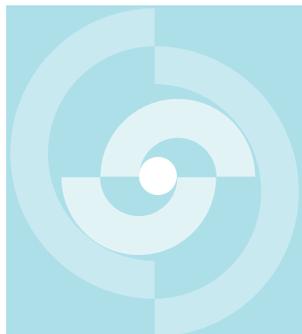
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TECHNICAL REPORT 90-18

COMPLEXATION OF Cu^{2+} , Ni^{2+} AND UO_2^{2+} BY RADIOLYTIC DEGRADATION PRODUCTS OF BITUMEN

L. R. VAN LOON
Z. KOPAJTIC

MAY 1990

PSI, Würenlingen and Villigen

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Preface

In the framework of its Waste Management Programme the Paul Scherrer Institute is performing work to increase the understanding of the geochemistry of nuclear waste relevant nuclides and the behaviour of solidification matrices. These investigations are performed in close cooperation with, and with the financial support of NAGRA. The present report is issued simultaneously as PSI report and a NAGRA NTB.

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Abstract

The radiolytic degradation of bitumen was studied under conditions which reflect those which will exist in the near field of a cementitious radioactive 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 Cu^{2+} , Ni^{2+} and UO_2^{2+} , 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 0.1 M. The composition of the bitumen water was analysed by GC-MS and IC. The major proportion of the bitumen degradation products in solution were monocarboxylic acids (acetic acid, formic acid, myristic acid, stearic acid ...), dicarboxylic acids (oxalic acid, phthalic acid) and carbonates.

The experimentally derived log K data are in good agreement with the literature and suggest that oxalate determines the speciation of Cu^{2+} , Ni^{2+} and UO_2^{2+} in the bitumen water below 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 radiolytic degradation products of bitumen will have no influence on radionuclide speciation in a cementitious near field and, as such, need not to be considered in the appropriate safety assessment models.

Résumé

La dégradation radiolytique du bitume a été étudiée dans les conditions analogues à celle qui existeraient dans le champ proche d'un dépôt de déchets radioactifs cimentés. La capacité potentielle de complexation des produits de dégradation a été étudiée et des expériences de complexation de Cu^{2+} , Ni^{2+} et UO_2^{2+} ont été réalisées. En général des complexes 1:1 avec le Cu^{2+} , le Ni^{2+} et l' UO_2^{2+} ont été produits pour une force ionique de 0,1 M et avec les valeurs de log K allant de 5,7 à 6,0 pour le Cu^{2+} , de 4,2 pour le Ni^{2+} et de 6,1 pour l' UO_2^{2+} . La composition de l'eau bitumeuse a été analysée par GC-MS et par IC. Les principaux produits de dégradation du bitume en solution sont des acides monocarboxyliques (acides acétique, formique, myristique, stéarique ...) des acides dicarboxyliques (oxalique, phthalique) et des carbonates. La valeur du log K mesurée pour $\text{pH} < 7$ de l'eau bitumeuse est comparable à celle des oxalates pour le Cu^{2+} , le Ni^{2+} et l' UO_2^{2+} . Cependant, pour les conditions de pH plus élevé, typiques pour un champ proche d'un dépôt cimenté, la compétition avec OH-ligands devient plus importante et l'oxalate cesse de jouer un rôle important pour la spéciation des radionuclides. La conclusion principale de cette étude est que les produits de dégradation du bitume n'auront pas d'influence sur la spéciation des radionuclides dans le champ proche du dépôt cimenté et que ces produits de dégradation radiolytique ne devraient pas être pris en considération dans les modèles d'analyse de sécurité.

Zusammenfassung

Das Komplexbildungsverhalten der durch die Radiolyse entstandenen Bitumen-Degradationsprodukte wurde unter endlagerrelevanten Bedingungen untersucht.

Die potentielle Komplexbildungskapazität der Degradationsprodukte wurde anhand von Komplexierungsexperimenten mit Cu^{2+} , Ni^{2+} und UO_2^{2+} studiert. In Lösungen mit einer Ionenstärke $I=0,1$ M wurden generell nur 1:1 Komplexe mit log K Werten von 5,7 - 6,0 für Cu^{2+} , 4,2 für Ni^{2+} und 6,1 für UO_2^{2+} gebildet. Die Zusammensetzung der Bitumenwässer wurde mittels GC-MS und IC ermittelt. Als Hauptkomponenten der Bitumenen-Degradation wurden Monocarbonsäuren (Ameisensäure, Essigsäure, Myristinsäure, Stearinsäure ...), Dicarbon-Säuren (Oxalsäure, Phthalsäure) und die Carbonate gefunden.

Die experimentell gefundenen log K Werte stimmen gut mit den Literaturwerten überein. Im Bereich unterhalb $\text{pH}=7$ dominieren die Oxalat-Komplexe mit Cu^{2+} , Ni^{2+} und UO_2^{2+} während bei höheren pH-Werten (typisch für Nahfeld-Umgebung) die Konkurrenzierung durch OH-Ionen immer stärker wird und die Rolle des Oxalats als Ligand an Bedeutung verliert. Das wichtigste Resultat dieser Untersuchungen ist deshalb die Feststellung, dass die radiolytische Bitumen-Degradationsprodukte im Nahfeld als potentielle Komplexbildner keine Bedeutung haben und somit für die Sicherheitsanalyse unwichtig sind.

1 Introduction

For more than twenty years bitumen has been used worldwide to solidify intermediate (ILW) and low level (LLW) radioactive waste. In Switzerland, about 5 wt % of the radwaste inventory is solidified in bitumen [18]. The largest proportion of waste is produced by the Cogema reprocessing plant in Marcoule (France) and is embedded in a Mexphalt 80/100 bitumen. A small amount (concentrates) also comes from the Gösigen nuclear power plant (Switzerland) and is solidified in Ebano B-15 bitumen.

A possible disadvantage of the use of bitumen could be its organic composition. It can be degraded by radiolytic [10], and microbial processes [31] and may form potential ligands for radionuclides. These ligands may influence the eventual fate of radionuclides, released from the solidified waste, in the near and the far fields of a repository. Although the gaseous degradation products of bitumen have been well studied [7], [8], [10], [13], [15], 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 (in presence of high alkalinity water) by external irradiation. The water soluble degradation products have been identified and partly quantified. In order to provide an insight into the complexation behaviour of the degradation products, tests have been made with Cu^{2+} because the complexation capacity can be easily estimated by titration as the free, uncomplexed Cu^{2+} is monitored by a Cu-ion sensitive electrode. Furthermore, Cu^{2+} builds relative stable complexes with many organic and inorganic ligands. Consequently, tests with Cu^{2+} give a good indication of the potential complexation capacity of the degradation products for radionuclides. The results derived from this series of experiments showed the presence of ligands among the degradation products and so additional studies, with safety relevant nuclides such as Ni^{2+} and UO_2^{2+} , have been performed to verify the Cu-results.

2 Materials and methods

2.1 Bitumen degradation

Two types of bitumen were studied. Mexphalt 80/100 and Mexphalt 90/30, because the 80/100 type straight run distillation bitumen is nowadays used instead of the initial R 90/40 blown bitumen for embedding liquid waste from the UP3 plant at La Hague (France). The former is a freshly distilled bitumen, whereas the latter type is oxidized and is thus very similar to the Mexphalt R 90/40 bitumen.

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. The dose to apply was estimated from the activity and composition of a bituminized waste product (WA-2) [23].

The cumulative dose absorbed at infinite time by a bituminized waste product (BWP) containing a fission product mixture from fuel reprocessing of a specific activity of 7.4 GBq/L (β, γ) is 0.2 MGy (which is accumulated almost completely after the first 200 years).

When the α -radionuclides with a long half life are included in the calculation (74 MBq/L) the total dose is estimated to be 5.2 MGy (Fig. 2.1) [15]. An important α -radiolysis is thus exclusively simulated by γ - irradiation. From the literature it is known that the relative amounts and not the nature of the radiolytic products are mainly depended on the type of radiation [8].

In practice, the matrix will be subjected to low dose rates but, to obtain data in a reasonable timescale, it has been necessary to accelerate the damage process by increasing the dose rate. In many organic materials, however, radiation effects are strongly dose rate dependent so that care must be taken when interpreting accelerated tests [7]. The irradiation experiments described in this work were performed at dose rates of 2.4 kGy/h and 11 kGy/h.

After irradiation, the water was collected and filtered through a 0.45 μm nominal pore size membrane filter (millipore type HA; 0.45 μm) and the solutions were stored in glass vials at 4°C.

Non-irradiated blanks were simultaneously prepared for comparison.

Table 2.1 summarizes the experimental conditions for the irradiated and non-irradiated samples.

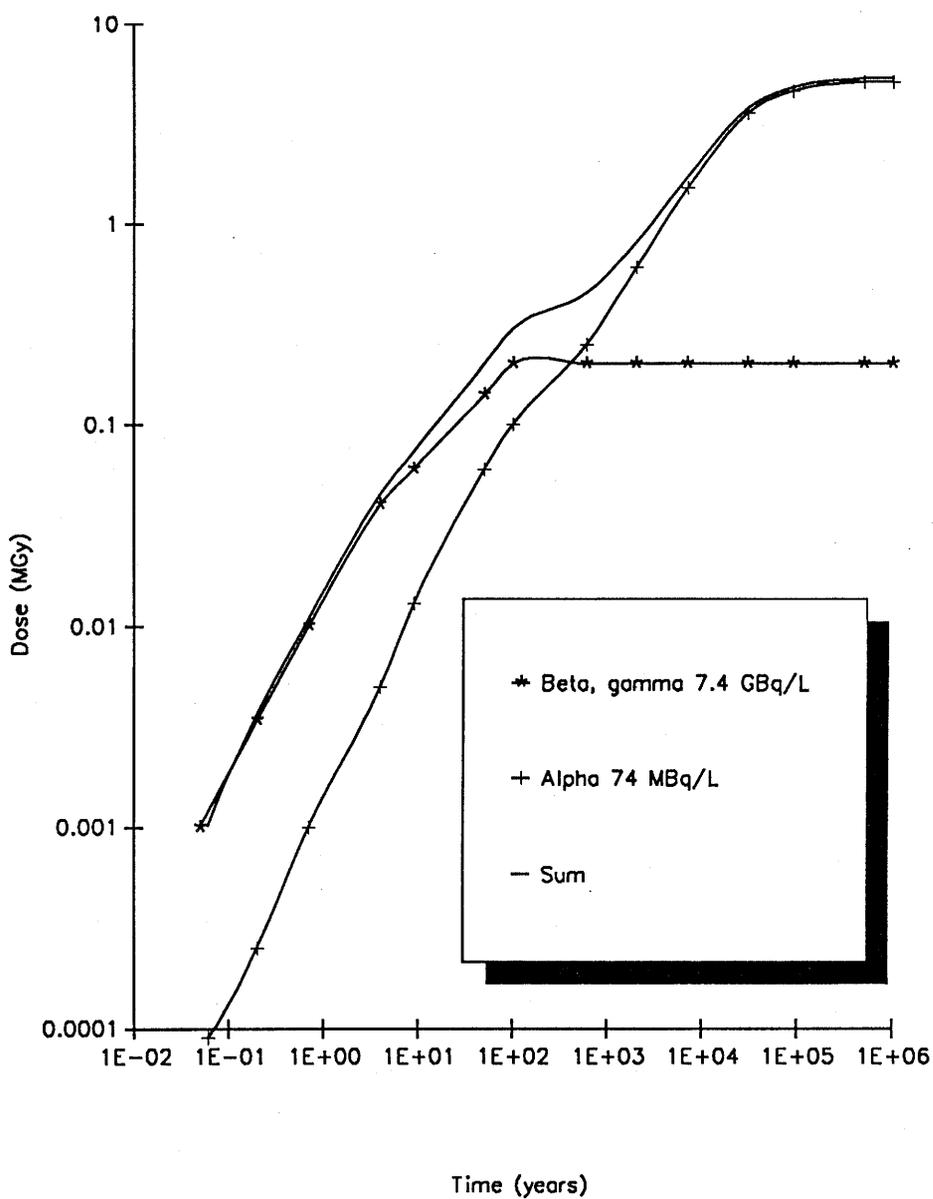


Fig. 2.1 Total absorbed dose for a BWP (Cogema, Marcoule) with a specific activity of 7.4 GBq/L (β, γ) and 74 MBq/L (α) as a function of time [15].

Bitumen type	Code	Weight bitumen (g)	Weight water (g)	pH	irradiation time days	Dose absorbed (MGy)
Mexphalt 80/100	B1	260	1040	12.5	90	* 5.10
Mexphalt 80/100	U1	361	1041	12.5	0	0
Mexphalt 90/30	B2	262	1049	12.5	60	* 3.78
Mexphalt 90/30	U4	251	1041	12.5	0	0
Mexphalt 80/100	B3	270	1075	12.5	21	6.00
Mexphalt 80/100	B4	277	1014	12.5	18.5	5.28

Table 2.1 Experimental conditions for the bitumen/water irradiations (Air atmosphere; T=45 °C; Dose rate 11 kGy/h and * 2.4 kGy/h). The bitumen surface/water ratio amounts: 0.126 cm⁻¹.

2.2 Qualitative and quantitative analysis of the degradation products

The qualitative analysis of the degradation products in irradiated and non-irradiated water samples were carried out by EMPA (Swiss Federal Laboratories for Materials Testing and Research) in Dübendorf.

The organic acids were converted to the more volatile methylesters. 200 ml of solution were adjusted to pH=12 with 1 M NaOH (to prevent loss due to volatilization) and taken to dryness in a rota-vapor before being taken up again in water free CH₃OH. The pH of the suspension was adjusted to 1 with freshly prepared methanolic HCl. The mixture was boiled under reflux for 1 hour (Fisher esterification). Afterwards, the mixture was cooled with ice and neutralized with NaHCO₃. The solution was analyzed by gas chromatography-mass spectrometry (GC-MS) [3].

Some of the carboxylic acids have been determined quantitatively by ion-chromatography (Dionex 2010 i).

2.3 Organic and inorganic carbon measurements

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 titration procedure could be applied because the CO_3^{2-} - concentration was two orders of magnitude higher than the organic acids contents.

2.4 Complexation of Cu^{2+} by bitumen degradation products

2.4.1 Measurement of Cu^{2+} by an ion sensitive electrode

The uncomplexed Cu^{2+} in solution was measured by a Cu-ion sensitive electrode (Cristal membrane electrode, Metrohm) in combination with a Ag/AgCl reference electrode (Metrohm).

The relationship between the measured potential, E , and the concentration of the uncomplexed, hydrated Cu^{2+} is given by the Nernst equation [6]:

$$E = E'_o + s \cdot \log [\text{Cu}] \quad (1)$$

The values of E'_o and s can be calculated from a calibration curve. From equation (1), the concentration of the uncomplexed Cu^{2+} ion can be derived. The amount of complexed Cu can be calculated by:

$$[\text{CuL}] = [\text{Cu}]_{\text{tot}} - [\text{Cu}^{2+}] \quad (2)$$

where $[\text{CuL}]$ = concentration of complexed Cu
 $[\text{Cu}]_{\text{tot}}$ = total concentration of Cu
 $[\text{Cu}^{2+}]$ = concentration of the free Cu^{2+}

2.4.2 Titration procedure

25 ml of the bitumen water (described in 2.1) were placed in a 50 ml titration vessel. The pH of the solution was adjusted to 3.5 with concentrated HClO_4 , after which the system was purged with prewetted nitrogen for 5 minutes to remove CO_2 . Afterwards the pH was finally adjusted to the desired value with 1 M NaOH and the ionic strength was adjusted to 0.1 M with 1 M NaClO_4 .

The solution was titrated with a 0.005 M $\text{Cu}(\text{NO}_3)_2$ solution. After each addition of Cu the pH of the system was measured and kept constant automatically with 0.01 M NaOH and 0.01 M HClO_4 at the desired pH.

All manipulations were performed at 25 °C under a nitrogen atmosphere and were controlled by a titroprocessor (Titrprocessor 670, Metrohm).

The Cu-electrode was calibrated for each curve from the results of a titration in the presence of the complexing agent in the range where no complexation occurs. ($10^{-3} \text{ M} > [\text{Cu}] > 10^{-4} \text{ M}$). In the region of high Cu-concentration, the proportion of complexed Cu was very small and the total Cu-concentration approximated the free Cu^{2+} concentration [6].

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

2.4.3 Complexation reactions

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



The stability constant of the complex ML is defined as:

$$K = \frac{[ML]}{[M][L]} \quad (4)$$

where: $[ML]$ = concentration of the complexed metal
 $[M]$ = concentration of the free metal
 $[L]$ = concentration of the free ligand

With the mass balance equations:

$$M_T = [M] + [ML] \quad (5)$$

$$L_T = [L] + [ML] \quad (6)$$

equation (4) can be rewritten as:

$$M_T = \frac{[M](1 + KL_T) + K[M]^2}{1 + K[M]} \quad (7)$$

where: M_T = total concentration of metal M in solution
 L_T = total concentration of ligand L in solution.

Fig. 2.2 is a graphical representation of the titration of a ligand L with a metal M. The curves have been calculated by equation (7).

When more ligands which contribute significantly to the complexation of the metal are present in solution, more complicated titration curves can be obtained (see Grauer [11] and Buffle and Altmann. [5] for details).

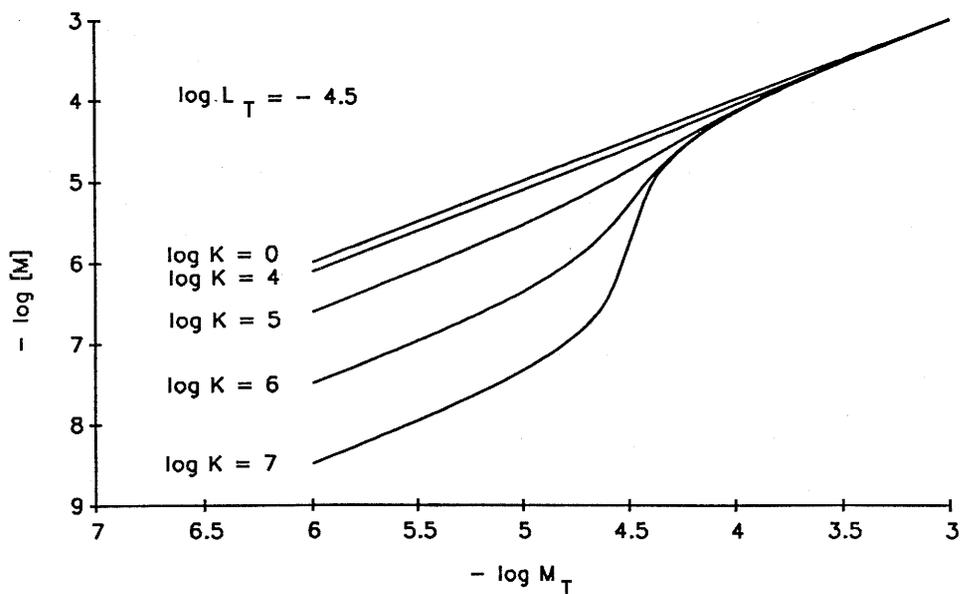


Fig. 2.2 Titration curve for a ligand L ($\log L_T = -4.5$) with different metals M forming 1:1 complexes with different stability constants.

2.5 Complexation of Ni^{2+} and UO_2^{2+} by bitumen degradation products

2.5.1 Theory of the Schubert method

No ion sensitive electrodes are available for Ni^{2+} or UO_2^{2+} and so other methods have to be used for studying the complex formation between these metals and 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 and co-workers [25], [26], [27].

The method ordinarily employed involves the use of trace-metal concentrations (where radioactive tracers are convenient), and a constant ionic medium. The advantage of this is the constancy of bulk cation concentration in both solution and resin phase and the consequent constancy of activity coefficients in both phases. Concentration may be used directly in the mass-action-law expression as a result. Another advantage is that the concentration of metal-bound ligand is negligible compared with the total ligand concentration, thereby simplifying the calculation of the free ligand concentration (the free ligand concentration equals the total ligand concentration if reactions with hydrogen ions are negligible). The procedure usually involves batch equilibration of known amounts of resin loaded with a cation in solutions of varying ligand concentration L for measurement of the total distribution coefficient K_d of the metal M [16].

The partition coefficient (K_d^o) of a metal M between an aqueous phase and the sodium form of a cation exchange resin may be expressed in terms of the equilibrium constant K_c for the reaction (8):



$$K_c = \frac{[\bar{M}] \cdot [Na]}{[M] \cdot [\bar{N}a]} \quad (9)$$

$$K_d^o = \frac{[\bar{M}]}{[M]} = K_c \cdot \frac{[\bar{N}a]}{[Na]} \quad (10)$$

where $[\bar{M}]$ and $[\bar{N}a]$ are the concentration of metal M and Na on the ion exchange resin (mol/kg).
 $[M]$ and $[Na]$ are the concentration of metal M and Na in solution (mol/l).

The stoichiometric partition coefficient will be constant provided that the value of K_c and the ratio of the Na concentration in both phases is constant. The latter condition is fulfilled when the Na concentration in the aqueous phase is high and the exchange is very low, i.e. when the amount of metal M in the system is very low (trace concentration).

pH-buffers are often used in complexation experiments and, as many of these buffering substances form complexes, a correction has to be performed. In cases when a side-reaction of M with buffer substance B occurs, according to:



$$\text{with } K_{MB} = \frac{[MB_m]}{[M][B]^m} \quad (12)$$

the partition coefficient of the metal M is given by

$$K_d^o = \frac{[\bar{M}]}{[M] + [MB_m]} \quad (13)$$

$$K_d^o = \frac{[\bar{M}]}{[M](1 + K_{MB}[B]^m)} \quad (14)$$

The buffer concentration is usually constant so that $1 + K_{MB}[B]^m$ can be considered to be constant.

$$K_d^o = \frac{[\bar{M}]}{[M]A} \quad (15)$$

$$\text{with } A = 1 + K_{MB}[B]^m$$

When a ligand L is introduced into the system, a complex is formed with M according to the equation:



and is characterized by the stability constant K_{ML}

$$K_{ML} = \frac{[ML_n]}{[M] \cdot [L]^n} \quad (17)$$

The partition coefficient can be written as:

$$K_d = \frac{[\bar{M}]}{[M] + [ML_n] + [MB_m]} \quad (18)$$

$$K_d = \frac{[\bar{M}]}{[M](1 + K_{ML}[L]^n + K_{MB} \cdot [B]^m)} \quad (19)$$

$$K_d = \frac{[\bar{M}]}{[M]A(1 + \frac{K_{ML}[L]^n}{A})} \quad (20)$$

$$K_d = \frac{K_d^0}{1 + \frac{K_{ML}[L]^n}{A}} \quad (21)$$

This can be expressed as:

$$\log \left(\frac{K_d^0}{K_d} - 1 \right) = \log K_{ML} + n \log [L] - \log A \quad (22)$$

where: K_d^0 = partition coefficient of M in the absence of ligand L
 K_d = partition coefficient in the presence of ligand L
 K_{ML} = stability constant of complex ML_n
 $[L]$ = free ligand concentration
A = correction term when a buffer, B, has complexing properties

Equation 22 forms the working equation of the Schubert method. Measuring the partition coefficient of traces of metal M in the presence and absence of different concentrations of the ligand L, and then plotting $\log \left(\frac{K_d^0}{K_d} - 1 \right)$ against $\log [L]$ yields a straight line. The slope n of the line represents the stoichiometry of the complex while the intercept with the Y-axis, $\log K_{ML}$, can be derived after correction for $\log A$.

It is evident, that the method only works when the complex formed is neutral or negatively charged and does not adsorb on the ion exchange resin. Otherwise, a modified version of the original Schubert method has to be applied [16], [24].

2.5.2 Experimental set-up of the Schubert method

2.5.2.1 Preparation of the Na-resin

10 g of a wet Dowex 50 W X-4 cation exchange resin in the H^+ - form (= 21 meq) were converted to the Na-form by washing the resin twice with 250 ml 0.1 M NaOH and equilibrating 3 times with 0.1 M $NaClO_4$.

After equilibration, the resin was air dried and stored in a glass vial.

2.5.2.2 Complexation experiments with Ni²⁺, UO₂²⁺ and oxalate About 100 mg of the Na-resin were transferred to 50 ml centrifuge tubes. 25 ml of a solution containing 0.12 M NaClO₄, 0.012 M NaOAc and different amounts of oxalate were added. The volume was then adjusted to 30 ml with 5 ml of a 6 · 10⁻⁶ M Ni²⁺ solution, spiked with Ni-63, or a 8.4 · 10⁻⁷ M UO₂²⁺ (U-233) solution. The final composition of the solutions was: 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 · 10⁻⁷ M and oxalate varied between 0 and 2 ppm. The solutions were buffered at pH=5 by the NaOAc to prevent hydrolysis as a side-reaction.

The resin/solution mixtures were placed in an end-over-end shaker and equilibrated for 20 hours at room temperature. Previous experiments [26], however, showed that equilibration already had been reached after 2 hours. After equilibration, Ni-63 and U-233 in solution were measured by liquid scintillation counting (Packard, Tricarb 2250 CA) using Instagel (Packard) as a scintillation cocktail. The partition coefficients of Ni and U (K_d^o and K_d) were calculated from the difference in radioactivity in solution before and after equilibration.

2.5.2.3 Complexation experiments with Ni²⁺, UO₂²⁺ and bitumen degradation products Different amounts of bitumen water (10, 15 or 20 ml in the case of UO₂²⁺; 35 or 70 ml in the case of Ni²⁺) were adjusted to pH=3 with concentrated HClO₄ to remove any carbonates. The pH was then adjusted to 5, a NaOAc buffer and NaClO₄ added and the volume was made up to 100 ml. The final composition of the solutions was 0.012 M NaOAc and 0.12 M NaClO₄. The oxalate concentration could be calculated from the dilution. With these mixtures, complexation experiments with Ni²⁺ and UO₂²⁺ were performed as described in 2.5.2.2.

2.5.3 Calculation of the correction term log A

The correction term A is defined as:

$$A = 1 + K_{MOAc} \cdot [OAc^-]^m \quad (23)$$

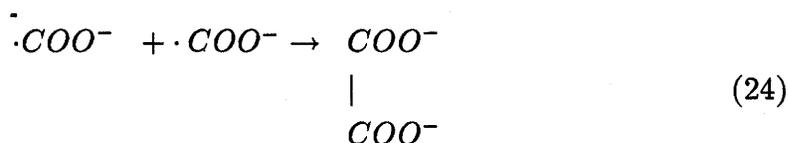
The concentration of the free acetate can be replaced by the total concentration because the metal concentration is very low. From the equilibrium pH and the Hendersson-Hasselbach equation, the acetate concentration can be calculated. The stability constants for Ni(OAc)⁺ and UO₂(OAc)⁺ at I=0.1 M are 10 and 10^{2.6} respectively [29], [30]. Under the experimental conditions used here, the 1:1 complexes of Ni²⁺ and UO₂²⁺ with OAc⁻ are the predominant side-reaction products (m=1). The correction term log A takes the value 0.03 for Ni and 0.55 for U.

3 Results and discussion

3.1 Composition of the bitumen water

Fig. 3.1 shows the chromatogram of the GC-MS analysis of the bitumen water B1. The composition of the bitumen water has been summarized in table 3.1. Most products found in the solution are fatty acids. This is not surprising, because fatty acids are abundant in bitumen [20]. Their concentration in solution, however, is very low. These fatty acids, in fact, cannot be considered as bitumen degradation products.

Beside fatty acids, 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 a product that is often found when carboxylic acids are irradiated. For example, when formic acid (HCOOH) is irradiated at high pH and oxygen atmosphere, oxalate is produced. The mechanism is probably the reaction of two $\cdot\text{COO}^-$ radicals [22].



In absence of oxygen, no oxalate was produced during irradiation of formic acid [22]. It is not difficult to imagine that $\cdot\text{COO}^-$ radicals are formed in the bitumen by decarboxylation of fatty acids. The reaction of two such radicals is a possible explanation for the occurrence of oxalate in the irradiated bitumen water. Since our experiments were performed under oxic conditions, the presence of oxalate is not unexpected. Under anoxic conditions (representing repository conditions more likely), the production of oxalate by irradiation could become questionable. Nevertheless, the presence of oxalate is important for the speciation of radionuclides and a more detailed discussion will be given in section 3.2.

The concentration of oxalate in the solution depends on the absorbed dose. Fig. 3.2 shows 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 3.2., together with the TOC and carbonate concentration. It is clear from this table that a large amount of carbonate is present in solution, presumably because irradiation of bitumen produces CO_2 . At a dose larger than 3 MGy, CO_2 -formation, in an oxygen atmosphere, becomes comparable to H_2 evolution [7]. The CO_2 produced is scavenged by the alkaline solutions and reacts to form CO_3^{2-} . No

effect of the difference in dose rate on the degradation products could be observed. The amount of oxalate only depended on the total absorbed dose. With IC, two additional low molecular weight products -acetate and formate- have also been detected. The quantities produced are displayed in fig. 3.2. The amount of acetate builded is independent on the total absorbed dose and so acetate seems not to be a radiolytic degradation product. The amount of formate produced, on the other hand, depends clearly on the total absorbed dose and is a radiolytic degradation product of the bitumen. The formation of formate can be explained by the condensation of two $\cdot\text{COOH}$ radicals [22].

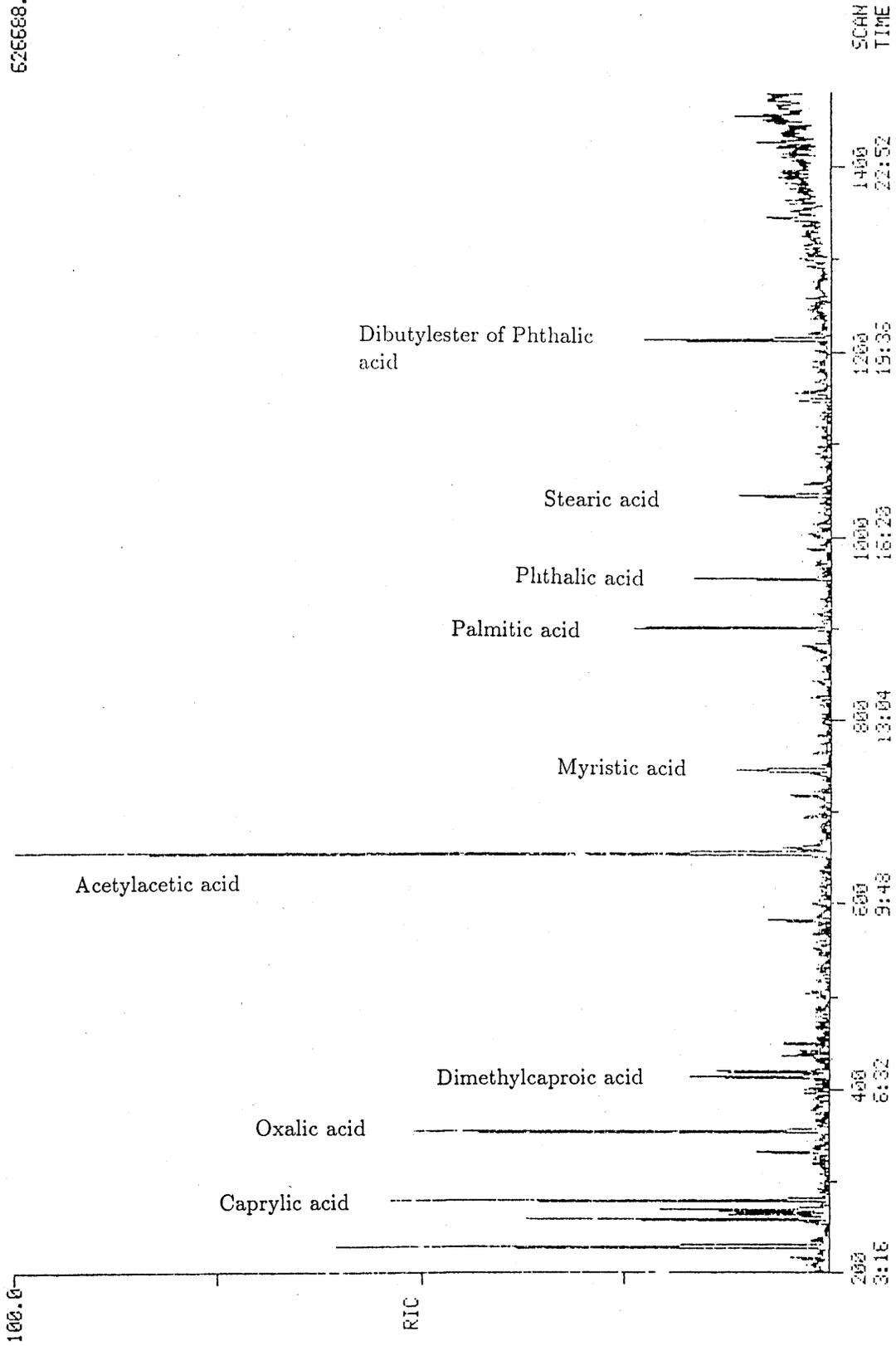


Fig. 3.1 Chromatogram of the GC-MS analysis of bitumen water B1

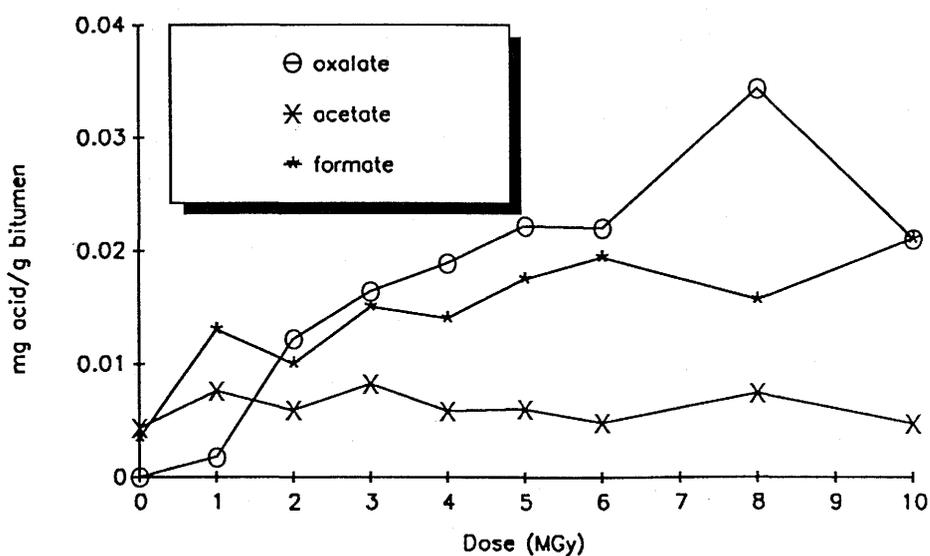


Fig. 3.2 Amount of oxalate, acetate and formate produced per gram of bitumen as a function of the absorbed dose. (Dose rate 11 kGy/h).

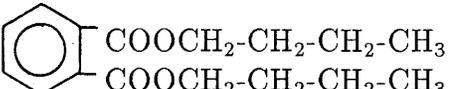
Name	Formula
Caprylic acid	$\text{CH}_3-(\text{CH}_2)_6 - \text{COOH}$
Myristic acid	$\text{CH}_3-(\text{CH}_2)_{12} - \text{COOH}$
Palmitic acid	$\text{CH}_3-(\text{CH}_2)_{14} - \text{COOH}$
Stearic acid	$\text{CH}_3-(\text{CH}_2)_{16} - \text{COOH}$
Dimethylcaproic acid	$\text{CH}_3-(\text{CH}_2)_3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

Table 3.1 Organic compounds in water after external irradiation of bitumen-water mixtures (B1)

Bitumen water	Oxalate mg/l	TOC mg/l	CO ₃ ²⁻ + HCO ₃ ⁻ meq/l	pH	Dose rate kGy/h	Dose MGy
B1	5.4	6.0	10.6	9.1	2.4	5.1
B2	3.3	4.5	n.d	12.5	2.4	3.5
B3	7.6	10.1	20.6	10.7	11	6.0
U1	< 0.1	0.9	1.7	12.7	0	0
U4	< 0.1	1.6	2.0	12.7	0	0
B4	5.2	6.6	14	11.8	11	5.3

Table 3.2 Concentration of oxalate, TOC and inorganic carbon in bitumen water with and without external irradiation. (n.d. = no data)

3.2 Complexation of Cu²⁺ by bitumen degradation products

Figs. 3.3, 3.4 and 3.5 show the titration curves of the irradiated bitumen waters (B2 and B3) with Cu²⁺. The free Cu²⁺ concentration ($-\log[\text{Cu}]_{free}$) is given as a function of the total Cu concentration ($-\log[\text{Cu}]_{tot}$). A straight line represents the case where no complexation occurs.

The experimental data can be reasonably well described by equation (7) with $\log K = 5.85-6.00$ and $\log L_T = -4.45$ for the B2 solution and $\log K = 5.65$ and $\log L_T = -4.10$ for the B3 solution. This suggests that only one ligand in the solution is important for the complexation of Cu²⁺. The other ligands either form much weaker complexes with Cu²⁺ or their concentration is low and their contribution can be neglected.

In table 3.3, an overview of the stability constants of Cu²⁺ and some carboxylic acids is given. No information about stability constants is available for the fatty acids. Examination of the homologous series of monocarboxylic acids (formate, acetate, propionate, butyrate) indicates that the stability constant decreases with increasing chain length. Based on this observation, the values for fatty acids were estimated to be smaller than 2 ($\log K \leq 2$).

From the composition data of the solution it is clear that only oxalate can contribute to the complexation of Cu²⁺. This is consistent with the observation that the titration data can be described well by a 1:1 complex with a stability constant $\log K = 5.7-6.00$. A direct comparison of the stability constant with literature data was not justifiable because the large spread observed in the reported values [12], [14], [29], [30]. A pragmatic approach was therefore adopted and the results of titrations of a pure oxalate solution under the same conditions were compared. Fig. 3.6 shows the titration of a pure oxalate solution (5 ppm) with Cu²⁺. The experimental results can be described very well by equation (7) with a $\log K$ value

5.7-6.00. The stability constant found for the pure oxalate solution is similar to the one observed for the bitumen water (B2 and B3). This verifies the fact that Cu^{2+} is mainly complexed by oxalate in the bitumen water.

The results of other titrations at different pH have been summarized in table 3.4. The same values for $\log K$ have been obtained at different pH values. The values range from 5.6 to 6.0 for both bitumen types. The only difference between the bitumen waters B2 and B3 is the amount of ligand (oxalate). The ligand concentration obtained from the titration with Cu^{2+} and from the IC analysis are very similar (table 3.5).

Fig. 3.7 and 3.8 display the titrations of the non-irradiated bitumen water (U1 and U4). The titration yields straight lines meaning that no complexation of Cu^{2+} and degradation products can be observed. This is consistent with the analytical data (table 3.2, no oxalate present in the solution).

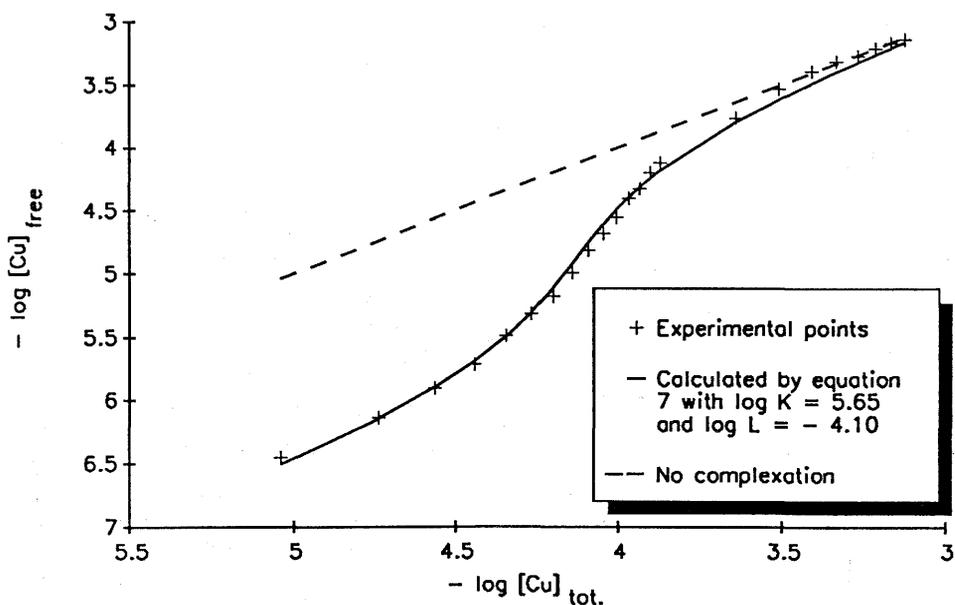


Fig. 3.3 Titration of bitumen water (B3) with Cu^{2+} at $\text{pH}=5.0$, $I=0.1 \text{ M}$ and $T=25 \text{ }^\circ\text{C}$.

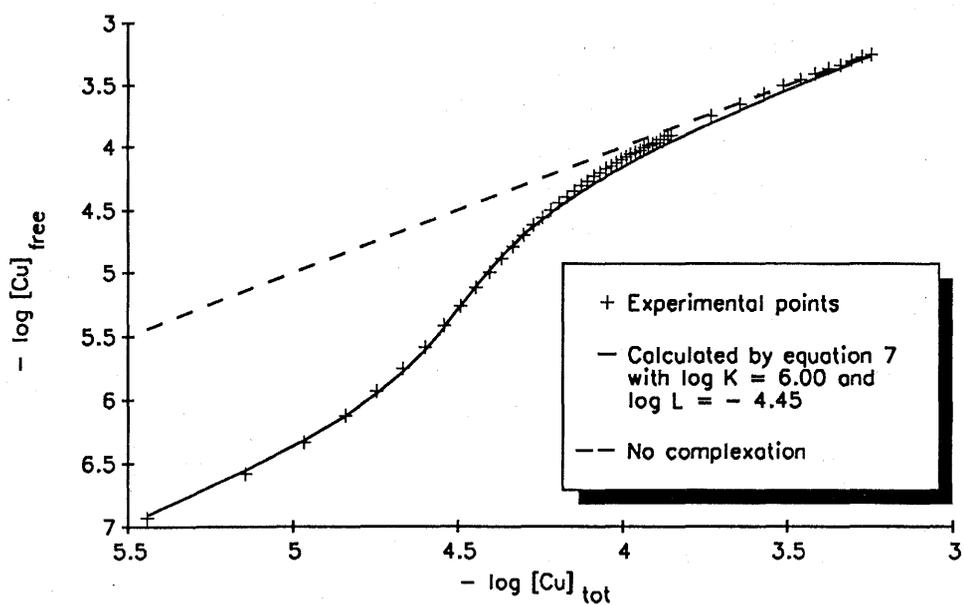


Fig. 3.4 Titration of bitumen water (B2) with Cu^{2+} at $\text{pH}=5.0$, $I=0.1 \text{ M}$ and $T=25 \text{ }^\circ\text{C}$.

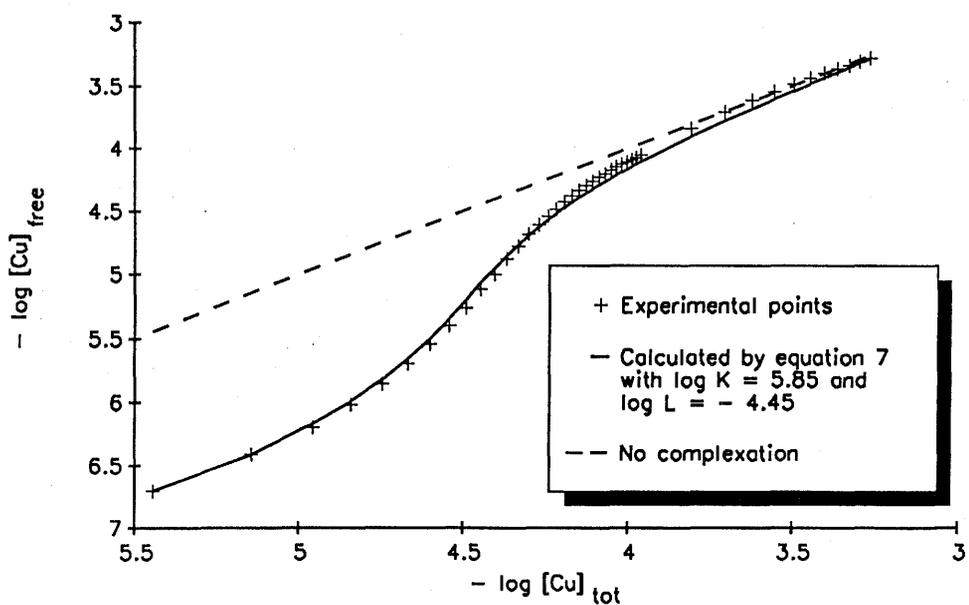


Fig. 3.5 Titration of bitumen water (B2) with Cu^{2+} at $\text{pH}=6.00$, $I=0.1 \text{ M}$ and $T=25 \text{ }^\circ\text{C}$.

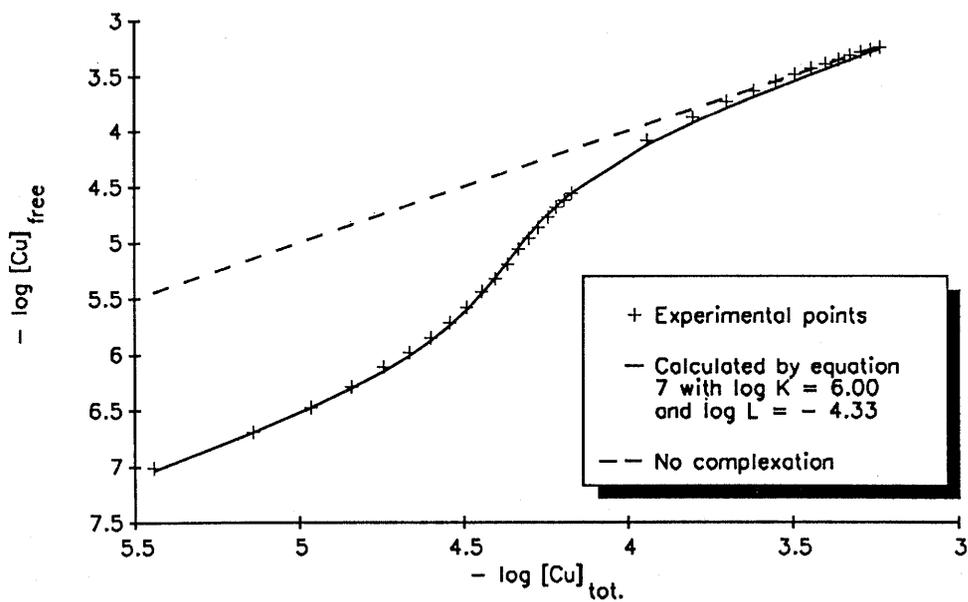


Fig. 3.6 Titration of a pure oxalate solution (5 ppm) with Cu^{2+} at $\text{pH}=6.0$, $I=0.1 \text{ M}$ and $T=25 \text{ }^\circ\text{C}$.

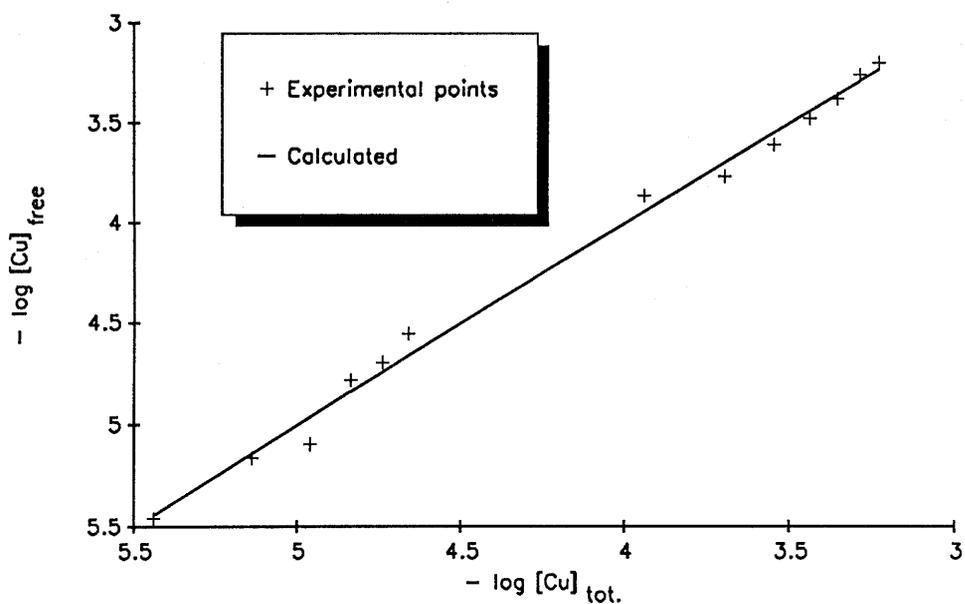


Fig. 3.7 Titration of non-irradiated bitumen water (U4) with Cu^{2+} at $\text{pH}=5$, $I=0.1 \text{ M}$ and $T=25 \text{ }^\circ\text{C}$.

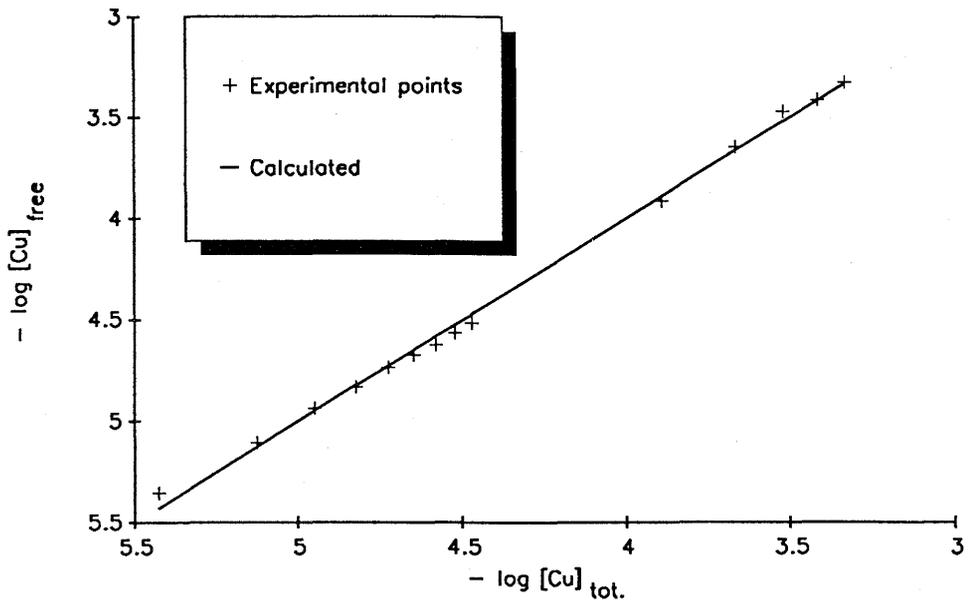


Fig. 3.8 Titration of non-irradiated bitumen water (U1) with Cu^{2+} at $\text{pH}=5$, $I=0.1 \text{ M}$ and $T=25 \text{ }^\circ\text{C}$.

Ligand	log K ₁ [29, 30] (I=0.1, T=25 °C)	log K ₁ [12] (I=0.1, T=25 °C)	log K ₁ [14] (I=0.1, T=25 °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 (I=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	–	–

Table 3.3 Stability constants of complexes between Cu²⁺ and some mono- and dicarboxylic acids.

- (a) estimated values
(m) monocarboxylic acids
(d) dicarboxylic acids

	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	5.50	-4.10	6.00	-4.33
pH = 5.0					5.65	-4.38
	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 3.4 Overview of the log K and log L_T values derived from titrations of bitumen water (B2 and B3) and oxalate with Cu²⁺ at different pH values and I=0.1 M.

	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

Table 3.5 Concentration of oxalate in bitumen water B2 and B3 determined by titration with Cu^{2+} and ion chromatography (IC).

3.3 Complexation of Ni^{2+} and UO_2^{2+} by bitumen degradation products

Fig. 3.9 and 3.10 show the results of the complexation study of Ni^{2+} and UO_2^{2+} with pure oxalate. The plot of $\log \left(\frac{K_d^o}{K_d} - 1 \right)$ against $\log L$ results in a straight line, the slope of which equals 1 for both Ni-oxalate and UO_2 -oxalate indicating that a 1:1 complex has been formed:



The stability constants of the complexes have been calculated by applying equation (26) to the individual experimental data, with $n=1$.

$$\log \left(\frac{K_d^o}{K_d} - 1 \right) - n \log [L] + \log A = \log K \quad (27)$$

This procedure gives a more accurate value of $\log K$ than the extrapolation method 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 [9].

Figs. 3.9 and 3.10, together with table 3.6, display the results of the complexation studies of Ni^{2+} and UO_2^{2+} with bitumen degradation products where it was assumed **a priori** that oxalate was the most important ligand present in the bitumen water. The $\log \left(\frac{K_d^o}{K_d} - 1 \right)$ values were plotted against the oxalate concentration in the solution (which was measured before the experiment began due to doubts about oxalate stability).

It is clear from figures 3.9 and 3.10 that the experimental data (and the calculated $\log K$ values) are completely consistent with that of the pure oxalate systems indicating that oxalate is the most important ligand present in the bitumen water.

The values of the stability constants ($\log K$) have been summarized in table 3.6 together with some values found in the literature. It is clear that the values determined by the Schubert method are in good agreement with the literature values.

The non-irradiated samples, U1 and U4, display some degree of complexation of Ni^{2+} and UO_2^{2+} . For comparison, the organic content of the non irradiated samples was normalized to oxalate, indicating that the complexing capacity of this system was equivalent to a solution containing 0.1 - 0.3 ppm oxalate.

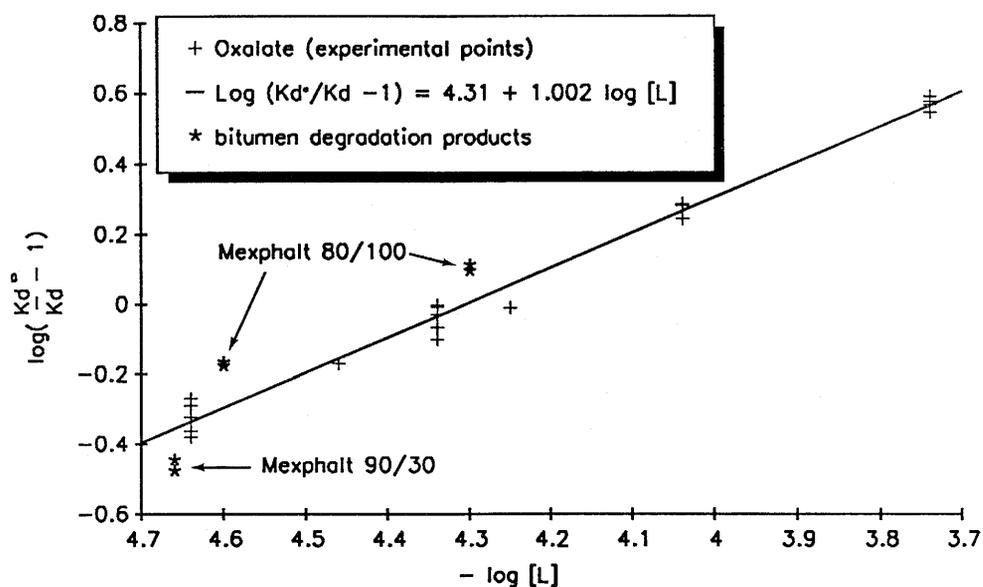


Fig. 3.9 Complexation of Ni^{2+} with oxalate and bitumen degradation products at $\text{pH}=5.0$ and $I=0.11 \text{ M}$ (Schubert method). The regression has been calculated for the pure oxalate solutions.

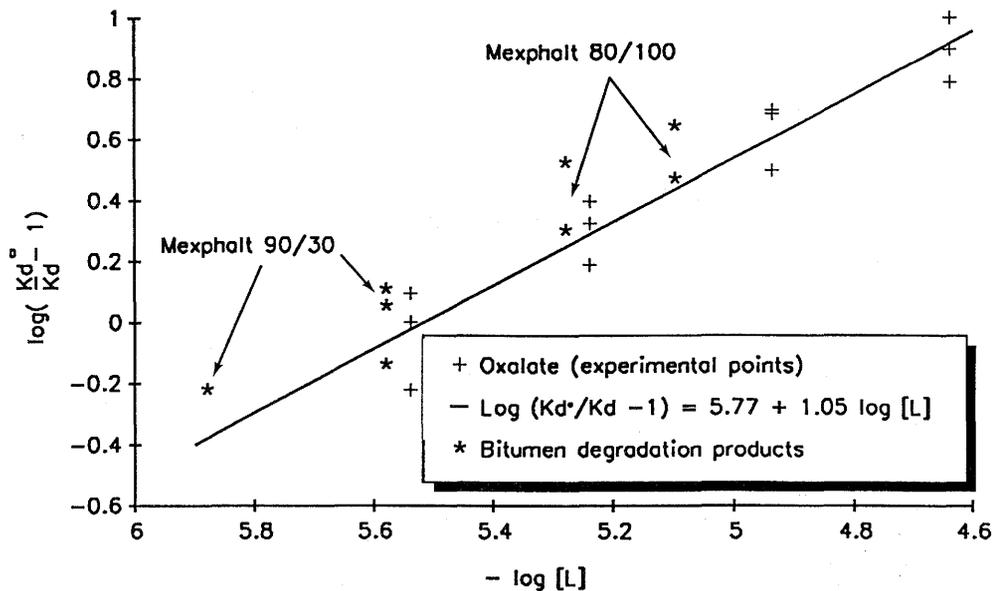


Fig. 3.10 Complexation of UO_2^{2+} with oxalate and bitumen degradation products at $\text{pH}=5.0$ and $I=0.11 \text{ M}$ (Schubert method). The regression has been calculated for the pure oxalate solutions.

	Ni^{2+}	UO_2^{2+}
Oxalate	4.27 ± 0.05	6.10 ± 0.11
Bitumen water	4.38 ± 0.02	6.09 ± 0.11
Mexphalt 80/100		
Bitumen water	4.17 ± 0.02	6.13 ± 0.11
Mexphalt 90/30		
Literature	$4.32 [14] *$	$5.96 [14] *$
	$5.3 [29, 30]$	$6.36 [12] *$
	$3.83 [12]$	

Table 3.6 Comparison of experimental stability constants ($\log K$) of complexes of oxalate, with Ni^{2+} and UO_2^{2+} at $\text{pH}=5$ and $I=0.11 \text{ M}$, with literature values
 (* corrected to $I=0.1 \text{ M}$ by the Davies equation [2])

4 Speciation of Ni and U in water in the presence of bitumen degradation products

In order to get an idea of the influence of bitumen degradation products on the behaviour of radionuclides released to the geosphere from the near field, a speciation calculation with the PHREEQE geochemical code has been performed [21]. A significant change in speciation indicates that an effect of the degradation products on the fate of radionuclides might be expected.

Parameter	Sediment USM	Cement SPP
Temperature	40	25
pH	7.5	13.2
Log P_{CO_2} [bar]	-2.5	-
Ionic strength [M]	0.21	0.23
E_h (mV)	- 237	+ 139
Na^+ [M]	1.85×10^{-1}	6.52×10^{-2}
K^+ [M]	5.00×10^{-4}	1.61×10^{-1}
Mg^{2+} [M]	2.64×10^{-3}	1.00×10^{-5}
Ca^{2+} [M]	4.19×10^{-3}	2.31×10^{-3}
Si [M]	2.00×10^{-4}	-
Fe_{tot} [M]	-	1.00×10^{-5}
NH_4^+ [M]	2.00×10^{-4}	-
Al [M]	-	2.00×10^{-4}
Cl^- [M]	1.98×10^{-1}	-
SO_4^{2-} [M]	5.00×10^{-5}	-
PO_4^{3-} [M]	-	-
C_{tot} [M]	$1.69 \cdot 10^{-3}$	4.72×10^{-5}
Alkalinity [N]	1.66×10^{-3}	2.31×10^{-1}
SiO_2 [M]	3.95×10^{-4}	2.00×10^{-4}
Saturated Solids	Calcite Dolomite Chalcedony	Calcite

Table 4.1 Composition of the USM [19] and SPP [1] water used for the PHREEQE calculations.

Two water types were utilized in the calculations, a cement pore water (SPP) [19] and a USM groundwater [1] (Table 4.1).

A modified thermodynamic database has been used [2]. The data for metal-oxalate interactions were selected from the PSI-MINEQL-database. The concentrations of Ni and U were set arbitrarily at 10^{-10} M. These values are perhaps a little bit too low for realistic conditions, but gives us some insight into the effects of the bitumen degradation products on the speciation of radionuclides.

4.1 Speciation of Ni and U in cement pore water (SPP)

A Swedish standard Portland cement water (SPP) was chosen as reference cement pore water. Such a water could be representative of a near field water at a low and intermediate level waste repository for a period of hundreds of years after repository closure [2]. The redox potential, however, is expected to drop to negative values within a time period of hundred years [28], so that a negative redox potential would probably more realistic. We have restricted our calculations for the case where an oxidic condition prevails.

The CO_2 produced during internal irradiation of the bitumen reacts with the alkaline cement pore water to produce CO_3^{2-} . Depending on the amount of CO_2 produced, CO_3^{2-} precipitates as CaCO_3 . As it is difficult to estimate the amount of CO_3^{2-} produced, a calculation with cement pore water in equilibrium with CaCO_3 was performed. The oxalate concentration was varied between 10^{-3} M and 10^{-9} M.

Oxalate	10^{-9} M	10^{-6} M	10^{-3} M
Species	%	%	%
$\text{Ni}(\text{OH})_3^-$	72.0	72.1	72.1
$\text{Ni}(\text{OH})_4^{2-}$	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

Table 4.2 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)

Table 4.2 shows the results of the Ni and U speciation calculation. The presence of CO_3^{2-} and oxalate in solution has no influence on the speciation of these radionuclides. The speciation of both elements in this alkaline environment is completely determined by the OH - ligands.

A part of the oxalate reacts with Ca^{2+} to form Ca-Oxalate (± 30 %).

4.2 Speciation of Ni and U in Untere Süsswasser Molasse (Lower Freshwater Molasse) water (USM)

The USM water occurs in a potential host rock for a high level/long lived intermediate waste repository site. It was used for the speciation calculation because it has a composition reasonably representative of several host rocks currently under investigation.

The USM water is a system already in equilibrium with CaCO_3 . Only oxalate was introduced as a "contaminant" to this water. Two different situations have been considered: a water (red) in equilibrium with pyrite (-237 mV) and an oxidizing (oxid) water (+237 mV). The results of the calculation are displayed in table 4.3.

Ni_{tot} U_{tot} Ox_{tot}	10^{-10} M		10^{-10} M		10^{-10} M	
	Oxid	Red	Oxid	Red	Oxid	Red
Ox^{2-}	36.9 %	36.9 %	36.9 %	36.9 %	39.1 %	39.1 %
CaOx°	54.9 %	54.9 %	54.9 %	54.9 %	53.1 %	53.1 %
MgOx°	8.1 %	8.1 %	8.1 %	8.1 %	7.8 %	7.8 %
Ni^{2+}	18.1 %	18.1 %	18.1 %	18.1 %	8.1 %	8.1 %
NiCO_3	76.0 %	76.0 %	75.9 %	75.9 %	37.4 %	37.4 %
NiHCO_3^+	1.4 %	1.4 %	1.4 %	1.4 %	0.6 %	0.6 %
$\text{Ni}(\text{CO}_3)_2^{2-}$	0.9 %	0.9 %	0.9 %	0.9 %	0.5 %	0.5 %
NiCl^+	2.5 %	2.5 %	2.5 %	2.5 %	1.1 %	1.1 %
NiCl_2	0.9 %	0.9 %	0.9 %	0.9 %	0.4 %	0.4 %
$\text{Ni}(\text{OH})^+$	0.1 %	0.1 %	0.1 %	0.1 %	-	-
NiOx°	-	-	-	-	39.2 %	39.2 %
$\text{Ni}(\text{Ox})_2^{2-}$	-	-	-	-	11.2 %	11.2 %
$\text{Ni}(\text{Ox})_3^{4-}$	-	-	-	-	1.3 %	1.3 %
$\text{U}(\text{OH})_5^-$	-	99.9 %	-	99.9 %	-	99.9 %
$\text{UO}_2(\text{CO}_3)_2^{2-}$	68.8 %	-	68.8 %	-	66.9 %	-
$\text{UO}_2(\text{CO}_3)_3^{4-}$	30.5 %	-	30.5 %	-	32.4 %	-
UO_2CO_3	0.6 %	-	0.6 %	-	0.5 %	-
$\text{UO}_2(\text{OH})_2$	0.1 %	-	0.1 %	-	0.1 %	-

Table 4.3 Speciation of Ni and U in a Lower Freshwater Molasse water under oxidizing and reducing conditions.

Oxalate has no significant influence on the U- and Ni-speciation at low concentrations. Only when the oxalate concentration is increased to 10^{-3} M, the Ni speciation alters and NiOx^\ominus becomes predominant. However 10^{-3} M is an unrealistic high concentration that will never be reached in a repository.

The speciation of Ni, in both oxidizing and reducing conditions, is mainly determined by CO_3^{2-} . For U, OH^- is the predominant ligand under reducing conditions, where all U is present as U(IV). The existence of the $\text{U}(\text{OH})_5^-$ species, however, is doubtful [4]. Under oxidizing circumstances, when U is present as U(VI), CO_3^{2-} is the predominant ligand.

5 Conclusions

Oxalate and CO_3^{2-} are the main radiolytic degradation products of bitumen, and the only ones that form relatively stable complexes with heavy metals and radionuclides. Calculations with the PHREEQE geochemical code show that these degradation products do not influence the speciation of Ni and U in a cement pore water (representing near field conditions for a LAW/MAW repository). In a groundwater (representing far field conditions), the speciation is independent on the oxalate present in the system. The speciation of Ni and U(VI) is determined by CO_3^{2-} , naturally present in the groundwater, whereas OH^- is the main ligand for U(IV).

The calculations clearly show that the radiolytic bitumen degradation products do not influence the speciation of Ni and U, so that they can be neglected for the safety assessment studies.

Element	$\log K_1$ [29, 30] (I=0.1, T=25 °C)	$\log K_1$ [17] (I=0.1, T=25 °C)
Am ³⁺	6.15	5.25
Eu ³⁺	4.81 (I=0.5)	5.36
NpO ₂ ⁺	4.04 (I=0.05)	4.04 (I=0.05, 20 °C)
PuO ₂ ²⁺	6.66 (I=?, 20 °C)	9.4 (I=1.0, 20 °C)
Pu ³⁺	9.31 (I=?, ? °C)	–
Cm ³⁺	5.96 (I=0.2, 20-25 °C)	5.25
Th ⁴⁺	8.23 (I=1)	8.8 (I=0.05)
Co ²⁺	3.84	–
Pa ⁴⁺	10.7 (I→0)	–
Zr ⁴⁺	9.8 (I=?, ? °C)	–

Table 5.1 Stability constants of complexes between radionuclides and oxalate

An additional evaluation for other radionuclides and other types of waters is recommended. A brief search of the literature, however, shows that many radionuclides do not form very stable complexes with oxalate [17], [29], [30]. Table 5.1 displays the stability constants of some radionuclides and oxalate. The $\log K$ values range from 3 to 10. For all these elements, the speciation is determined completely by OH-ligands. Consequently, a significant influence of the radiolytic bitumen degradation products on their fate is not to be expected. A more fundamental study on the influence of organic compounds on the speciation of radionuclides in different environments is ongoing at PSI and will further evaluate our results (W. Hummel, personal communication).

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