

TECHNICAL REPORT 91-32

**CHEMISTRY OF THE
REDOX SENSITIVE ELEMENTS**

LITERATURE REVIEW

D. SUTER

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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 radionuclide transport in the geosphere. These investigations are performed in close cooperation with, and with the financial support of, NAGRA. The present report is issued simultaneously as a PSI report and a NAGRA NTB.

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SUMMARY

As part of the safety assessment for a nuclear waste repository, the migration of the radioactive elements from the waste matrix to the biosphere has to be modelled. The geosphere is an important barrier and a consideration of the retention of the radioactive isotopes needs knowledge of sorption coefficients and solubilities. Important long-lived isotopes in the high level radioactive waste are the fission products selenium, technetium, palladium and tin, and the actinide neptunium, which are all redox sensitive elements. A transport model using conservative sorption values predicts mainly doses from these five elements. Since the individual oxidation states of the redox sensitive elements have different and largely unknown sorption properties and solubilities, the realistic doses might be far less.

The relevant literature about the chemistry of the five elements is summarized and is planned to serve as the basis for an experimental programme. For every element, the literature about the general chemistry, selected sorption studies, geochemistry, and analytical methods is reviewed. It was found that the knowledge about some of these points is very limited. Even the general chemistry of some of the elements is not well known, because they have only limited applications and research concentrates only on certain aspects. Most of the sorption studies in the context of nuclear waste concentrate on a few of the relevant elements and others have been neglected up to now.

The simulation of a realistic system in the laboratory poses some problems, which have to be solved as well. The literature about this subject is also critically reviewed.

The elements which are most mobile under realistic far-field conditions are identified and it is recommended to concentrate research on these at the beginning.

ZUSAMMENFASSUNG

Als Teil der Sicherheitsbetrachtung für ein Endlager für radioaktive Abfälle muss die Migration der radioaktiven Elemente von der Abfallmatrix bis in die Biosphäre modelliert werden. Die Geosphäre ist eine wichtige Barriere und der Einbezug der Rückhaltung der radioaktiven Isotope setzt die Kenntnis von Sorptionskoeffizienten und Löslichkeiten voraus. Wichtige langlebige Isotope im hochaktiven Abfall sind die Spaltprodukte Selen, Technetium, Palladium und Zinn, sowie das Aktinid Neptunium, welche alle redoxsensitiv sind. Ein Transportmodell mit konservativen Sorptionswerten sagt hauptsächlich Dosen von diesen Elementen voraus. Da die einzelnen Oxidationsstufen der redoxsensitiven Elemente unterschiedliche und weitgehend unbekannte Sorptionseigenschaften und Löslichkeiten aufweisen, könnten die realistischen Dosen geringer sein.

Die relevante Literatur über die Chemie der fünf Elemente wird zusammengefasst und soll als Grundlage für die Planung eines experimentellen Programmes dienen. Für jedes Element wird die Literatur über die allgemeine Chemie, ausgewählte Sorptionsstudien, Geochemie und analytische Methoden zusammengefasst. Es zeigt sich, dass das Wissen über einige Punkte sehr gering ist. Von einigen Elementen ist sogar die allgemeine Chemie nicht sehr gut bekannt, weil diese nur beschränkte Anwendungen haben und sich die Forschung darauf konzentriert. Die meisten Sorptionsstudien im Zusammenhang mit dem radioaktiven Abfall konzentrieren sich auf einige der relevanten Elemente, während andere bisher vernachlässigt wurden.

Die Simulation eines realistischen Systems im Labor stellt spezielle Probleme, welche ebenfalls gelöst werden müssen. Die Literatur zu diesem Thema wurde kritisch durchgesehen.

Die Elemente, welche unter realistischen Bedingungen am mobilsten sind werden identifiziert und es wird empfohlen, die Forschung zu Beginn auf diese zu konzentrieren.

RÉSUMÉ

Dans le cadre des études du contrôle de sécurité d'un dépôt de déchets nucléaires, la migration des éléments radioactifs depuis la matrice de déchets jusqu'à la biosphère doit être modélisée. La géosphère est une importante barrière et la prise en considération de la rétention des isotopes radioactifs nécessite la connaissance des coefficients de sorption et des solubilités. Parmi les éléments radioactifs importants, les produits de fission tel que le sélénium, le technetium, le palladium et l'étain et l'actinide neptunium sont tous redox sensibles. Un modèle de transport mettant en jeu des coefficients conservateurs prédit des doses principalement pour ces cinq éléments. Puisque les états d'oxydation individuels des éléments ont des propriétés de sorption et des solubilités relativement peu connues, les doses réelles peuvent être assez différentes.

Les études importantes au sujet de ces cinq éléments sont résumées, et devront servir de base au programme expérimental. Pour chaque élément, la littérature concernant la chimie générale, les études de sorption sélective, la géochimie, et les méthodes analytiques sont revues. On doit constater que la connaissance de ces points est très limitée. Pour certains d'entre-eux la chimie générale, même, n'est pas bien connue, parce qu'ils ont seulement des applications limitées pour certains aspects. La plupart des études de sorption dans le cadre des déchets nucléaires concernent certains de ces éléments, les autres ont été négligés jusqu'à présent.

La simulation d'un système réaliste au laboratoire pose certaines problèmes qui doivent être résolus. La littérature à ce sujet est a été revue de façon critique.

Les éléments qui sont les plus mobiles dans les conditions les plus réalistes ont été identifiés et il est recommandé de concentrer la recherche à ce sujet.

1. INTRODUCTION

It is planned to dispose of nuclear waste in deep geologic formations in order to isolate it from the environment. The waste matrix itself, the steel containers, the back-fill material and the surrounding rocks act as barriers to hinder migration of the radioactive elements to the biosphere. Intrusion of water into the repository could lead to leaching of the radioactive elements and migration through the barriers into surface waters from where they could enter the food chain. Government regulations set a limit for radiation doses resulting from such an exposure to radioactivity from a nuclear waste repository. In order to predict the doses under a given set of conditions (waste matrix, man-made barrier, geologic formations), reliable models for the migration through these barriers have to be developed. One experimental research group at Paul Scherrer Institute is studying the interaction of radioactive waste elements with the rocks in the far-field of a potential repository. These data are used in mathematical models describing the migration through the geosphere.

Some of the elements present in nuclear waste exist in several oxidation states within the range of redox potentials that is likely to be encountered in a repository and the surrounding rocks. Among these elements, the fission products selenium, technetium, palladium and tin and the actinide neptunium, contribute appreciably to the expected radiation doses from a repository (Fig. 1). The calculated contribution from some of the elements is relatively high, because conservative assumptions have been used for computation. Realistic calculations based on experimental studies might yield considerably lower values.

Due to the reducing capacity of the steel containers in the repository, the radionuclides are released from the near-field in a reduced form. In the reducing environment of the far-field, they will stay in a reduced form, but redox reactions can not be excluded. Since the chemical properties of the same element in different valence states vary widely, the migration behavior of these elements depends strongly on the redox potential. The oxidation state can change during the migration through the geosphere by reaction with dissolved and solid reactants. The bulk of the redox capacity of the geosphere is present in the form of reducing minerals. This redox capacity can act by direct redox reactions of the solid with adsorbed ions or by dissolution of the solid and reaction in solution. There are only few studies dealing with the problem of the reaction between a redox sensitive element and a redox active rock.

It can not be excluded that such reactions play an important role in the retention of radionuclides, in addition to normal sorption on the rock surfaces.

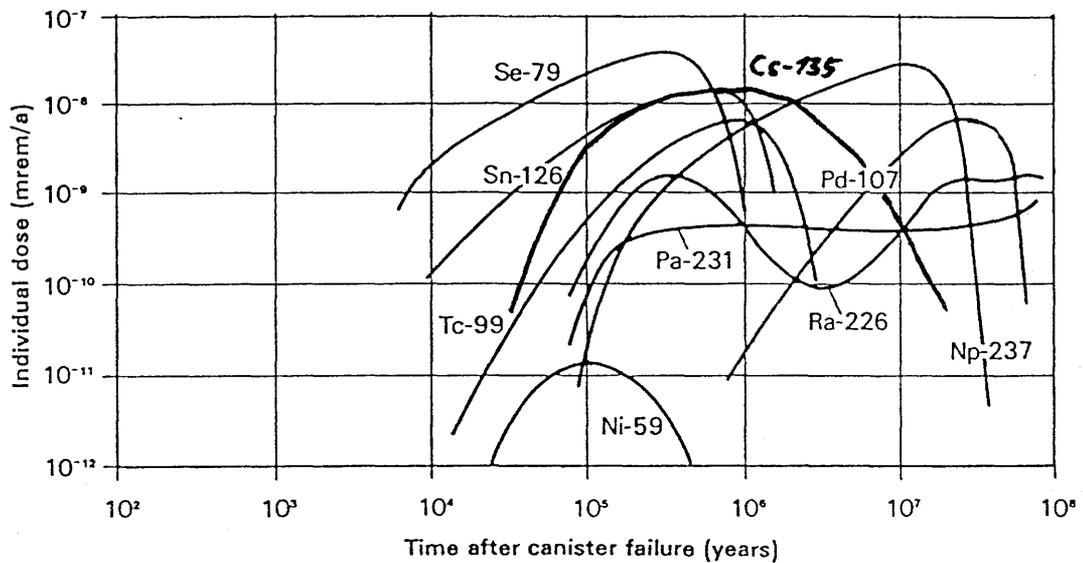


Figure 1. Contribution of isotopes to the annual individual dose from a high-level waste repository as a function of time (after NAGRA, 1985, the Cs-135 contribution is recalculated from the results of Jakob et al., 1989).

The rocks which are to be examined come for example from the Grimsel Test Site, where migration experiments are performed. Here, experiments in the laboratory have to provide sorption data as input for computer models, which are used to predict migration in the field experiment. Other rock samples are from potential sites of future nuclear waste repositories. Under consideration are presently marl, opalinus clay and the lower freshwater molasse. In these cases, sorption data is used to model migration through the geosphere, which is part of the safety assessment.

A study like this can never be as complete as one would like it to be. Some of the elements discussed are somewhat exotic from a chemical point of view and even basic information is incomplete. Many studies of the sorption of radionuclides are only phenomenological; they concentrate on adsorption on one particular rock system and discuss it only in terms of the amount that is sorbed without trying to understand the reasons for different adsorption behavior on different rocks. Where a large number of studies is available, the ones with more chemical information and higher quality were chosen, but when little information is available, studies of lesser quality have been included, to provide at least some information. Since this report deals with the chemical behavior of redox sensitive elements, only a limited number of representative sorption data are given here for illustrative purposes. The sorption data apply only for the conditions given in the publication cited and different values may be obtained for other systems. Readers who are interested in additional sorption studies will find a number of them referenced in the report by McKinley and Hadermann (1984).

2. REDOX CONDITIONS

Retention of the redox sensitive elements discussed in this report depends to a large extent on the redox conditions in the environment. In this chapter the general problem of the reproduction of the geological redox conditions in the laboratory is discussed. Particular problems of the individual elements will be presented in the chapters on the individual elements.

It is generally accepted that reducing conditions exist in the far field of a repository, because the rocks contain a number of reducing minerals. They can reduce adsorbed radionuclides directly and/or they are dissolved and reduce the radionuclides in solution. For this reason, the redox conditions can be simulated best by letting the minerals/rocks equilibrate with the water at the desired pH, carbon dioxide concentration and water chemistry. This is what happens in a real system. In order to avoid oxidation of the reducing compounds in the experimental system, glove boxes, filled with nitrogen or a mixture of nitrogen and carbon dioxide have to be used. In such a system, the residual atmospheric oxygen concentration is in the range of 1 ppm, corresponding to an oxygen concentration in solution of around 10^{-9} M, which is in the concentration range of the sorbate elements used in the sorption experiments. The sensitivity of the elements towards oxidation by dissolved oxygen varies from very sensitive (e.g. Tc(IV)) to insensitive (e.g. Se(IV)). It should be kept in mind that oxidation kinetics of adsorbed ions can be considerably different from oxidation kinetics in solution (Tamura et al., 1976, Tamura et al. 1980, Davies and Morgan, 1989, Wehrli and Stumm, 1989). The residual oxygen in the system might also oxidize the most accessible part of the reduction capacity of the system (either dissolved or on the surface of the rocks), which could alter the extent of sorption/reduction. For this reason, additional methods for removal of oxygen from the system have to be considered. There are a few studies on the oxidation of reducing minerals (White et al., 1985, White and Yee, 1985, Pirhonen et al., 1991).

2.1 Hydrazine as Reducing Reagent

Several methods have been used to set the redox conditions artificially. One of the more widely used in the past was the introduction of hydrazine into the system as a "redox buffer". A number of problems with regard to this method have been summarized by Kelmers et al. (1984):

1. Hydrazine can undergo a number of different redox reactions, depending on the conditions (pH value). Some of them are definitely not reversible. Reversibility is a fundamental requirement for a "buffer" of any type.

2. Hydrazine dissociation leads to a change in pH.

3. Reaction between hydrazine and carbonate can lead to the formation of carbamates. This reaction can deplete carbonate in the system and carbamate can form undesirable complexes.

4. The reaction between hydrazine and technetium has not been studied in detail and the reaction product has only been assumed to be Tc(IV).

5. The reduction of neptunium(V) to neptunium(IV) is extremely slow. It is however faster at very low pH values and it also can be catalyzed by iron (El-Naggar et al., 1982).

6. Hydrazine reacts with clays and alters the rock system in an undesirable way.

7. Hydrazine reacts with some plastics used as part of the experimental system, and this can lead to the destruction of the experimental apparatus.

These points show that use of hydrazine as a redox buffer is undesirable.

An acceptable way of using hydrazine to reduce a stock solution of Np(V) to Np(IV) has been published recently (Rösch et al., 1990). After reduction, neptunium is sorbed on an ion exchange column, which is washed to remove an excess of hydrazine.

2.2 Electrochemical Reduction

As an alternative method of achieving a certain oxidation potential in an experimental rock/water circulating column system, the use of a potentiostat with a porous electrode has been suggested. The electrode was used to precondition the solution and was removed before the tracer was added (Meyer et al., 1984). This method is certainly superior to the methods which introduce chemicals into the system, but there is still the possibility, that the treatment may produce chemical species which are not representative of the natural situation and which lead to undesirable side reactions.

2.3 Hydrogen as Reductant

Another "clean" reductant is hydrogen, which can be just bubbled through the solution or it can be activated with a palladium catalyst (Bruno et al., 1985). The reactions of hydrogen with other elements can, however, be kinetically hindered and the products depend on the reaction conditions and on the presence of catalysts. The elements to be conditioned might be reduced and precipitated on the electrode, which is not desirable. Hydrogen has been shown to reduce Mn(VII) to Mn(VI) in solution, and to Mn(IV) in the presence of a platinum catalyst (Guppy and Atkinson, 1989). Hydrogen in solution does not influence the oxidation state of technetium (Guppy et al., 1989).

3. SELENIUM

3.1 Solution Chemistry

The chemistry of selenium is in many respects similar to the chemistry of sulfur, which belongs to the same periodic group of elements. Selenium exists in the oxidation states -II, 0, IV and VI. The selenide anion (Se^{2-}) is very similar to the sulfide anion (S^{2-}) and forms many minerals which correspond to the sulfides of the same cations (Howard, 1977). Selenide minerals are highly insoluble. The oxidation of selenide to selenite (SeO_3^{2-}) is rapid under oxidizing conditions, whereas the oxidation of selenide to selenate (SeO_4^{2-}) is slow (Masscheleyn et al., 1990). Selenous acid (H_2SeO_3) and selenic acid (H_2SeO_4) resemble sulfurous and sulfuric acid, respectively. In contrast to the sulfur analog sulfite, selenite is quite stable towards oxidation by oxygen in aqueous solutions over a wide range of pH values. Selenous acid is reduced by hydrogen sulfide to a precipitate, which consists of selenium and sulfur (Gmelin, 1949).

Acid	pK ₁	pK ₂
H_2Se	3.81	14.96
H_2SeO_3	2.57	7.30
H_2SeO_4	-1.97 ^{a)}	1.91

References: Wagman et al. (1982), except ^{a)} Bard et al. (1985)

Native selenium exists in several different allotropic forms. Amorphous selenium can form a red, dark or black powder, depending on particle size. The crystalline form is more stable and amorphous selenium can be transformed to hexagonal crystals (Gmelin, 1942). There is relatively little known about their reactivity, but it appears to depend strongly on the modification (Schulek and Körös, 1960). The reaction of elemental selenium with sulfide produces the anion selenosulphide (SSe_x)²⁻, which leads to an increased mobility of selenium (Gmelin, 1942, 1949, Schulek and Körös, 1960).

Elemental selenium and sulfite form the anion selenosulfate (SSeO_3^{2-}) (Gmelin, 1942, 1949, Warren, 1968). Selenite is reduced to elemental selenium fairly quickly, but the oxidation of native selenium can be very slow, depending on its allotropic form (Geering et al., 1968, Howard, 1977). Selenium metal is oxidized to Se(IV) fairly quickly in a warm 1:1 solution of nitric acid (Frost and Griffin, 1977). There are several compilations of thermodynamic data of selenium available (Wagman et al. 1982, Phillips et al., 1988, Baeyens and McKinley, 1989).

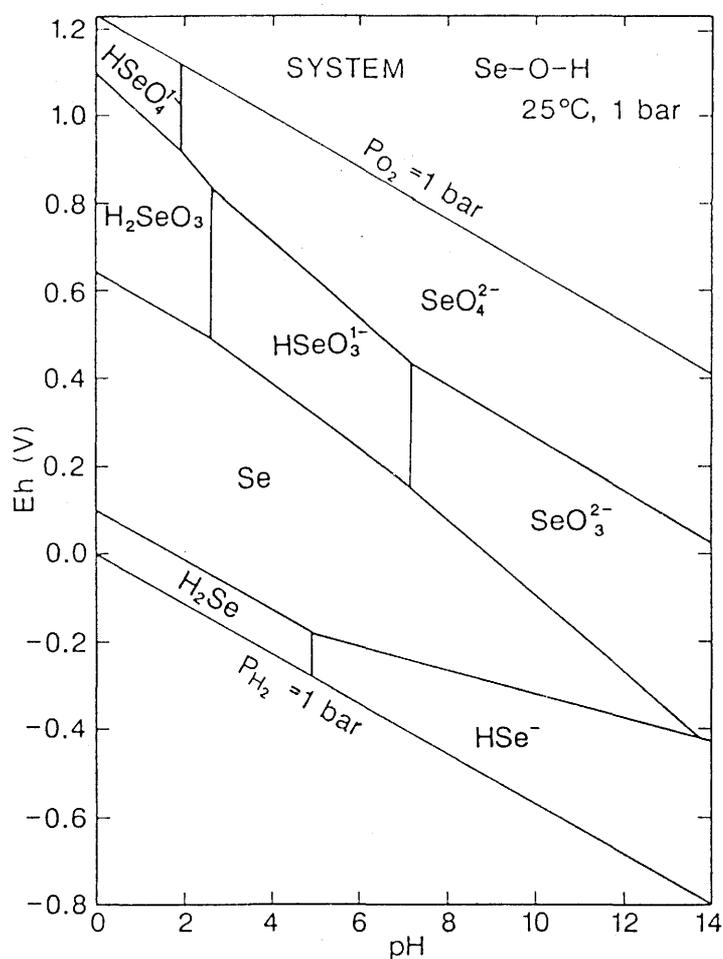


Figure 2. Eh-pH diagram for the system Se-O-H (Brookins, 1988). The activity of Se is 10^{-6} M.

3.2 Sorption Studies

3.2.1 Sorption on Pure Phases

Adsorption of the oxyanions of selenium on iron, aluminum and manganese oxides has been studied by several authors (Hingston et al., 1972, 1974, Balistrieri and Chao, 1987, 1990, Hayes et al., 1988, Zhang and Sparks, 1990). On amorphous iron oxyhydroxide and manganese dioxide selenite adsorbs more strongly than selenate and selenate does not adsorb on manganese dioxide. Adsorption of both species decreases with increasing pH value. Phosphate, silicate and molybdate compete with selenite for surface sites on both oxides (Balistrieri and Chao, 1990). Adsorption of selenite on goethite also decreases from high values at pH 4-6 to almost zero at pH 10 (Fig. 3) (Hingston et al., 1972, Balistrieri and Chao, 1987); very little of the adsorbed selenite can be desorbed by washing at constant pH value over a period of up to 15 days (Hingston et al., 1974). Similar behavior for the adsorption of selenite on gibbsite ($\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$) was found, but here, desorption was readily achieved (Hingston et al., 1972, 1974) The different desorption behavior might be explained by different types of surface complexes (monodentate vs. bidentate) (Hingston et al., 1974).

An EXAFS study of the adsorption of selenate and selenite on goethite ($\alpha\text{-FeOOH}$) showed that selenate forms a weakly bonded, outer-sphere complex and selenite forms a strongly bonded inner-sphere complex on the surface of the iron oxyhydroxide (Hayes et al., 1987). A kinetic study of the same system using pressure-jump relaxation showed a one-step mechanism for selenate adsorption leading to an outer-sphere complex. Selenite forms an outer-sphere complex first and a second step leads to an inner-sphere complex (Zhang and Sparks, 1990).

Sorption of selenium on a number of clay minerals has also been measured. It was found that adsorption of both selenate and selenite on kaolinite and montmorillonite decreases with increasing pH (Frost and Griffin, 1977, Bar-Yosef and Meek, 1987).

Silicates (augite, hornblende, vermiculite) were found to sorb substantial quantities of selenate ($>10^{-2}$ moles/kg) and only a small fraction of it could be desorbed. Sulfides (galena, sphalerite), carbonates (calcite, smithsonite), phosphates (apatite) and oxides (PbO) also take up selenate.

Desorption from sphalerite was not measurable, while desorption from apatite and calcite was possible to a large extent. There is no detailed interpretation given (Bird and Lopata, 1980).

Selenite is adsorbed by calcite and an anion exchange mechanism was proposed for this reaction (Cowan et al., 1990). The sorption capacity of calcite is smaller than the capacity of goethite, kaolinite and montmorillonite, but calcite can still be an important sorbent in a calcite rich environment. Phosphate and sulfate compete strongly with selenite for the sorption sites on calcite.

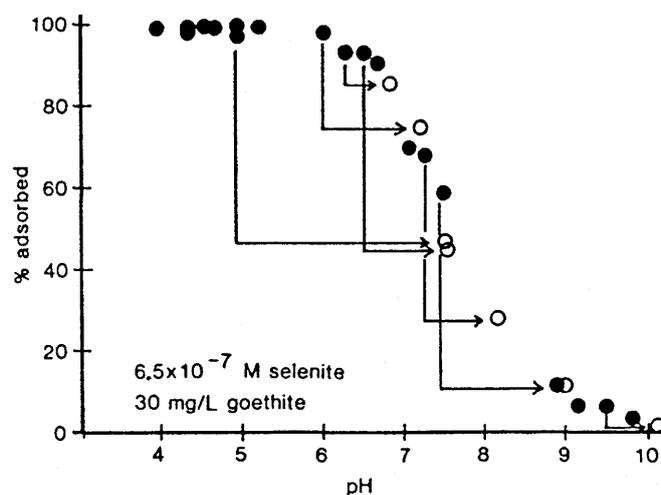


Figure 3. The adsorption (closed symbols) and desorption (open symbols) of selenite on goethite in 0.1 M KCl as a function of the equilibrium pH (Balistrieri and Chao, 1987).

3.2.2 Sorption on Natural Rocks

The sorption of selenium on basalts under oxidizing and reducing conditions was examined (Ames et al., 1982). Under oxidizing conditions, adsorption and desorption kinetics was observed over a wide concentration range and adsorption was modelled by a Freundlich isotherm. Reducing conditions were achieved by addition of hydrazine, which probably reduced all oxidized species of selenium to Se(0), which was then irreversibly deposited on the surface of the rocks. The disadvantages of using hydrazine to establish reducing conditions have been discussed before.

In another study, adsorption of selenium on the components of a natural rock has been investigated using autoradiography (Ticknor et al., 1989). Comparison of sorption under reducing conditions (system under nitrogen gas) and oxidizing conditions (system under air) indicated an increased sorption of selenium on the reducing (ferrous iron containing) minerals in the absence of oxygen; this could be interpreted as reduction of selenite to elemental selenium.

Sorption of selenium on rocks and fracture-filling minerals was studied under different conditions (Ticknor et al., 1988). The sorption coefficients for all rocks and conditions studied were less than 100 ml/g.

3.3 Geochemistry

In contrast to other elements discussed in this report, selenium is present in the environment in considerable concentrations. It is an essential trace element, but at elevated concentrations, it is a poison for animals and humans. For these reasons it has been of interest to different areas of environmental research and a number of useful studies on the behavior of selenium in nature have been published.

3.3.1 Selenium in Natural Waters

Selenium profiles in lakes and the sea give interesting information about the biogeochemical cycle of selenium. From the thermodynamic point of view, selenate should be the predominant inorganic species in oxygenated natural waters, but since oxidation is slow, there is often a considerable fraction of selenium present as selenite (Uchida et al., 1980, Cutter, 1982, Takayanagi and Wong, 1985). Se(VI) and organic selenium compounds are the major species in surface waters. With increasing depth, the concentrations of these species decrease and the concentration of Se(IV) increases. In the anoxic layer, the concentration of organic selenium compounds increases sharply, probably because of the decomposition of biological matter or by diffusion from the underlying sediment (Takayanagi and Wong, 1985). In one case a low concentration of selenide was found near the sediment (Cutter, 1982) (Fig. 4).

In a recent study, the geochemistry of selenium in the sediments of a coastal salt marsh was studied and the speciation was shown to depend on the seasonal variation of redox conditions (Velinsky and Cutter, 1991).

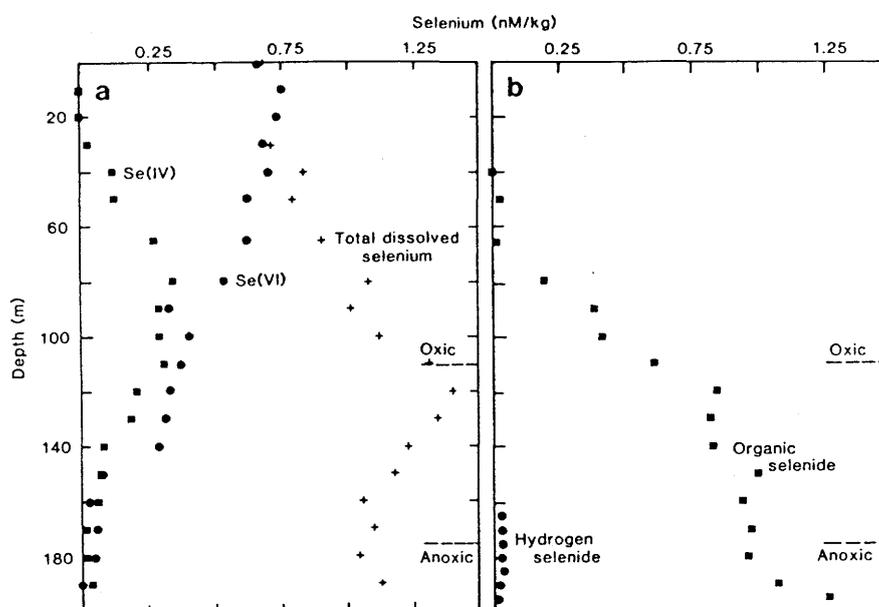


Figure 4. (a) Saanich Inlet profile of selenite, selenate and total dissolved selenium. (b) Profile of hydrogen selenide and organic selenide in the Saanich Inlet (Cutter, 1982).

Organisms play an important role in the transformation reactions between different redox states, because they take up inorganic selenium and when the organisms are degraded, selenium is released in the form of organic compounds (Cutter, 1982, Takayanagi and Wong, 1985, Masscheleyn et al., 1990). Bacteria present in soils, sediments and sewage sludge were found to be able to transform selenite and selenate to methylated selenium compounds (Chau et al., 1976, Reamer and Zoller, 1980). Bacteria can form elemental selenium from selenite (Reamer and Zoller, 1980).

Other bacteria were found to oxidize elemental selenium to selenite (Sarathchandra and Watkinson, 1981).

In a study of selenium species in surface waters, the nonvolatile seleno amino acids and the dimethylselenonium ion as well as the volatile methylated forms, dimethyl selenide and dimethyl diselenide, have been identified (Cooke and Bruland, 1987). The speciation of selenium in natural water has been modelled in a recent publication (Campanella et al., 1989). Extensive compilations of data on the occurrence of selenium in freshwaters (Cutter, 1989) and marine systems (Siu and Berman, 1989) have been published.

3.3.2 Selenium in the Geosphere

Under strongly reducing conditions selenium is usually associated with sulfur, because both elements coexist in the form of similar anions, S^{2-} and Se^{2-} , respectively, which undergo similar reactions and form mixed sulfide minerals. Under oxidizing conditions, selenium and sulfur are separated, because sulfur is easily oxidized to the very soluble sulfate, but selenium is only oxidized to selenate by strong oxidants and it usually stays in the less mobile forms of elemental selenium or selenite (Berrow and Ure, 1989).

In natural waters and under both reducing and oxidizing conditions, selenium is largely associated with iron minerals. In a reducing environment selenium may be present in the elemental form, or it is incorporated as selenide in the lattice of sulfide minerals, or it may form a pure selenium mineral. Tischendorf (1966) has published an extensive compilation on the selenium content of sulfur minerals and the selenium/sulfur ratios, which are typically in the range from 1:1,000 to 1:50,000. Selenium minerals are ferroselite ($FeSe_2$), clausthalite ($PbSe$), stilleite ($ZnSe$), cadmoselite ($CdSe$), berzelianite (Cu_2Se) and eucairite ($AgCuSe$) (Howard, 1977). In roll-type uranium bodies, selenium is concentrated as elemental selenium and ferroselite at the redox front (Howard, 1977). Native selenium has also been found in the sediments of ponds contaminated with selenium (Weres et al., 1989). In the absence of metal ions which form sparingly soluble selenium compounds, elemental selenium is the solubility controlling solid (Early et al., 1984). A compilation of data on selenium in the geosphere is given by Berrow and Ure (1989).

In a study of the selenium distribution in the overburden of coal and uranium deposits, selenium was found to be associated with detrital grains and with organic carbon (Naftz and Rice, 1989).

3.3.3 Volatile Selenium Compounds

It has been pointed out above, that selenium can form volatile organic compounds (Chau et al., 1976, Reamer and Zoller, 1980, Cooke and Bruland, 1987). The presence of bacteria which produce these compounds could therefore alter the migration behavior of selenium by orders of magnitude. This aspect should be considered for migration modelling and the question should be dealt with by microbiologists, who can judge the likelihood of the existence of such bacteria in the geosphere and the extent of volatilization.

Lerman (1989) pointed out another possibility for the volatilization of selenium. Selenium dioxide has a relatively high vapor pressure and especially at elevated temperature, this could lead to an increased migration in the vapor phase, in addition to transport by water flow.

3.4 Experiments

The mobility of selenium in the geosphere is determined by its adsorption on rocks, the retention of selenium colloids, and the coprecipitation of selenium ions with chemically similar ions. These mechanisms depend strongly on the oxidation state of the selenium. For this reason it is important to consider the behavior of every oxidation state expected in the far-field of a repository.

Selenite is the most soluble among the reduced forms of selenium and therefore potentially most mobile. To model its retention, adsorption of selenite by the rocks has to be studied. Selenite might be reduced by reducing components of the water or the rock, which leads to the formation of elemental selenium or selenide. It is important to determine, if such reactions occur, because they could strongly affect retention. In case of a reduction, the distribution coefficient will not simply be a function of the sorption properties of selenite and the rocks, but also a function of the redox equilibrium and of the sorption properties of the products formed. The determination of the oxidation state of adsorbed selenium can help distinguish between adsorption and a coupled adsorption/reduction reaction. The oxidation state can be determined by

spectroscopic methods (e.g. EXAFS) on the surface or by several chemical methods in solution after desorption.

Elemental selenium is very insoluble, but it forms colloids, which can be transported by waterflow. The size of the colloids depends on the conditions during their formation, but there is almost no information available in the literature. Interaction of native selenium with sulfur anions like sulfite and sulfide leads to mixed sulfur/selenium anions, which means an increase of the solubility and therefore also of the mobility. Since sulfide can frequently be found in reducing groundwaters and sulfur is usually present in considerably higher concentrations than selenium, such an interaction can play an important role.

Selenide forms very insoluble salts with many cations. There are no adsorption data for selenide available, but by analogy to other adsorbents, it can be concluded, that it forms relatively stable complexes on surfaces with the same elements as in solution. In the case of a large presence of sulfide, selenide will most likely share the fate of sulfur. If sulfide is precipitated, selenide will be included in the sulfide lattice, as it is observed in every sulfide mineral found in nature. This is another possible way for the deposition of selenium, and knowledge of the behavior of sulfide is required to predict such a mechanism.

3.4.1 Handling of Selenium

Stability of Selenium Solutions

To assess the stability of selenium(IV) and selenium(VI) solutions at ppb levels, a number of storage tests have been performed (Cheam and Agemian, 1980). Different container materials have been used and solutions of selenium in distilled water and natural water have been stored at different pH values over long periods of time. Polyethylene containers and a pH of 1.5 were found to provide optimum conditions for the preservation of both types of water for up to 125 days. The low pH inhibits growth of algae and bacteria which take up selenium. The analytical results will be perturbed by such bacteria, unless these organisms are digested to release selenium (Cheam and Agemian, 1980). In another study Raber et al. (1983) tested a large number of polymeric and metallic materials with respect to sorption of selenium. A review by Robberecht and Van Grieken (1982) also considers the problem of sorption loss.

Preparation of Pure Selenate Solutions

A number of methods have been suggested for the removal of traces of selenite (SeO_3^{2-}) from a solution of selenate (SeO_4^{2-}). Selenite can be selectively adsorbed on aluminium oxide in acid (Knab and Gladney, 1980) or on kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) at pH 7.5 (Alemi et al., 1988). Alternatively, selenite can be removed from a selenate solution by extraction with ammonium sec-butyl dithiophosphate (Ahlrichs and Hossner, 1987).

3.5 Analytical Methods

Reviews of methods for analysis of both inorganic and organic selenium compounds have been written by Robberecht and Van Grieken (1982), Raptis et al. (1983), Lewis and Veillon (1989) and Tan and Rabenstein (1989).

3.5.1 Methods for Preconcentration

Since selenium concentrations in natural waters are generally very low, preconcentration methods have been developed. Selenite can be preconcentrated by extraction of its complex with ammonium 1-pyrrolidinedithiocarbamate into chloroform and back-extraction into nitric acid. Total selenium can be preconcentrated by addition of an acid solution of sodium tellurite and hydrazine sulfate to the sample. The mixture is boiled for 15 minutes and the precipitate that forms is filtered off and redissolved in a small amount of acid (Takayanagi and Wong, 1983).

3.5.2 Radioactive Tracers

Selenium can be measured by counting the gamma radiation of the ^{75}Se tracer. Due to the relatively short half life of this isotope ($t_{1/2}=120$ days), corrections for decay have to be made during long term experiments. It should be noted that commercial ^{75}Se tracer in the form of sodium selenite always contains a considerable amount of sodium selenate (Ahlrichs and Hossner, 1987).

3.5.3 Neutron Activation Analysis

For a method involving neutron activation and separation of selenium by ion exchange, a detection limit of ca. 10 ppb is given (Knab and Gladney, 1980).

3.5.4 Electrochemical Methods

The redox couple Se(IV)/Se(VI) is not reversible at a platinum electrode and the redox potential of a selenite/selenate solution can not be determined using an electrode (Runnells et al., 1987, Runnells and Lindberg, 1990).

Selenium(VI) can not be reduced at a mercury electrode, but Se(IV) is electroactive and can be reduced in acid solution to Se(-II). This allows determination of selenium by adsorptive cathodic stripping voltammetry in the presence of copper, where Cu_2Se is adsorbed on the hanging mercury drop electrode. Se(VI) can be quantitatively reduced to Se(IV) by UV irradiation at pH 8.2. The detection limit is 0.01 nM for a deposition time of 15 minutes (van den Berg and Khan, 1990).

3.5.5 X-ray Fluorescence Spectrometry

Selenium can be precipitated as elemental selenium and determined by x-ray fluorescence (XRF). All selenium species are reduced to elemental selenium by treatment with sulfur dioxide/hydroxylamine hydrochloride or stannous chloride. Selenium is then filtered off and determined by x-ray fluorescence. A reasonable precision (better than 15 %) can only be reached for selenium levels of above 1 μg (Howard, 1977). Another method uses ascorbic acid to reduce selenite or thiourea to reduce both selenate and selenite and the elemental selenium formed is sorbed on activated carbon for quantitative determination by X-ray fluorescence spectrometry. The detection limit is 50 ng/l for Se(IV) and 60 ng/l for total selenium (Robberecht and Van Grieken, 1980).

3.5.6 Spectrophotometric Methods

Se(IV) can be determined fluorimetrically by complexation with 2,3-diaminonaphthalene to form 4,5-benzopiazselenol. The excitation wavelength is 380 nm and the fluorescence intensity is measured at 520 nm. The detection limit after preconcentration is about 20 pM for a 1 liter sample (Takayanagi and Wong, 1983).

The formation of a piaszelenol can also be used for the spectrophotometric determination of selenium. Se(IV) reacts with 4,5,6-triaminopyrimidine to a piaszelenol, which has an absorption maximum at 362 nm. The detection limit, after preconcentration by adsorption of Se(IV) on iron hydroxide, is 0.1 ppm (Bodini and Alzamora, 1983). Another method is the reaction of Se(IV) with 5,5-dimethyl-1,3-cyclohexanedione (dimedone) in acid aqueous solution to give a benzoxaselenol with an absorption maximum at 313 nm. The product can be extracted into chloroform where it has an absorption maximum at 300 nm. The detection limit is 0.1 ppm (Bodini et al., 1990).

3.5.7 Atomic Absorption Spectrometry

Selenite can be determined by atomic absorption spectrometry. Selenate has to be transformed to selenite by heating the solution which has been acidified with hydrochloric acid (Brimmer et al., 1987, Pettersson and Olin, 1991). If the solution is boiled for half an hour, selenate is reduced quantitatively to selenite by chloride, but the vessel has to be closed to avoid losses by evaporation of volatile selenium compounds (Brimmer et al., 1987). The selenite is reduced to the hydride by reaction with sodium borohydride. The hydride is stripped from the solution with helium gas, trapped in a liquid nitrogen cooled U tube and detected by atomic absorption spectrometry. The same stripping apparatus can be used to separate the volatile methyl selenium species. The detection limit for this system is 0.5 ng, which corresponds to 5 ppt for 100 ml of solution. (Cutter, 1978). Methods for the reduction of selenium species have been reviewed by Bye (1983).

3.5.8 Gas Chromatography

Another method for the determination of Se(IV) is the derivatization of selenite with 1,2-diamino-3,5-dibromobenzene to 4,6-dibromopiazselenol, which can be extracted and determined by gas chromatography, using an electron capture detector (Uchida et al., 1980).

3.5.9 Ion Chromatography

The soluble selenium species selenite and selenate can be quantitatively measured by ion chromatography (Bar-Yosef and Meek, 1987).

3.5.10 Determination of Elemental Selenium

Se(0) in sediments can be determined as the difference between the extract with the thiophyllic reagent sodium sulfide, which solubilizes Se(0) (and also compounds like Se_2S_4) by formation of polysulfide species of the form S_nSe^{2-} , and the extract with a basic solution of sodium chloride and sulfate. Since the former extract contains not only Se(0), but also selenide, selenate and part of the organic selenium, these have to be accounted for by the second extraction, which contains the above mentioned selenium compounds, but not Se(0).

The resulting selenium concentrations can be determined by X-ray fluorescence analysis or atomic absorption spectroscopy, using a hydride generator (Weres et al., 1989). Another method to resolubilize elemental selenium is the reaction with sulfite at neutral pH. The product is the anion selenosulfate SSeO_3^{2-} (Warren, 1968, Velinsky and Cutter, 1990). Alternatively elemental selenium can be extracted by carbon disulfide (CS_2) (Howard, 1977). Red amorphous selenium is soluble in carbon disulfide, but black crystalline selenium is not (Oremland et al., 1989).

3.5.11 X-ray Absorption Spectroscopy (EXAFS, XANES)

X-ray absorption spectroscopy methods like EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near edge structure) allow the determination of the geometry and oxidation state of atoms adsorbed on the surface of a solid phase. With this method, it was possible to show that selenite forms inner-sphere complexes and selenate forms outer-sphere complexes on goethite (Hayes et al., 1987, Brown et al., 1989). The concentrations required for these methods are above trace levels.

4. TECHNETIUM

4.1 Solution Chemistry

Technetium is a transition metal with the electron configuration $[\text{Kr}]4d^55s^2$. There are many possible oxidation states from VII downwards. Not all of these oxidation states have been well characterized, due to their limited stability. The speciation in solution is complicated by the interaction of redox reactions, complex formation, hydrolysis, polymerisation and colloid formation (Hughes and Rossotti, 1987). In the aqueous phase, Tc(VII) and Tc(IV) are the dominant species, while the lower oxidation states are stable only in the presence of suitable complex formers.

Technetium(VII) forms the pertechnetate anion TcO_4^- , which is the common species in oxidizing media. Pertechnetic acid, HTcO_4 , is a strong acid. The reported dissociation constants differ widely, but it is unlikely, that undissociated pertechnetic acid exists in appreciable quantities even at very low pH values. There are no complexes of pertechnetate known in aqueous solution. Some pertechnetate salts are moderately soluble (CsTcO_4 solubility 0.014 M, AgTcO_4 solubility 0.02 M at 20°C).

Pertechnetate can be reduced by metal ions such as Fe(II), Sn(II), Cr(II), Cu(I), Ti(III), Pu(III) or metals such as Fe, Zn/HCl, Na/Hg, Zr, Al, Hg. In concentrated hydrochloric acid, pertechnetate is instantly reduced to $\text{Tc}^{\text{V}}\text{OCl}_4^-$ and slowly further to $\text{Tc}^{\text{IV}}\text{Cl}_6^{2-}$. The rate of this reaction is strongly dependent on the concentration of HCl. Reduction of Tc(VII) to Tc(V) can be achieved with hypophosphorous acid in chloride media, dithiolate ligands, thiourea and ascorbic acid in the presence of iron. Dithionite reduces Tc(VII) to Tc(V) quantitatively between pH 11 to 13, and to a mixture of Tc(V) and Tc(IV) at lower pH values. Hydrazine and sodium tetrahydroborate reduce Tc(VII) to Tc(IV), while hydroxylamine reduces Tc(VII) to Tc(I) and other oxidation states. The reduction by sulfite in dilute acid is slow, but quantitative. The products are sulfite complexes of Tc(III), Tc(IV) or Tc(V) (Hughes and Rossotti, 1987). Technetium(VII) is not reduced to lower oxidation states by hydrogen, probably for kinetic reasons (Guppy et al., 1989).

Technetium (VI) is unstable; it disproportionates to Tc(VII) and Tc(IV) in neutral media, and to Tc(VII) and Tc(V) in alkaline media. There are many indications that the technetate ion, TcO_4^{2-} , exists, both in solution and in solids.

The acid H_2TcO_4 is moderately strong with pK values of ca. 0 and 9 (Hughes and Rossotti, 1987).

Technetium(V) as the oxotechnetium(V) ion is only stable in aqueous solution in the form of complexes with appropriate ligands. In solution Tc(V) disproportionates to Tc(IV) and Tc(VII) via Tc(VI). (Davison and Jones, 1982).

Technetium(IV) is the second important oxidation state. The existence of the Tc^{4+} aquo ion has been suggested for very strongly acidic solutions, but under most conditions, hydrolyzed species like TcO^{2+} or $\text{Tc}(\text{OH})_2^{2+}$, $\text{TcO}(\text{OH})^+$ and $\text{TcO}(\text{OH})_2$ are present. For very concentrated hydroxide solutions, the hydroxo complex $\text{Tc}(\text{OH})_6^{2-}$ has been suggested. Tc(IV) can form dimers and polymers and the sparingly soluble oxide $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$. Oxidation of Tc(IV) to Tc(VII) by air is slow, and a number of complexes are resistant to oxidation by oxygen (Hughes and Rossotti, 1987).

Technetium(III) disproportionates to Tc(IV) and Tc(0) at pH values above 4, but it can be stabilized by certain ligands such as tripolyphosphate, phosphate or carbonate. It has been suggested that TcO^+ is the dominant species in acid solution below pH 3.5. Tc(III) is easily oxidized by air to Tc(VII) via Tc(IV) (Hughes and Rossotti, 1987).

Technetium(II) is expected to exist only under highly reducing conditions. Technetium(+I, 0, -I) are not important in aqueous media (Hughes and Rossotti, 1987).

The lower oxidation states of technetium can be oxidized to Tc(VII) by a number of oxidants. Ce(IV) in dilute acid oxidizes Tc very rapidly to Tc(VII), while oxidation by bromate (BrO_3^-), bromine (Br_2), permanganate (MnO_4^-), iodate (IO_4^-), peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$) in the presence of Ag^+ , hydrogen peroxide (H_2O_2) and air is slow in acid solution (Vine and Wahl, 1982).

There are several literature reviews dealing with the solution chemistry of technetium (Schwochau, 1983, Hughes and Rossotti, 1987, 1988). Since the technetium isotope $^{99\text{m}}\text{Tc}$ is widely used in nuclear medicine for imaging purposes, a

major fraction of the studies of technetium complexes deals with organic ligands which are quite different from those encountered in natural waters. These studies are not very relevant to this review.

Several reviews of the organic chemistry of technetium have been published (Jones and Davison, 1982, Davison and Jones, 1982, Hughes and Rossotti, 1987).

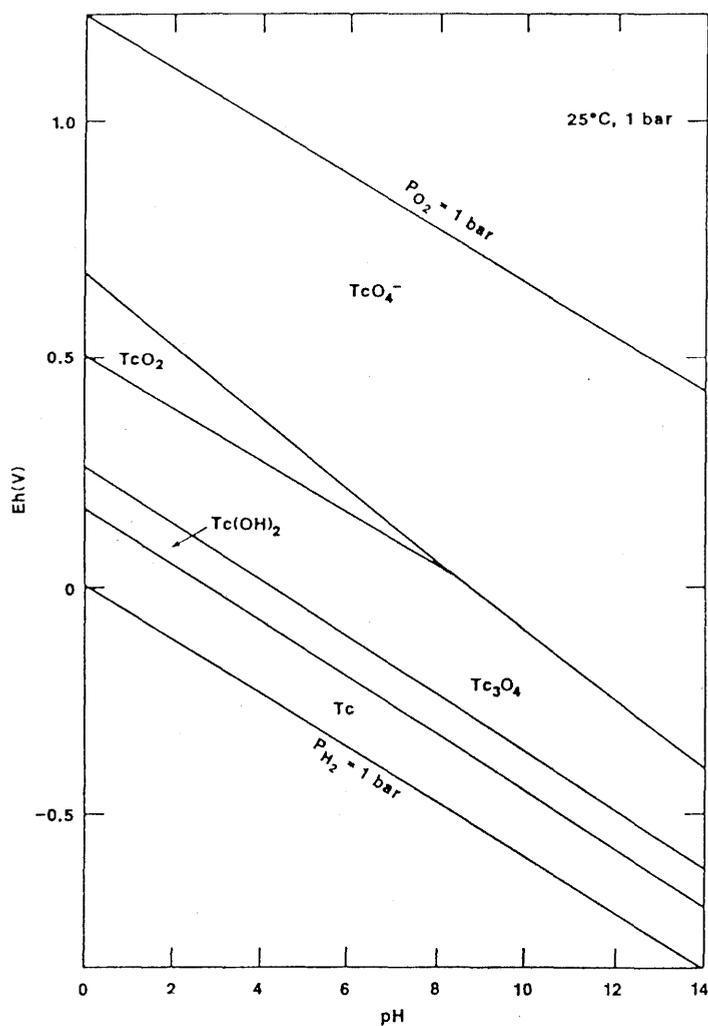


Figure 5. Eh-pH diagram for the system Tc-O-H (Brookins, 1988). The assumed activity for dissolved technetium is 10^{-8} M.

4.2 Sorption Studies

4.2.1 Sorption on Pure Phases

Rocks and minerals containing mostly silicates, aluminosilicates and feldspars adsorb very little technetium(VII), whereas adsorption is significant on rocks containing sulfides of copper, iron and lead. Technetium(VII) sorbs more efficiently on sulfides whose metal ion is in a lower oxidation state. From a comparison of different sulfide minerals, it was concluded that both metal ions in low oxidation state and sulfide ions can reduce Tc(VII) (Winkler, 1989).

Powdered iron and lead eliminate technetium(VII) from solution. It is concluded that a reduction of technetium occurs on the surface of these solids (Strickert et al., 1980).

In one study, it was conclusively shown by Fourier transform infrared spectroscopy of the product that technetium(VII) is reduced on the surface of magnetite (Fe_3O_4) to $\text{Tc}^{\text{IV}}\text{O}_2$ (Haines et al., 1987). It was also shown that the extent of adsorption on reducing solids depends on the oxygen content of the system (Vandergraaf et al., 1984, Wood et al., 1987) (Fig. 6). This can be explained by the fact that oxygen is reduced by magnetite more quickly than technetium(VII).

In the presence of oxygen, the extent of reduction of technetium by reducing solids is decreased in comparison to that under anoxic conditions, probably because reduced technetium is reoxidized by oxygen (Lieser and Bauscher, 1987). In contrast to technetium(VII), soluble technetium(IV) is rapidly removed from solution by iron(III) oxyhydroxides (Walton et al., 1986). Experiments with technetium(IV) are difficult, because it is relatively insoluble and easily oxidized to technetium(VII) by traces of oxygen present in the system.

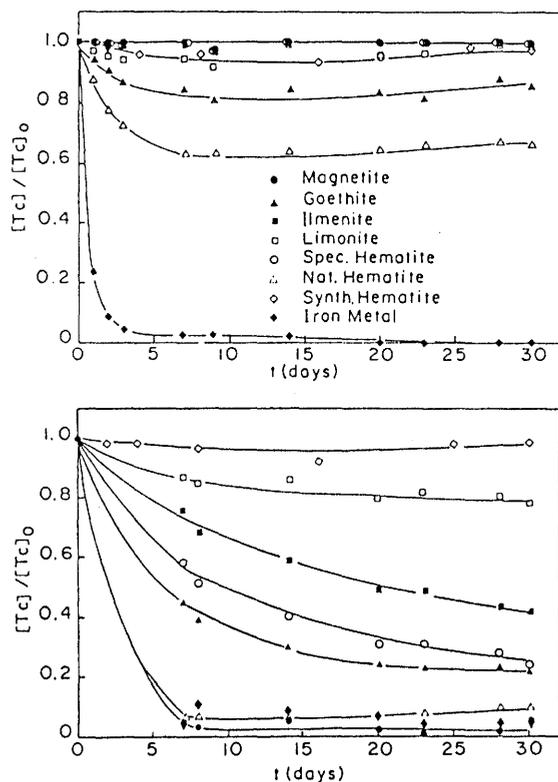


Figure 6. Decrease in technetium concentration as a function of time for solutions in contact with iron metal and iron minerals under (a) oxic and (b) anoxic conditions (Vandergraaf et al., 1984).

4.2.2 Sorption on Natural Rocks

Sorption of technetium under oxic conditions is very low. This can be explained by the fact that the stable species is the pertechnetate anion, which is very soluble and sorbs very weakly. Under reducing conditions, the relatively insoluble Tc(IV) is the predominant oxidation state; it forms the solid phases TcO_2 or $TcO(OH)_2$, respectively (Lieser and Bauscher, 1987, 1988).

Sorption under anoxic conditions is increased if reducing minerals are present in the natural rock (Winkler et al., 1988). In a comparison between different rocks (basalt, granite, shales), it was shown that if the rock/water system exhibited a redox potential which lay in the stability field of Tc(VII), there was virtually no adsorption, but if the potential lay in the stability field of Tc(IV), technetium was strongly adsorbed (Bondietti and Francis, 1979).

In two other studies on the adsorption of technetium on basalt under anoxic conditions, strongly contrasting results were obtained. In one case no adsorption was observed, while in the other, a considerable fraction of technetium was adsorbed (Kelmers et al., 1984, Meyer et al., 1984). It was shown that traces of oxygen, for example present in the plastic material of the tubing, can affect sorption values strongly (Meyer et al., 1985). Grinding the rock with a crusher made from steel can introduce metal iron, which reduces technetium and produces results which are not representative of the natural situation (Meyer et al., 1984). All this leads to the conclusion that some of the discrepancies between published studies are caused by experimental problems.

To attain reducing conditions, hydrazine has sometimes been used as a so called "redox buffer". This method has been criticized, because it only demonstrates, that hydrazine reduces technetium, but not that a certain rock will reduce technetium (Meyer et al., 1984). The use of hydrazine has been discussed in the chapter on redox conditions.

4.3 Geochemistry

Because all isotopes of technetium are radioactive and have relatively short half lives on a geological time scale, no primordial technetium exists, but it has been found in the geological environment in trace concentrations. This technetium either formed by the action of cosmic radiation on molybdenum, ruthenium or niobium or is a product of the spontaneous fission of uranium (Onishi et al., 1981). It has also been released into the environment by reprocessing plants, nuclear power stations and by nuclear bomb explosions (Riley and Siddiqui, 1982). Concentrations in natural waters have been measured, but oxidation states have not been determined. A review of technetium in the environment has been published by Luxenburger and Schüttelkopf (1984) and in the proceedings of a meeting on the same subject by Desmet and Myttenaere (1986).

4.4 Experiments

For practical purposes, it is generally assumed that only the relatively stable oxidation states Tc(IV) and Tc(VII) exist in the geosphere. Thermodynamically this seems to be quite realistic, but other oxidation states must be involved as intermediates in the redox reactions between Tc(IV) and Tc(VII) and changing conditions can influence these reactions.

Technetium(IV) forms sparingly soluble oxides, which limits its mobility in a reducing environment. Technetium(VII) exists in the form of the very soluble pertechnetate anion. Reduction of Tc(VII) and oxidation of Tc(IV) occur very easily. For this reason, the most important question for the modelling of migration concerns changes of the oxidation state.

Because of its chemical properties, technetium is a very difficult element to study. Tc(IV) is very sensitive to oxidation by small traces of oxygen, which makes its handling very difficult and can lead to erroneous results. The first aim will be to establish well controlled redox conditions in the laboratory. This means that no change of the redox state will be caused by oxygen traces present in the experimental system. Meaningful sorption measurements can only be performed, if this goal can be achieved. Working in the glove-box under a controlled atmosphere of nitrogen or nitrogen/carbon dioxide will exclude oxygen to a large extent, but traces of oxygen can be introduced when material is brought into the boxes and when samples are removed for analysis. Stable redox conditions in the experimental system have to be achieved, either by making sure there is no depletion of the redox determining components during the reaction or by controlling the redox conditions artificially. Since these problems are much more pronounced for technetium than for most of the other elements of interest, it is recommended that a study of technetium is deferred until reliable methods for controlling oxidation states have been introduced and work on the elements which pose fewer problems is finished.

4.5 Analytical Methods

An extensive review of analytical methods for technetium has been published by Long and Sparkes (1988).

4.5.1 Methods for Preconcentration

Technetium can be preconcentrated by several methods. Liquid extraction, coprecipitation, adsorption on ion exchangers, and electrodeposition have been used for this purpose (Riley and Siddiqui, 1982).

4.5.2 Radioactive Tracers

Technetium-99 ($t_{1/2} = 2.1 \times 10^5$ years) is the only long-lived isotope which can be obtained in weighable amounts. It is a beta emitter with no gamma radiation and can be measured by liquid scintillation spectrometry. The detection limit is around 10^{-10} mol/l ^{99}Tc , depending on equipment and the required accuracy. Technetium-99m is a tracer, which is frequently used for medical applications. It is a gamma and beta emitter with a half life of 6 hours. Technetium-95m, which is a gamma emitter with a half-life of 60 days, can also be used as a tracer. Technetium-97m has a half life of 91 days.

4.5.3 Electrochemistry

A number of electroanalytical methods for technetium are available. Polarography, voltammetry, inverse voltammetry, coulometry and other methods involving solid electrodes have been used (Jovtshev et al., 1975, Russell, 1982, Hughes and Rossotti, 1987, 1988, El-Reefy et al., 1989). Many electrochemical reactions of technetium are thermodynamically irreversible. Slow kinetics can lead to uncertainties in the identification of the reaction products. The formation of the different oxidation states in the reduction of pertechnetate, as well as the actual value of the polarographic half-wave potential ($E_{1/2}$) are influenced by the pH value, electrode material, the nature of the supporting electrolyte and the presence of oxidants and complexing

agents. The influence of these different conditions has been extensively reviewed by Hughes and Rossotti (1987).

4.5.4 Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) has been used to analyze the product of the reaction between pertechnetate in solution and magnetite. By comparing the Tc-O vibration bands in different technetium compounds with the observed band on the magnetite surface, the researchers could show that TcO_2 is formed on the surface of the magnetite (Haines et al., 1987).

4.5.5 Selective Determination of Individual Oxidation States

Separation and selective measurement of individual oxidation states of technetium can be achieved by different methods such as solvent extraction, coprecipitation or adsorption. The pertechnetate ion (TcO_4^{2-}) can be separated by extraction with tetraphenylarsonium ion in chloroform (Vine and Wahl, 1982) or by similar methods with other organic complex formers. Technetium(IV) can be coprecipitated with molybdenum oxinate ($\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$), tetraphenylarsonium perrhenate ($(\text{C}_6\text{H}_5)_4\text{AsReO}_4$), potassium hexachlororhenate (K_2ReCl_6) or manganese dioxide (MnO_2) (Vine and Wahl, 1982).

5. PALLADIUM

5.1 Solution Chemistry

Palladium is a noble metal with the electron configuration $[\text{Kr}]4d^{10}5s^0$. It exists in the Pd(0) metal form and as the Pd(II) ion. Due to its noble character, Pd(II) can be reduced to the metal relatively easily. Upon reduction, Pd(II) can form metallic colloids (Klotz et al., 1985). There is relatively little information available about the hydrolysis of Pd(II). The following values are available: $\text{p}K_1 = 1.9$, $\text{p}K_2 = 3.8$, $\text{p}K_3 = 15.9$, $\text{p}K_4 = 29.4$ ($I=0$) (Nabivanets and Kalabina, 1970, Baes and Mesmer, 1976, Baeyens and McKinley, 1989, Wood, 1991).

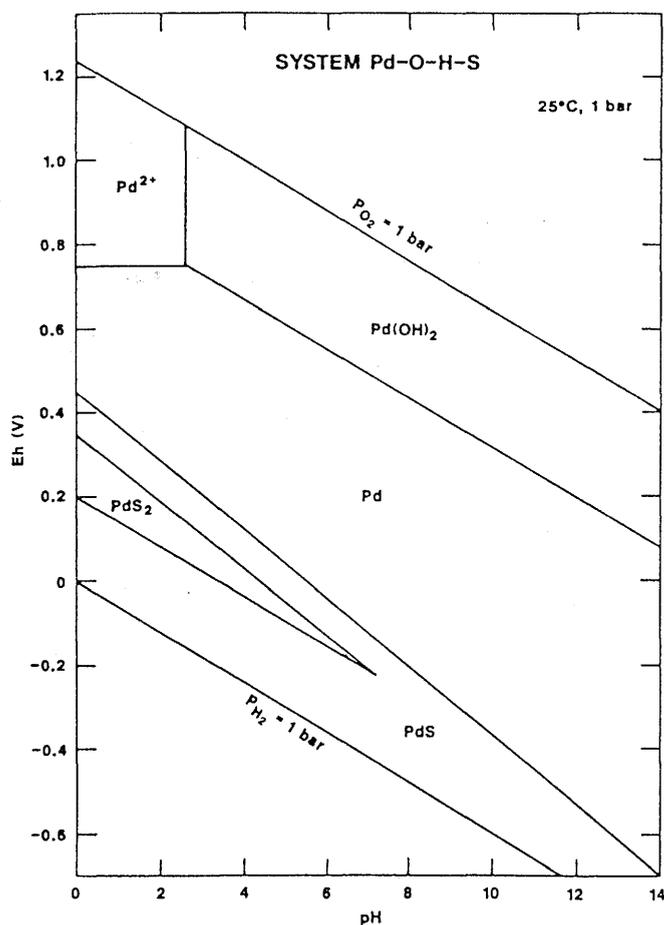


Figure 7. Eh-pH diagram for the system Pd-O-H-S (Brookins, 1982). Assumed activities are: $\text{Pd}=10^{-8}$ M, $\text{S}=10^{-3}$ M.

At higher concentrations, hydroxo polymers are formed even at low pH values. The solubility product of $\text{Pd}(\text{OH})_2$ is 1.1×10^{-29} (Nabivanets and Kalabina, 1970). Palladium has a high electronegativity and a high polarizability. It is a soft acid, which forms strong complexes with soft ligands like sulfide, chloride, bromide or cyanide and weak complexes with hard ligands like carbonate, sulfate, nitrate or fluoride. Chloro and bromo complexes of palladium(II) have been studied by Elding (1972a,b, 1973) and by Tait et al. (1991). Two compilations of thermodynamic data of palladium compounds have been published recently (Phillips et al., 1988, Baeyens and McKinley, 1989).

5.2 Sorption Studies

5.2.1 Sorption on Pure Phases

In a recent study, adsorption of palladium(II) on pyrite (FeS_2), galena (PbS) and sphalerite (Zn,FeS) has been measured and reduction of Pd(II) to Pd(0) on the surface of the minerals has been demonstrated by high resolution X-ray photoelectron spectroscopy (XPS). It was also shown that the extent of the reduction depends on solution parameters such as pH and chloride concentration, as well as on the surface structure (e.g. defects) (Hyland and Bancroft, 1990).

5.2.2 Sorption on Natural Rocks

Very few adsorption studies have been performed for palladium. An early compilation of sorption coefficients (Vandergraaf, 1982) cites only one (unpublished) study. Subsequently, some preliminary sorption experiments on several different sands were carried out and a range of sorption coefficients have been published ($1 < R_s < 650 \text{ cm}^3/\text{g}$) (Klotz et al., 1985). The expected formation of colloids was not observed in this study.

5.3. Geochemistry

5.3.1 Palladium in the Geosphere

Due to its noble character and its catalytic properties, palladium is of commercial interest and its occurrence in the geosphere has been studied for a long time. The majority of the deposits of the platinum group elements are of magmatic origin, but secondary deposits have been found, which give interesting clues to the geochemical cycle of palladium. Palladium is relatively mobile, because it forms soluble chloride complexes, which can be transported by water. Palladium is often enriched in base metal sulfides; such enrichment can be explained by an adsorption/reduction mechanism as described above (Hyland and Bancroft, 1990). When these rocks are weathered, the sulfides are decomposed by oxidation and palladium is released. Palladium metal particles can accrete to form the larger particles found in alluvial deposits (Cousins, 1973, Bowles, 1986).

Under reducing conditions, the solubility limiting phase is palladium metal and the solubility is very low. Under oxidizing conditions the solubility limiting phase is PdO or Pd(OH)₂ and, due to the presence of dissolved hydroxo complexes, the solubility is higher by several orders of magnitude (Nabivanets and Kalabina, 1970).

Palladium is mobile in acid soils, probably as a chloride complex. Examination of its association with soil components has shown that it is present predominantly in the so called magnetic fraction (mainly magnetite), in the clay portion and in the organic fraction (Fuchs and Rose, 1974). The association with magnetite and organic matter can be explained by an adsorption/reduction mechanism. Palladium was found to be more mobile than platinum.

5.3.2 Palladium in Natural Waters

Speciation calculations show that palladium in natural waters is predominantly present in the form of the dihydroxo complex (Baeyens and McKinley, 1989). In seawater, the relatively high chloride concentration leads to the predominance of chloro complexes, which suppress hydrolysis of Pd(II) (Kump and Byrne, 1989). It was found that amino acids compete with chloride as complexing agents for palladium

in seawater, even at the relatively low concentrations present in natural waters (Li and Byrne, 1990).

5.4 Experiments

Palladium as a noble metal is expected to exist in the metal form under the reducing conditions encountered in both the near-field and the far-field of a repository. Even in the case of an unexpected intrusion of oxygen, palladium metal will not be oxidized. If palladium metal is the solubility limiting phase, the solubility can vary over a wide range from 10^{-17} M in a crystalline groundwater up to 10^{-2} M in a cement pore water (Baeyens and McKinley, 1989). This low solubility under far-field conditions leads to a very small mobility and the priority of palladium in an experimental program is therefore not very high.

The only mechanism which could lead to an increased mobility of palladium is the formation of colloids (Klotz et al., 1985). They could already exist in the waste matrix or they could be formed during leaching of the waste matrix in the reducing near-field environment. These possibilities, however, do not belong to the scope of this study, which is only concerned with the far-field.

There is one point, which could justify some research on palladium, even under the conditions mentioned. As Hyland and Bancroft (1990) have shown, the oxidation state of palladium on the surface of solids can be measured conveniently. For this reason, palladium is a suitable model reductant for studies of any redox reaction on reducing mineral surfaces, which can be expected to occur between some elements and some minerals.

5.5 Analytical Methods

5.5.1 Preconcentration Methods

Several methods for preconcentration of palladium have been developed. Silica gel treated with γ -aminopropyltriethoxysilane can be used to remove the chloro complex of palladium(II) from solution in a pH region from 2-5 (Tong et al., 1990). Another solid-liquid extraction method uses dimethyl glyoxime, acenaphthenequinone dioxime or a mixture of both on naphthalene as carrier to remove palladium from solution. After stripping with dimethylformamide-n-butylamine the concentration of palladium can be determined with atomic absorption spectrometry. The sensitivity of this method is around 4×10^{-8} g/ml, depending on the ligand used for extraction (Usami et al., 1990).

5.5.2 Radioactive Tracers

The palladium isotope which could be used as a tracer is ^{103}Pd , but it is not commercially available and its relatively short half life of 17 days requires corrections for long-term experiments. The long-lived isotope present in nuclear fuel waste is ^{107}Pd with a half-life of 6.5×10^6 years.

5.5.3 Spectrophotometry

Palladium can be determined spectrophotometrically. There are a number of suitable ligands which form strong complexes with palladium, but some are relatively insoluble in water, so extraction into an organic liquid phase is required. Some ligands, however, form a complex which is sufficiently soluble in water and a relatively simple procedure can then be used.

A convenient method is the complexation of palladium with xylenol orange in strongly acidic solution, where palladium is selectively complexed. The complex can be measured spectrophotometrically at 518 nm in a concentration range of 0.2 - 4 ppm (Otomo, 1963). Alternatively palladium can be complexed by sulfochlorophenolazorhodanine, but the ligand does not seem to be available commercially. The palladium

complex absorbs at 488 nm and the detection limit is 0.004 $\mu\text{g/ml}$ (Shiundu et al., 1990). Another method uses 2-(5-bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropyl-amino)aniline to form a palladium complex which absorbs at 612 nm and allows a detection limit of 2 $\mu\text{g/l}$ (Sakai and Ohno, 1988). 4-(3,5-dichloro-2-pyridylazo)-1,3-diaminobenzene is another sensitive and selective complex former for the spectrophotometric determination of palladium, but it also seems to be unavailable commercially (Kai et al., 1983).

Methods have been developed to increase selectivity and sensitivity. Chelation with 2-(5-bromopyridylazo)-5-diethylaminophenol, followed by separation using reversed phase liquid chromatography, enables the palladium complex to be determined spectrophotometrically at a wavelength of 565 nm with a molar absorptivity of 34000. The detection limit is 5.3×10^{-10} g (Zhao and Fu, 1990).

5.5.4 Atomic Absorption Spectrometry

Palladium can also be determined by atomic absorption spectrometry (Lockyer and Hames, 1959, Hyland and Bancroft, 1990). The detection limit on a modern instrument is around 2 ppb, corresponding to ca. 2×10^{-8} M.

5.5.5 Inductively Coupled Plasma-Mass Spectrometry

This sensitive method allows the determination of palladium at low concentrations. The detection limit is around 0.1 ppb, corresponding to ca. 10^{-9} M (Wernli, 1990).

5.5.6 Electrochemistry

In the presence of an excess of ligand, the electrode potentials of palladium complexes can be determined and the potentials obey the Nernst equation. If the ligand/metal ratio is below four, the response of the metal electrode is poor, probably due to the dependence of the exchange current on the concentration of the free ligand (Hancock et al., 1977).

5.5.7 X-ray Photoelectron Spectroscopy (XPS)

With high-resolution X-ray photoelectron spectroscopy (XPS, or ESCA for electron spectroscopy for chemical analysis), the binding energy of electrons of an atom on a solid surface can be determined. This method allows different oxidation states of an element to be distinguished and this helps decide whether an adsorbed Pd(II) ion stays in this oxidation state or is reduced to Pd metal (Hyland and Bancroft, 1990).

6. TIN

6.1 Solution Chemistry

Tin can exist in several oxidation states ranging from -4 to +4, but only the +2 and +4 states are important in aqueous media. In hydrochloric acid solution, tin(II) and tin(IV) ions form a dimeric interaction complex, which shows an optical interaction absorption (Browne et al., 1951). SnO_2 is only soluble to an appreciable extent in strong acid or strong base, whereas SnO is much more soluble. The solubility of tin under different redox conditions is discussed by Early et al. (1984). Thermodynamically SnO is unstable toward oxidation to SnO_2 by water, but this reaction is very slow under laboratory conditions. Tin(II) hydrolyzes to a number of mono- and polynuclear hydroxo species; probably SnOH^+ , $\text{Sn}_2(\text{OH})_2^{2+}$ and $\text{Sn}_3(\text{OH})_4^{2+}$ predominate. The hydrolysis constants (pK) given for these complexes are 3.4, 4.77 and 6.88 respectively (Baes and Mesmer, 1976). In alkaline solutions, the main species is $[\text{Sn}(\text{OH})_3]^-$, but there is also evidence for the dinuclear ion $[\text{Sn}_2(\text{OH})_4\text{O}]^{2-}$ (Harrison, 1989). The main species present in alkaline tin(IV) solutions is $[\text{Sn}(\text{OH})_6]^{2-}$, which can be dehydrated in less basic solutions to give ions such as $[\text{SnO}_3]^{2-}$ (Harrison, 1989).

Thermodynamic data for tin compounds have been compiled by Phillips et al. (1988). An extensive monograph on tin has been published by Harrison (1989), but it deals mostly with organic tin compounds, which are studied for their ecotoxic properties.

6.2 Sorption Studies

6.2.1 Sorption on Natural Rocks

Within the US Waste/Rock Interaction Technology Program, adsorption of tin on salt, basalt, tuff and granite has been measured under oxidizing and reducing conditions. Adsorption on all rock samples was considerably stronger under oxidizing

conditions (Serne and Relyea, 1981). A limited number of sorption measurements has been performed on tuff (Daniels et al., 1982, Thomas, 1987). Sorption coefficients obtained under nitrogen were smaller than those obtained in air by a factor of about 2.

Desorption ratios were considerably larger in most cases, which indicates either kinetic problems or precipitation. The latter author concludes, that "there are not enough measurements of tin to draw any correlations of sorption with mineralogy."

6.3 Geochemistry

6.3.1 Tin in Natural Waters

Values of tin trace concentrations in rivers and in the oceans are given by Byrd and Andreae (1982). Inorganic species are dominant, but methylated forms have been identified as well. Oxidation states have not been determined. It is expected that most of the tin found in the oceans is brought in by atmospheric transport and only a fraction by river transport. Its origin is mainly anthropogenic. Tin(IV) is scavenged by marine particulate matter and sediments with a high sorption coefficient (Nyffeler et al., 1984).

6.3.2 Tin in the Geosphere

An extensive monograph on the geology of tin deposits has been published by Taylor (1979).

6.4 Experiments

Both oxidation states of tin (II, IV) form insoluble (hydr)oxides at neutral pH values. For this reason tin is not very mobile.

Redox reactions between Sn(II) and Sn(IV) are two-electron reactions, which are relatively slow. This should make it possible to study the sorption of one oxidation state at a time. On the other hand, redox reactions caused by reductants from the rocks might be difficult to study, because of the slow kinetics. Distinction between the two oxidation states is also difficult. Mössbauer spectroscopy can be used in solids and selective complexation might be possible in solution, but no method was found in the literature.

6.5 Analytical Methods

6.5.1 Radioactive Tracers

The gamma emitting isotope ^{113}Sn ($t_{1/2}=115$ d) is a convenient tracer (Patton and Penrose, 1989). Several other isotopes with half-lives of the same order of magnitude can be used as well.

6.5.2 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy has been used successfully for the determination of tin in a matrix of dissolved tungsten minerals in alkaline solution (Leclere, 1974). The detection limit is in the range of 0.04 - 0.2 ppm, depending on the type of flame used. Hydride generation and cryogenic trapping has been used to measure traces of tin in natural waters (Byrd and Andreae, 1982). The detection limit given for this method is 1.7×10^{-12} M.

6.5.3 Polarography

Tin can also be determined by differential pulse polarography (Leclere, 1974).

6.5.4 Separation Methods

In two recent studies of tin in sediments, tin was separated from other elements and concentrated by extraction with methylisobutylketone (Koide and Goldberg, 1985, Patton and Penrose, 1989).

6.5.5 Mössbauer Spectroscopy

By use of $^{119\text{m}}\text{Sn}$ Mössbauer spectroscopy, the structure, bonding and valence of tin in chemical compounds and solids can be determined. Some applications of this method have been reviewed by Zuckerman (1967).

7. NEPTUNIUM

7.1 Solution Chemistry

Neptunium can exist in the oxidation states +III, +IV, +V, +VI and +VII. The hydrolysis constants have been determined by several authors (Moskvin, 1971, Sevost'yanova and Khalturin, 1976, Lierse et al., 1985).

Neptunium(III) exists in acid solutions in the form of the violet $\text{Np}^{3+}(\text{aq})$ ion. It is a weak acid with an estimated pK value of greater than 7. In alkaline solutions it precipitates as the insoluble hydroxide. Np(III) is easily oxidized.

Neptunium(IV) forms the yellow-green $\text{Np}^{4+}(\text{aq})$ ion in acid solution. Hydrolysis of Np(IV) starts at around pH 1 (pK = 2.3). In the neutral pH region, various hydrolysis products, including polynuclear species, are formed. In alkaline solutions, Np(IV) precipitates as the metastable $\text{Np}(\text{OH})_4$, which is slowly transformed to the stable NpO_2 .

Neptunium(V) exists in the form of the linear oxo cation NpO_2^+ , a green ion, which hydrolyzes to the yellow $\text{NpO}_2(\text{OH})_2^-$ anion in alkaline solution. The published pK₁ values vary between 2 and 5 (Lierse et al., 1985). Np(V) is the dominant species at redox potentials (E_{H}) of between 100 and 800 mV, i.e. under aerobic conditions and pH values of natural waters.

Neptunium(VI) is only found at very high redox potentials. In acid solution, it forms the linear oxo cation NpO_2^{2+} , which is pink/red colored. In alkaline solutions it exists either as $\text{NpO}_4^{2-}(\text{aq})$ or $\text{NpO}_2(\text{OH})_4^{2-}(\text{aq})$. The pK₁ value of Np(VI) is 5.17. At higher concentrations polynuclear species are formed.

Neptunium(VII) is only stable in alkaline solution, where it is present as $\text{NpO}_5^{3-}(\text{aq})$ or $\text{NpO}_2(\text{OH})_6^{3-}(\text{aq})$. In acid solutions, it oxidizes water (Nilsson and Carlsen, 1989).

The standard potentials of the redox pairs of neptunium have been measured by several authors. The published values are summarized as follows (Riglet et al., 1989):

$$E^{\circ}(\text{NpO}_2^{2+}/\text{NpO}_2^{+}) = 1.16 \text{ V/normal hydrogen electrode}$$

$$E^{\circ}(\text{Np}^{4+}/\text{Np}^{3+}) = 0.21 \text{ V/normal hydrogen electrode}$$

A literature survey of the redox reactions of neptunium has been published by Newton (1975). Reactions of Np(V) with Cr(II), Co(III), V(III), of Np(VI) with H_2O_2 , and of Np(VII) with Hg(I), as well as some redox reactions between different actinide elements are discussed, and some additional redox reactions are summarized.

The most important inorganic ligand for neptunium in natural systems is carbonate. Np(IV) complexes are the strongest, but NpO_2^{+} and NpO_2^{2+} also form strong carbonato complexes (Maya, 1983, 1984, Bidoglio et al., 1985, Grenthe et al., 1986 a,b). Np(V) can form sparingly soluble, mixed carbonato complexes with alkali or alkaline earth ions. (Allard et al., 1980, Lieser and Mühlenweg, 1988).

The complexing abilities of the neptunium ions follow the order $\text{Np(IV)} > \text{Np(VI)} > \text{Np(V)}$ (Patil et al., 1978). The stabilities of neptunium with a number of inorganic and organic ligands have been determined. They are not discussed here, because there are two extensive reviews available (Patil et al., 1976, 1978).

Solid, non-crystalline neptunium(IV) dioxide dissolves very slowly under anaerobic conditions, but much faster in the presence of oxygen, where the released neptunium is in an unidentified oxidized form (Lieser et al., 1985).

Extensive reviews of the chemistry of neptunium have been published (Kim, 1986, Nilsson and Carlsen, 1989). Thermodynamic data of neptunium compounds have been compiled, e.g. by Phillips et al. (1988). General information can be found in Fahey (1986).

It was observed that the redox pair $\text{Np}^{4+}/\text{NpO}_2^{+}$ is not readily reversible (Cross et al., 1989). This is in contrast to the redox pairs $\text{Np}^{3+}/\text{Np}^{4+}$ and $\text{NpO}_2^{+}/\text{NpO}_2^{2+}$, and can be explained by the fact that, unlike the transformations between Np^{4+} and NpO_2^{+} , these redox reactions do not involve the breaking of neptunium-oxygen bonds (Nilsson and Carlsen, 1989).

7.2 Sorption Studies

7.2.1 Sorption on Pure Phases

Three major factors control sorption on minerals; adsorption of hydrolyzed species, chemisorption on surfaces which contain strong complexing ions, and redox reactions with ferrous iron containing minerals (Beall and Allard, 1981). The typical feature of adsorption of hydrolyzed species is the onset of adsorption at the same pH value for very different minerals (and also on other surfaces like glass vessel surfaces). Minerals which contain complex formers (e.g. phosphate in apatite) complex neptunium with the surface ligands (Fig. 8). Sorption of neptunium is also enhanced by reduction of Np(V) to Np(IV) by ferrous iron containing minerals like pyrite and biotite; this occurs even in the presence of oxygen, but more strongly under anoxic conditions (Beall and Allard, 1981, Bidoglio and De Plano, 1986). If Np(V) is adsorbed on reducing minerals, the fraction of adsorbed neptunium, which is reduced, varies from mineral to mineral. In a study of the adsorption of Np(V) on biotite, chalcopyrite, galena and pyrite, galena showed the highest adsorption at pH 8.8, but only 18 % of the adsorbed neptunium was reduced to Np(IV). Chalcopyrite showed low adsorption at pH 6.3, but almost all of the adsorbed neptunium was reduced to Np(IV). The oxidation state of adsorbed neptunium was determined in solution after desorption (Meyer et al., 1984). It is essential to know in which oxidation state an element is adsorbed. Unless there is a chemical interpretation, sorption measurements on such a complex system will only result in a collection of numbers, which can show a general trend, but no reliable model calculations can be obtained from such data (Fig. 9).

7.2.2 Sorption on Natural Rocks

In a study of the interaction of neptunium(VI) with basalt and olivine, it was shown that Np(V) and Np(IV) is adsorbed on the surface. It was concluded, that ferrous iron in the rocks reduces adsorbed neptunium (Susak et al., 1983). Adsorption studies on soils have shown that in an oxidizing environment, neptunium is adsorbed preferentially on clay and organic matter (Sheppard et al., 1984).

As in the case of technetium, hydrazine has been used as a "redox buffer" for experiments with neptunium. The same reservations regarding this method apply here and the reader is referred to the discussion of this point in the chapter on redox conditions.

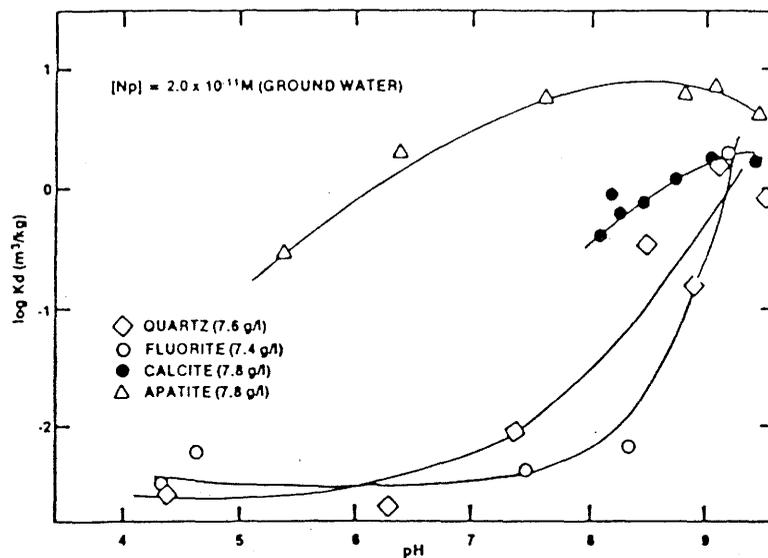


Figure 8. Distribution coefficients (K_d) for Np(V) on some minerals (Beall, 1981).

7.3 Geochemistry

Neptunium is present in the geosphere only as traces from human activities such as nuclear bomb explosions and fuel reprocessing plants. There are some studies on its distribution, but usually, only total concentrations have been determined (Nilsson and Carlsen, 1989).

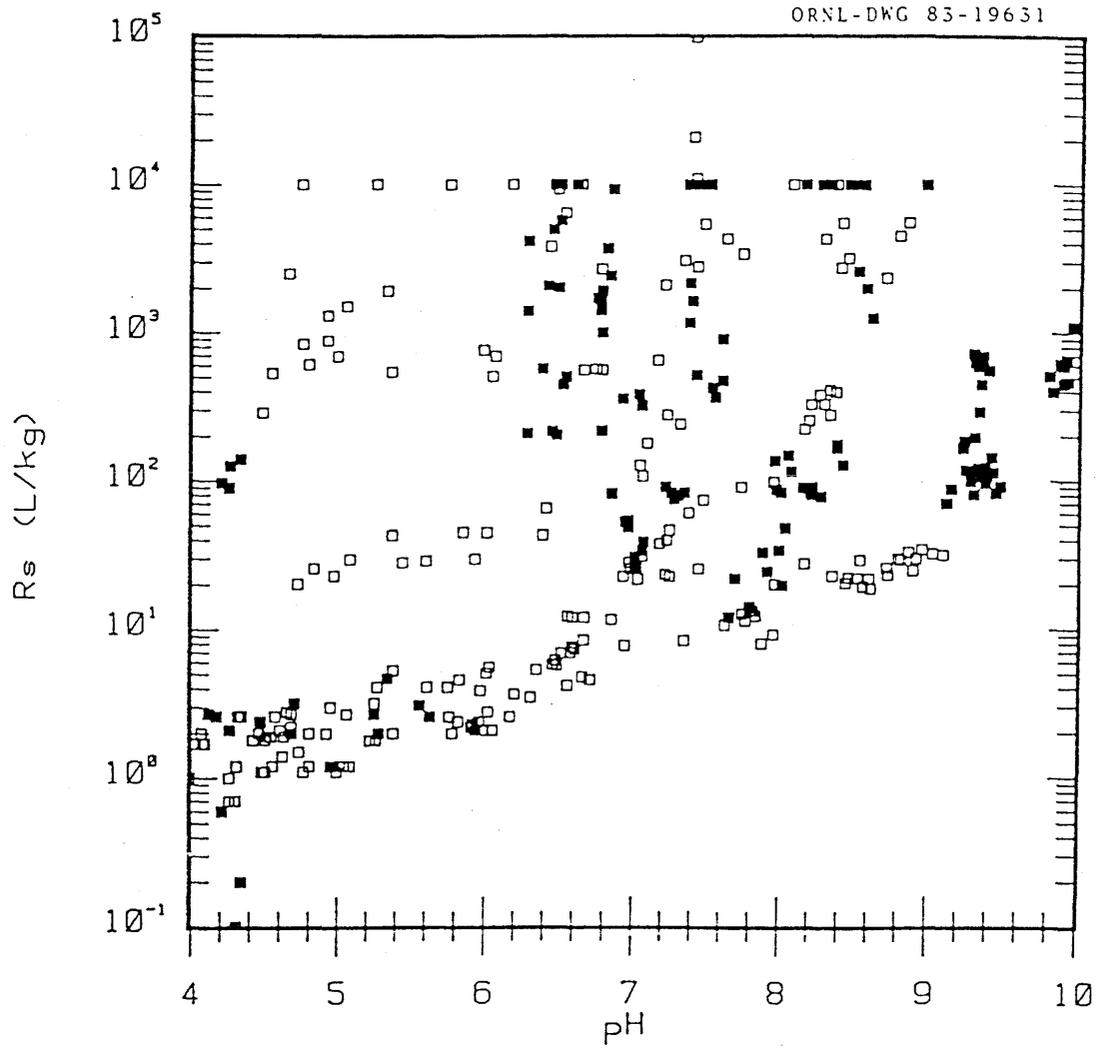


Figure 9. Sorption ratios for Np(V) on 18 different minerals (iron-containing minerals and sulfides). Open symbols oxic conditions (air saturated), closed symbols anoxic conditions (controlled atmosphere) (Meyer et al., 1984).

7.4 Experiments

Neptunium exists in several different oxidation states, but in a natural environment, only the oxidation states IV and V are relevant. Np(V) is fairly soluble, whereas Np(IV) is very insoluble.

Adsorption of Np(V) on rocks can be studied without many problems, as long as there is no reduction by the sorbent. If there is a reduction, the derived distribution coefficient is useless, unless the extent of the reduction is quantified. Desorption studies and subsequent determination of the oxidation state in solution can give some information about the extent of reduction, but there is always a degree of uncertainty about changes of oxidation state during desorption.

The sorption of Np(IV) can be estimated by the substitution of Np(IV) by its analog, Th(IV), which is not redox active and therefore easier to handle. There are, however, also disadvantages with this method. Sorption of Th(IV) might be somewhat different from sorption of Np(IV). Redox effects, which might occur in the neptunium system can not be observed with thorium. For this reason, thorium experiments should at least be complemented by some neptunium experiments.

7.5 Analytical Methods

There are a number of methods available for the determination of neptunium and reviews of this subject have been published (Bajo, 1982, Fahey, 1986).

7.5.1 Radioactive Tracers

^{237}Np has a half-life of 2.14×10^6 years and can be measured by α -spectrometry and ^{239}Np ($t_{1/2} = 2.33$ d) by γ -spectrometry. ^{235}Np has a short half-life ($t_{1/2} = 410$ d) and can be measured either by counting of the low energy x-ray emission or by liquid scintillation measurement of the Auger electrons.

The isotopes ^{237}Np , ^{238}Np ($t_{1/2} = 2.12$ d) and ^{239}Np are produced by neutron irradiation in a nuclear reactor, the isotopes ^{235}Np and ^{236}Np ($t_{1/2} = 1.55 \times 10^5$ y) are formed by cyclotron irradiation of ^{235}U with deuterons and protons, respectively (Niese, 1990).

7.5.2 Spectrophotometry

Neptunium can be determined spectrophotometrically as the complex with arsenazo III (Savvin, 1964).

7.5.3 Laser Induced Photoacoustic Spectroscopy (LIPAS)

A relatively new approach for the determination of species is the laser induced photoacoustic spectroscopy (LIPAS). Neptunium speciation can be determined even at concentrations around 10^{-9} M (Cross et al., 1989).

7.5.4 Electrochemical Methods

Neptunium can be determined by differential pulse polarography in the Np(IV) oxidation state. The redox pair Np(IV)/Np(III) is reversible and the detection limit is 2×10^{-7} M (Cauchetier, 1979).

Classic voltametry was used for the redox couple Np(VI)/Np(V) and cyclic voltametry for the redox pairs Np(VI)/Np(V) and Np(IV)/Np(III) (Riglet et al., 1989).

The determination of Np(V) and Np(VI) at pH 8 and 11 was investigated by voltammetry, but no useful results were obtained because the peaks were either irreproducible or entirely absent (Cross et al., 1989).

7.5.5 Selective Determination of Individual Oxidation States

There are several methods available for the selective determination of individual oxidation states of neptunium. These states can be determined directly by spectrophotometry, provided the concentrations are high enough and there is no interference (Moskvin, 1971, Sevost'yanova and Khalturin, 1976). A standard method is the extraction of Np(IV) by 2-thenoyltrifluoroacetone (TTA) in an organic solvent (Foti and Freiling, 1964). Tricaprylmethylammonium nitrate (TCMA) has been used as an alternative to TTA for extractions from saline solutions (Cleveland et al., 1985). The precipitation of all oxidation states except Np(VI) by lanthanum fluoride is a method for the selective determination of Np(VI) (Foti and Freiling, 1964).

Np(VI) can also be selectively sorbed on silica gel in the pH range 6-7 and Np(IV) is adsorbed selectively on barium sulfate in acid solution (Inoue and Tochiyama, 1977). Np(IV) can also be selectively sorbed on hydrated antimony pentoxide (Török and Ruf, 1982).

7.5.6 Mössbauer Spectroscopy

The environment of a neptunium ion in a solid can be investigated by Mössbauer spectroscopy. The coordination number and the oxidation state of neptunium can be obtained by this method (Jové et al., 1988).

8. ANALOGS

Sometimes chemical analogs are used to study the sorption of radionuclides. This can have advantages for the handling of a system, for example if actinides are replaced by lanthanides, but there is never a perfect analog. If, however, one wants to study one particular property of an element, an analog may be found. To study the adsorption of neptunium in the oxidation state IV, one could replace it by thorium(IV), but this means that the redox properties and the influence of the small fraction of neptunium present in other oxidation states must be ignored.

In the case of redox sensitive elements, many properties, like redox chemistry, hydrolysis and complexation are important, and an analog for all these properties is unlikely to be found. For this reason, the use of chemical analogs is not considered in this report.

9. CONCLUSIONS FOR EXPERIMENTS

The literature study shows that there are several problems which have to be addressed in order to get reliable data about interactions with rock and solubilities of the redox sensitive radioactive waste elements in the far-field of a repository.

When planning experiments, in a first step it has to be assured that the redox conditions in the natural geological environment can be reproduced in the laboratory. The exclusion of oxygen from the laboratory atmosphere is the most important aspect. The inert atmosphere in the glove-boxes contains only traces of oxygen. Some of the elements of interest are kinetically inert towards oxidation by oxygen and should not be affected by these traces, while others can be easily oxidized. Another aspect is the influence of oxygen on the reducing components of the rocks. The total reducing capacity of most rocks is much larger than the oxygen content of the inert atmosphere. There is however the possibility that the most accessible sites on the surface of the rocks are oxidized and that this affects the interaction of the redox sensitive elements with the reducing minerals.

In the literature there are several methods to exclude oxygen and to set reducing conditions. All of them have limitations and it is recommended to test the most promising methods, particularly for experiments with the most sensitive elements.

It is also worthwhile to study the redox capacity of the rock as an independent parameter under the influence of different oxidants (oxygen, oxidizing radioactive waste elements or other oxidants like organics). Dissolution of the rocks by infiltrating water leads to the release of reducing compounds. The resulting changes in surface structure and water chemistry can alter the behavior of the redox sensitive elements and it is recommended to study these aspects as well.

The second aspect is the control of the oxidation state of the radioactive elements during a sorption experiment. In most experimental studies, only total concentrations are measured and oxidation states are not determined. Sorption and solubility of different oxidation states can vary considerably and if the oxidation state is not known, sorption data are of very limited use. To interpret a sorption experiment in a reliable way, oxidation states in solution and on the surface of the rock should be known.

Methods to determine individual oxidation states in solution are well known for some of the elements, but not for all. Methods for measurements of oxidation states on solid surfaces are now available, but they require sophisticated and expensive equipment, and only relatively high concentrations can be determined. An alternative for surface measurement is desorption and measurement in solution, but there is the danger of a shift in redox equilibrium during desorption. This could produce results which do not reflect the true distribution of oxidation states on the surface.

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11. REFERENCES

11.1 Introduction

Jakob, A., Hadermann, J. and Rösel F. (1989), Radionuclide Chain Transport with Matrix Diffusion and Non-linear Sorption, PSI-Bericht Nr. 54 / NTB 90-13, Nagra

McKinley, I.G. and Hadermann, J. (1984), Radionuclide Sorption Database for Swiss Safety Assessment, EIR-Bericht Nr. 550 / NTB 84-40

NAGRA (1985), Project Gewähr 1985, Nuclear Waste Management in Switzerland: Feasibility Studies and Safety Analyses, NGB 85-09

11.2 Redox Conditions

Bruno, J., Grenthe, I, Muñoz, M. (1985), Studies on the Radionuclide Coprecipitation - Solid Solution Formation, The $\text{UO}_2(\text{s})\text{-La}(\text{OH})_3(\text{s})$ Coprecipitation as an Analog for the $\text{UO}_2(\text{s})\text{-Pu}(\text{OH})_3(\text{s})$ System, Mat. Res. Soc. Symp. Proc. 50, 717

Davies, S.H.R. and Morgan, J.J. (1989), Manganese(II) Oxidation Kinetics on Oxide Surfaces, J. Coll. Int. Sci. 129, 63

El-Naggar, H.A., Gourisse, D. and Masoud, M.S. (1982), Neptunium Reduction by Hydrazine and Hydroxylamine, Radiochimica Acta 31, 51

Guppy, R.M. and Atkinson, A. (1989), The Evolution of Redox Conditions in a Radwaste Repository: Preliminary Investigations, AERE-R-13615, UK Department of the Environment Report DOE/RW/89/103

Guppy, R.M., Atkinson, A. and Valentine, T.M. (1989), Studies of the Solubility of Technetium under a Range of Redox Conditions, Harwell Laboratory, AERE R 13467

Kelmers, A.D., Kessler, J.H., Arnold, W.D., Meyer, R.E., Cutshall, N.H., Jacobs, G.K. and Lee, S.Y. (1984), Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Report for October-December 1983, NUREG/CR-3851 Vol.1, ORNL/TM-9191/V1

Meyer, R.E., Arnold, W.D. and Case, F.I. (1984), Valence Effects on the Sorption of Nuclides on Rocks and Minerals, NUREG/CR-3389, ORNL-5978

Pirhonen, V.O., Pitkänen, P. and Takala, J. (1991), Design and Preliminary Results of Redox Capacity Measurements of Granitic Rocks and Minerals, Scientific Basis for Nuclear Waste Management, Mat. Res. Soc. Symp. Proc., in print

Rösch, F., Hung, T.K., Dittrich, S., Ludwig, R., Buklanov, G.V., Dreyer, R. and Khalkin, V.A. (1990), Electromigration Studies of Carrier-Free $^{239}\text{Np(V)}$ in Aqueous Solutions, *Isotopenpraxis* 26, 355

Tamura, H., Goto, K. and Nagayama, M. (1976), The Effect of Ferric Hydroxide on the Oxygenation of Ferrous Ions in Neutral Solutions, *Corr. Sci.* 16, 197

Tamura, H., Kawamura, S. and Hagayama, M. (1980), Acceleration of the Oxidation of Fe^{2+} Ions by Fe(III)-Oxyhydroxides, *Corr. Sci.* 20, 963

Wehrli, B. and Stumm, W. (1989), Vanadyl in Natural Waters, Adsorption and Hydrolysis Promote Oxygenation, *Geochim. Cosmochim. Acta* 53, 69

White, A.F. and Yee, A. (1985), Aqueous Oxidation-Reduction Kinetics Associated with Coupled Electron-Cation Transfer from Iron-Containing Silicates at 25°C, *Geochim. Cosmochim. Acta.* 49, 1263

White, A.F., Yee, A. and Flexser, S. (1985), Surface Oxidation-Reduction Kinetics Associated with Experimental Basalt-Water Reaction at 25°C, *Chem. Geol.* 49, 73

11.3 Selenium

Ahrlachs, J.S. and Hossner, L.R. (1987), Selenate and Selenite Mobility in Overburden by Saturated Flow, *J. Environ. Qual.* 16(1), 95

Alemi, M.H., Goldhamer, D.A. and Nielsen, D.R. (1988), Selenate Transport in Steady-State, Water-Saturated Soil Columns, *J. Environ. Qual.* 17(4), 608

Ames, L.L., Salter, P.F., McGarrah, J.E. and Walker, B.A. (1982), Selenium Sorption on a Columbia River Basalt, PNL-SA-10750

Baeyens, B. and McKinley, I.G. (1989), A PHREEQE Database for Pd, Ni and Se, PSI-Bericht Nr. 34

Balistreri, L.S. and Chao, T.T. (1987), Selenium Adsorption by Goethite, Soil Sci. Soc. Am. J. 51, 1145

Balistreri, L.S. and Chao, T.T. (1990), Adsorption of Selenium by Amorphous Iron Oxyhydroxide and Manganese Dioxide, Geochim. Cosmochim. Acta 54, 739

Bard, A.J., Parsons, R. and Jordan, J. (1985), Standard Potential in Aqueous Solution, Dekker, New York

Bar-Yosef, B. and Meek, D. (1987), Selenium Sorption by Kaolinite and Montmorillonite, Soil Sci. 144(1), 11

van den Berg, C.M.G. and Khan, S.H. (1990), Determination of Selenium in Sea Water by Adsorptive Cathodic Stripping Voltammetry, Anal. Chim. Acta 231, 221

Berrow, M.L. and Ure, A.M. (1989), in: Ilnat, M. (Ed.), Occurrence and Distribution of Selenium, CRC Press, Boca Raton, Fl.

Bird, G.W. and Lopata, V.J. (1980), Solution Interaction of Nuclear Waste Anions with Selected Geological Materials, in: Northrup, C.J.M., Ed., Scientific Basis for Nuclear Waste Management, Vol. 2, Plenum Press, New York and London

Bodini, M.E. and Alzamora, O. (1983), Spectrophotometric Determination of Trace Amounts of Selenium with 4,5,6-Triaminopyrimidine, Talanta 30(6), 409

Bodini, M.E., Pardo, J. and Arancibia, V. (1990), Spectrophotometric Determination of Selenium(IV) with 5,5-Dimethyl-1,3-cyclohexanedione, Talanta, 37, 439

Brimmer, S.P., Fawcett, W.R. and Kulhavy, K.A. (1987), Quantitative Reduction of Selenate Ion to Selenite in Aqueous Samples, Anal. Chem. 59, 1470

Brookins, D.G. (1982), Eh-pH Diagrams for Geochemistry, Springer-Verlag, Berlin

Brown Jr., G.E., Parks, G.A. and Chisholm-Brause, C.J. (1989), In-Situ X-Ray Absorption Spectroscopic Studies of Ions at Oxide-Water Interfaces, Chimia, 43, 248

Bye, R. (1983), Critical Examination of Some Common Reagents for Reducing Selenium Species in Chemical Analysis, Talanta 30(12), 993

Campanella, L., Ferri, T. and Morabito, R. (1989), A Selenium Speciation Model for the Studies of Natural Water, *Analisis*, 17(9), 507

Chau, Y.K., Wong, P.T.S., Silverberg, B.A., Luxon, P.L. and Bengert, G.A. (1976), Methylation of Selenium in the Aquatic Environment, *Science* 192, 1130

Cheam, V. and Agemian, H. (1980), Preservation and Stability of Inorganic Selenium Compounds at ppb Levels in Water Samples, *Anal. Chim. Acta* 113, 237

Cooke, T.D. and Bruland, K.M. (1987), Aquatic Chemistry of Selenium: Evidence of Biomethylation, *Environ. Sci. Technol.* 21, 1214

Cowan, C.E., Zachara, J.M. and Resch C.T. (1990), Solution ion effects on the surface exchange of selenite on calcite, *Geochim. Cosmochim. Acta* 54, 2223

Cutter, G.A. (1978), Species Determination of Selenium in Natural Waters, *Anal. Chim. Acta* 98, 59

Cutter, G.A. (1982), Selenium in Reducing Waters, *Science* 217, 829

Cutter, G.A. (1989), in: Ihnat, M. (Ed.), Occurrence and Distribution of Selenium, CRC Press, Boca Raton, Fl.

Early, T.O., Jacobs, G.K. and Drewes, D.R. (1984), Geochemical Controls on Radionuclide Releases from a Nuclear Waste Repository in Basalt, in: Geochemical Behavior of Disposed Radioactive Waste, ACS Symposium Series 246

Frost, R.R. and Griffin, R.A. (1977), Effect of pH on Adsorption of Arsenic and Selenium from Landfill Leachate by Clay Minerals, *Soil Sci. Soc. Am. J.* 41, 53

Geering, H.R., Cary, E.E., Jones, L.H.P. and Allaway, W.H. (1968), Solubility and Redox Criteria for the Possible Forms of Selenium in Soils, *Soil Sci. Soc. Amer. Proc.* 32, 35

Gmelin (1942), Gmelins Handbuch der Anorganischen Chemie, Selen, Teil A, Verlag Chemie, Weinheim/Bergstrasse

Gmelin (1949), Gmelins Handbuch der Anorganischen Chemie, Selen, Teil B, Verlag Chemie, Weinheim/Bergstrasse

Hayes, K.F., Papelis, C. and Leckie, J.O. (1988), Modeling Ionic Strength Effects on Anion Adsorption at Hydrous Oxide/Solution Interfaces, *J. Coll. Int. Sci.* 125, 717

Hayes, K.F., Roe, A.L., Brown Jr., G.E., Hodgson, K.O., Leckie, J.O. and Parks, G.A. (1987), In Situ X-ray Absorption Study of Surface Complexes: Selenium Oxyanions on α -FeOOH, *Science* 238, 782

Hingston, F.J., Posner, A.M. and Quirk, J.P. (1972), Anion Adsorption by Goethite and Gibbsite, I. The Role of the Proton in Determining Adsorption Envelopes, *J. Soil Sci.* 23(2), 177

Hingston, F.J., Posner, A.M. and Quirk, J.P. (1974), Anion Adsorption by Goethite and Gibbsite, II. Desorption of Anions from Hydrous Oxide Surfaces, *J. Soil Sci.* 25(1), 16

Howard III, J.H. (1977), Geochemistry of Selenium: Formation of Ferroselite and Selenium Behavior in the Vicinity of Oxidizing Sulfide and Uranium Deposits, *Geochim. Cosmochim. Acta* 41, 1665

Knab, D. and Gladney, E.S. (1980), Determination of Selenium in Environmental Materials by Neutron Activation and Inorganic Ion Exchange, *Anal. Chem.* 52, 825

Lerman, A. (1989), Volatile Radionuclides: Limiting Concentrations and Transport Rates in an Unsaturated Rock Pore Space, Migration '89 Conference, Abstract No. 2A-3

Lewis, S.A. and Veillon, C. (1989), in: Inhat, M. (Ed.), Occurrence and Distribution of Selenium, CRC Press, Boca Raton, FL.

Masscheleyn, P.H., Delaune, R.D., and Patrick, W.H. (1990), Transformations of Selenium as Affected by Sediment Oxidation-Reduction Potential and pH, *Environ. Sci. Technol.* 24, 91

Naftz, D.L. and Rice, J.A. (1989), Geochemical Processes Controlling Selenium in Ground Water After Mining, Powder River Basin, Wyoming, U.S.A., *Appl. Geochem.* 4, 565

Oremland, R.S., Hollibaugh, J.T., Maest, A.S., Presser, T.S., Miller, L.G. and Culbertson, C.W. (1989), Selenate Reduction to Elemental Selenium by Anaerobic

Bacteria in Sediments and Culture: Biogeochemical Significance of a Novel, Sulfate-Independent Respiration, *Appl. Environ. Microbiol.* 55(9), 2333

Pettersson, J. and Olin, Å. (1991), The Rate of Reduction of Selenium(VI) to Selenium(IV) in Hydrochloric Acid, *Talanta* 38(4), 413

Phillips, S.L., Hale, F.V., Silvester, L.F. and Siegel, M.D. (1988), Thermodynamic Tables for Nuclear Waste Isolation, NUREG/CR-4864, Vol. 1

Raber, E., Garrison, J. and Oversby, V. (1983), The Sorption of Selected Radionuclides on Various Metal and Polymeric Materials, *Radioactive Waste Management and the Nuclear Fuel Cycle* 4(1), 41

Raptis, S.E., Kaiser, G. and Tölg, G. (1983), A Survey of Selenium in the Environment and a Critical Review of its Determination at Trace Levels, *Fresenius Z. Anal. Chem.* 316, 105

Reamer, D.C. and Zoller, W.H. (1980), Selenium Biomethylation Products from Soil and Sewage Sludge, *Science* 208, 500

Robberecht, H.J. and Van Grieken, R.E. (1980), Sub-Part-per-Billion Determination of Total Dissolved Selenium and Selenite in Environmental Waters by X-ray Fluorescence Spectrometry, *Anal. Chem.* 52, 449

Robberecht, H. and Van Grieken, R. (1982), Selenium in Environmental Waters: Determination, Speciation and Concentration Levels, *Talanta* 29, 823

Runnells, D.D., Lindberg, R.D. and Kempton, J.H. (1987), Irreversibility of Se(VI)/Se(IV) Redox Couple in Synthetic Basaltic Ground Water at 25°C and 75°C, in: *Scientific Basis for Nuclear Waste Management X*, *Mat. Res. Soc. Symp. Proc.* 84

Runnells, D. and Lindberg, R.D. (1990), Selenium in Aqueous Solutions: The Impossibility of Obtaining a Meaningful Eh Using a Platinum Electrode, With Implications for Modeling of Natural Waters, *Geology* 18, 212

Sarathchandra, S.U. and Watkinson, J.H. (1981), Oxidation of Elemental Selenium to Selenite by *Bacillus megaterium*, *Science*, 211, 600

Schulek, E. and Körös (1960), Contributions to the Chemistry of Selenium and Selenium Compounds - V, The Hydrolysis of Selenium, *J. Inorg. Nucl. Chem.* 13, 58

Siu, K.W.M. and Berman, S.S. (1989), in: Ilnat, M. (Ed.), Occurrence and Distribution of Selenium, CRC Press, Boca Raton, Fl.

Takayanagi, K. and Wong, G.T.F. (1983), Fluorimetric Determination of Selenium(IV) and Total Selenium in Natural Waters, *Anal. Chim. Acta* 148, 263

Takayanagi, K. and Wong, G.T.F. (1985), Dissolved Inorganic and Organic Selenium in the Orca Basin, *Geochim. Cosmochim Acta* 49, 539

Tan, K.S. and Rabenstein, D.L. (1989), in: Ilnat, M. (Ed.), Occurrence and Distribution of Selenium, CRC Press, Boca Raton, Fl.

Ticknor, K.V., Harris, D.R. and Vandergraaf, T.T. (1988), Sorption/Desorption Studies of Selenium on Fracture-Filling Minerals under Aerobic and Anaerobic Conditions, TR-453, Atomic Energy of Canada Limited

Ticknor, K.V., Vandergraaf T.T. and Kamineni, D.C. (1989), Radionuclide Sorption on Primary and Fracture-filling Minerals from the East Bull Lake Pluton, Massey, Ontario, Canada, *Appl. Geochem.* 4, 163

Tischendorf, G. (1966), Zur Verteilung des Selens in Sulfiden, *Freiberger Forschungshefte C* 208, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig

Uchida, H., Shimoishi, Y. and Tôei, K. (1980), Gas Chromatographic Determination of Selenium(-II,0), -(IV), and -(VI) in Natural Waters, *Environ. Sci. Technol.* 14, 541

Velinsky, D.J. and Cutter, G.A. (1990), Determination of Elemental Selenium and Pyrite-Selenium in Sediments, *Anal. Chim. Acta* 235, 419

Velinsky, D.J. and Cutter, G.A. (1991), Geochemistry of Selenium in a Coastal Salt Marsh, *Geochim. Cosmochim. Acta* 55, 179

Wagman, D.D. et al. (1982), The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C1 and C2 organic substances in SI units, *J. Phys. Chem. Ref. Data* 11, supp. 2, 1

Warren, C.G. (1968), The Synthesis of Ferroselite from an Aqueous Solution at Low Temperature, *Econ. Geol.* 63, 418

Weres, O., Jaouni, A. and Tsao, L. (1989), The Distribution, Speciation and Geochemical Cycling of Selenium in a Sedimentary Environment, Kesterson Reservoir, California, U.S.A., *Appl. Geochem.* 4, 543

Zhang, P. and Sparks, D.L. (1990), Kinetics of Selenate and Selenite Adsorption/Desorption at the Goethite/Water Interface, *Environ. Sci. Technol.* 24, 1848

11.4 Technetium

Bondiotti, E.A. and Francis, C.W. (1979), Geologic Migration Potentials of Technetium-99 and Neptunium-237, *Science* 203, 1337

Brookins, D.G. (1982), *Eh-pH Diagrams for Geochemistry*, Springer-Verlag, Berlin

Davison, A. and Jones, A.G. (1982), The Chemistry of Technetium V, *Int. J. Appl. Radiat. Isot.* 33, 875

Desmet, G. and Myttenaere, C., Eds. (1986), *Technetium in the Environment*, CEC Radiation Protection Programme, Elsevier, London and New York

El-Reefy, S., Ruf, H. and Schorb, K. (1989), Inversvoltammetrie des Technetiums im Tetraphenylarsoniumchlorid-Chloroform-Extrakt am hängenden Quecksilbertropfen, *KfK* 4639

Guppy, R.M., Atkinson, A. and Valentine, T.M. (1989), Studies of the Solubility of Technetium under a Range of Redox Conditions, Harwell Laboratory, AERE R 13467

Haines, R.I., Owen, D.G. and Vandergraaf, T.T. (1987), Technetium-Iron Oxide Reactions under Anaerobic Conditions: A Fourier Transform Infrared, FTIR Study, *Nucl. J. Canada* 1:1, 32

Hughes, M.A. and Rossotti, F.J.C. (1987), A Review of Some Aspects of the Solution Chemistry of Technetium, Harwell, AERE-R 12820

Hughes, M.A. and Rossotti, F.J.C. (1988), Voltammetric Studies of the Solution Chemistry of Technetium, AERE-R-13382

Jones, A.G. and Davison, A. (1982), The Chemistry of Technetium I, II, III and IV, *Int. J. Appl. Radiat. Isot.* 33, 867

Jovtschev, M., Koch, H. and Kupsch, H. (1975), Zur Elektrochemie des Technetiums, *Isotopenpraxis* 11(11), 369

Kelmers, A.D., Kessler, J.H., Arnold, W.D., Meyer, R.E., Cutshall, N.H., Jacobs, G.K. and Lee, S.Y. (1984), Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Report for October-December 1983, NUREG/CR-3851 Vol.1, ORNL/TM-9191/V1

Lieser, K.H. and Bauscher, Ch. (1987), Technetium in the Hydrosphere and in the Geosphere, I. Chemistry of Technetium and Iron in Natural Waters and Influence of the Redox Potential on the Sorption of Technetium, *Radiochim. Acta* 42, 205

Lieser, K.H. and Bauscher, Ch. (1988), Technetium in the Hydrosphere and in the Geosphere, II. Influence of pH, of Complexing Agents and of Some Minerals on the Sorption of Technetium, *Radiochim. Acta*, 44/45, 125

Long, S.E. and Sparkes, S.T. (1988), A Literature Survey of Techniques for the Analytical Determination of Technetium-99, Harwell, AERE-R 12742

Luxenburger, H.J. and Schüttelkopf, H. (1984), Vorkommen und Verhalten von Tc in der Umwelt (Literaturstudie), Kernforschungszentrum Karlsruhe KfK 3418

Meyer, R.E., Arnold, W.D. and Case, F.I. (1984), Valence Effects on the Sorption of Nuclides on Rocks and Minerals, NUREG/CR-3389, ORNL-5978

Meyer, R.E., Arnold, W.D. and Case, F.I. (1985), Valence Effects on the Sorption of Nuclides on Rocks and Minerals II, NUREG/CR-4114, ORNL-6137

Onishi, Y., Serne, R.J., Arnold, E.M., Cowan, C.E. and Thompson, F.L. (1981), Critical Review: Radionuclide Transport, Sediment Transport, and Water Quality Mathematical Modeling; and Radionuclide Adsorption/Desorption Mechanisms, NUREG/CR-1322, PNL-2901

Riley, J.P. and Siddiqui, S.A. (1982), The Determination of Technetium-99 in Seawater and Marine Algae, *Anal. Chim. Acta* 139, 167

Russell, C.D. (1982), Electrochemistry of Technetium, *Int. J. Appl. Radiat. Isot.* 33, 883

Schwochau, K. (1983), The Present Status of Technetium Chemistry, *Radiochim. Acta* 32, 139

Sparkes, S.T. and Long, S.E. (1988), The Chemical Speciation of Technetium in the Environment: A Literature Survey, Harwell, AERE-R 12743

Strickert, R., Friedman, A.M. and Fried, S. (1980), The Sorption of Technetium and Iodine Radioisotopes by Various Minerals, *Nucl. Technol.* 49, 253

Vandergraaf, T.T., Ticknor, K.V. and George, I.M. (1984), Reactions Between Technetium in Solution and Iron-Containing Minerals Under Oxidic and Anoxic Conditions, in: *Geochemical Behavior of Disposed Radioactive Waste*, ACS Symposium Series 246

Vine, E.N. and Wahl, A.C. (1982), The Chemical Behavior of Tracer-level Technetium Isotopes, *J. Appl. Radiat. Isot.* 33, 861

Walton, F.B., Paquette, J., Ross, J.P.M. and Lawrence, W.E. (1986), Tc(IV) and Tc(VII) Interactions with Iron Oxyhydroxides, *Nucl. Chem. Waste Mgmt.* 6, 121

Winkler, A., Brühl, H., Trapp, Ch. and Bock, W.-D. (1988), Mobility of Technetium in Various Rocks and Defined Combinations of Natural Minerals, *Radiochim. Acta* 44/45, 183

Winkler, A. (1989), Untersuchungen zur Mobilität von Technetium (und Selen) in Norddeutschen Grundwasserleitern und Technetium im Kontakt mit natürlich vorkommenden Mineralien, *Berliner Geowissenschaftliche Abhandlungen, Reihe A, Band 117*, Selbstverlag Fachbereich Geowissenschaften, FU Berlin

Wood, M.I., Ames, L.L. and McGarrah, J.E. (1987), Tc Behavior in the Basalt-Synthetic Groundwater System as a Function of Temperature and Initial Oxygen Content, in: *Scientific Basis for Nuclear Waste Management X*, *Mat. Res. Soc. Symp. Proc.* 84, 695

11.5 Palladium

Baes, C.F. and Mesmer, R.E. (1976), *The Hydrolysis of Cations*, J. Wiley and Sons

Baeyens, B. and McKinley, I.G. (1989), A PHREEQE Database for Pd, Ni and Se, PSI-Bericht Nr. 34

Bowles, J.F.W. (1986), The Development of Platinum-Group Minerals in Laterites, *Econ. Geol.* 81, 1278

Brookins, D.G. (1982), *Eh-pH Diagrams for Geochemistry*, Springer-Verlag, Berlin

Cousins, C.A. (1973), Notes on the Geochemistry of the Platinum Group Elements, *Trans. Geol. Soc. South Africa* 76, 77

Elding, L.I. (1972a), Palladium(II) Halide Complexes. I. Stabilities and Spectra of Palladium(II) Chloro and Bromo Aqua Complexes, *Inorg. Chim. Acta* 6(4), 647

Elding, L.I. (1972b), Palladium(II) Halide Complexes. II. Acid Hydrolysis and Halide Anations of Palladium(II) Chloro and Bromo Aqua Complexes, *Inorg. Chim. Acta* 6(4), 683

Elding, L.I. (1973), Palladium(II) Halide Complexes. III. Acid Hydrolysis and Halide Anations of cis- and trans-Dichlorodiaquapalladium(II) and -Dibromodiaquapalladium(II), *Inorg. Chim. Acta* 7(4), 581

Fuchs, W.A. and Rose, A.W. (1974), The Geochemical Behavior of Platinum and Palladium in the Weathering Cycle in the Stillwater Complex, Montana, *Econ. Geol.* 69, 332

Hancock, R.D., Finkelstein, N.P. and Evers, A. (1977), A Linear Free-Energy Relation Involving the Formation Constants of Palladium(II) and Platinum(II), *J. inorg. nucl. Chem.* 39, 1031

Hyland, M.M. and Bancroft, G.M. (1990), Palladium Sorption and Reduction on Sulphide Mineral Surfaces: An XPS and AES Study, *Geochim. Cosmochim. Acta* 54, 117

Kai, F., Sakanashi, Y., Satoh, S. and Uchikawa, S. (1983), 4-(3,5-Dichloro-2-Pyridylazo)-1,3-Diaminobenzene as a New Sensitive and Selective Reagent for Palladium(II), *Anal. Letters*, 16(A13), 1013

Klotz, D., Lang, H. and Moser, H. (1985), Experimentelle Untersuchungen zur Migration von Radionukliden der Elemente I, Sr, Cs, Co und Pd im Deckgebirge des Endlagerortes Gorleben, *GSF-Bericht* 24/85

Kump, L.R. and Byrne, R.H. (1989), Palladium Chemistry in Seawater, *Environ. Sci. Technol.* 23, 663

Li, J.-H. and Byrne R.H. (1990), Amino Acid Complexation of Palladium in Seawater, *Environ. Sci. Technol.* 24(7), 1038

Lockyer, R. and Hames, G.E. (1959), The Quantitative Determination of some Noble Metals by Atomic-absorption Spectroscopy, *Analyst*, 84, 385

Nabivanets, B.I. and Kalabina, L.V. (1970), State of Palladium(II) in Perchlorate Solutions, *Russ. J. Inorg. Chem.* 15(6), 818

Otomo, M. (1963), The Spectrophotometric Determination of Palladium(II) with Xylenol Orange, *Bull. Chem. Soc. Japan* 36(8), 889

Phillips, S.L., Hale, F.V., Silvester, L.F. and Siegel, M.D. (1988), Thermodynamic Tables for Nuclear Waste Isolation, *NUREG/CR-4864*, Vol. 1

Sakai, T. and Ohno, N. (1988), Flow-Injection Spectrophotometric Determination of Palladium in Catalysts and Dental Alloys with 2-(5-Bromo-2-Pyridylazo)-5-(N-Propyl-N-Sulfopropylamino)Aniline, *Anal. Chim. Acta* 214, 271

Shiundu, P.M., Wentzell, P.D. and Wade, A.P. (1990), Spectrophotometric Determination of Palladium with Sulfochlorophenolazorhodanine by Flow Injection, *Talanta*, 37(3), 329

Tait, C. D., Janecky, D. R. and Rogers, P. S. Z. (1991), Speciation of Aqueous Palladium(II) Chloride Solutions Using Optical Spectroscopies, *Geochim. Cosmochim. Acta* 55, 1253

Tong, A., Akama, Y. and Tanaka, S. (1990), Selective Preconcentration of Au(III), Pt(IV) and Pd(II) on Silica Gel Modified with γ -Aminopropyltriethoxysilane, *Anal. Chim. Acta* 230, 179

Usami, S., Fukami, T., Kinoshita, E., Puri, B.K. and Satake, M. (1990), Column Chromatographic Preconcentration of Palladium with Dimethyl Glyoxime and Acenaphthenequinone Dioxime on Naphthalene, *Anal. Chim. Acta* 230, 17

Vandergraaf, T.T. (1982), A Compilation of Sorption Coefficients for Radionuclides on Granites and Granitic Rocks, AECL TR-120

Wernli, B. (1990), Private Communication

Wood, S.A. (1991), Experimental Determination of the Hydrolysis Constants of Pt^{2+} and Pd^{2+} at 25°C from the Solubility of Pt and Pd in Aqueous Hydroxide Solutions, *Geochim. Cosmochim. Acta* 55, 1759

Zhao, Y. and Fu C. (1990), Pre-column Chelation Liquid Chromatographic Separation and Determination of Trace V, Cu, Co, Pd, Fe and Ni, *Anal. Chim. Acta* 230, 23

11.6 Tin

Baes, C.F. and Mesmer, R.E. (1976), *The Hydrolysis of Cations*, J. Wiley and Sons

Browne, C.I., Craig, R.P. and Davidson, N. (1951), Spectrophotometric and Radiochemical Investigation of the Interaction between Tin(II) and -(IV) in Hydrochloric Acid Solutions, *J. Am. Chem. Soc.* 73, 1946

Byrd, J.T. and Andreae M.O. (1982), Tin and Methyltin Species in Seawater: Concentrations and Fluxes, *Science* 218, 565

Daniels, W.R., Wolfsberg, K., Rundberg, R.S. et al. (1982), Summary Report on the Geochemistry of Yucca Mountain and Environs, LA-9328-MS

Early, T.O., Jacobs, G.K. and Drewes, D.R. (1984), Geochemical Controls on Radionuclide Releases from a Nuclear Waste Repository in Basalt, in: *Geochemical Behavior of Disposed Radioactive Waste*, ACS Symposium Series 246

Harrison, P.G., (Ed). (1989), Chemistry of Tin, Blackie & Son Ltd., Glasgow and London

Koide, M. and Goldberg, E.D. (1985), Determination of ^{99}Tc , ^{63}Ni and $^{121\text{m}+126}\text{Sn}$ in the Marine Environment, *J. Environ. Radioactivity* 2, 261

Leclere, B. (1974), Application de la Spectrophotométrie d'Absorption Atomique et de la Polarographie à Tension Sinusoïdale Surimposée aux Dosages de l'Etain et du Molybdène dans les Minerais de Tungstène, Thèse présentée à l'Université Scientifique et Médicale de Grenoble

Nyffeler, U.P., Li, Y.-H. and Santschi, P.H. (1984), A Kinetic Approach to Describe Trace-Element Distribution Between Particles and Solution in Natural Aquatic Systems, *Geochim. Cosmochim. Acta* 48, 1513

Patton, T.L. and Penrose, W.R. (1989), Fission Product Tin in Sediments, *J. Environ. Radioactivity* 10, 201

Phillips, S.L., Hale, F.V., Silvester, L.F. and Siegel, M.D. (1988), Thermodynamic Tables for Nuclear Waste Isolation, NUREG/CR-4864, Vol. 1

Serne, R.J. and Relyea, J.F. (1981), The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program, PNL-SA-9787

Taylor, R.G. (1979), Geology of Tin Deposits, Elsevier Scientific Publishing Company, Amsterdam

Thomas, K.W. (1987), Summary of Sorption Measurements Performed with Yucca Mountain, Nevada, Tuff Samples and Water from Well J-13, LA-10960-MS

Zuckerman, J.J. (1967), Applications of $^{119\text{m}}\text{Sn}$ Mössbauer Spectroscopy to Chemical Problems, *Mössbauer Effect Methodology* 3, 15

11.7 Neptunium

Allard, B., Kipatsi, H. and Liljenzin, J.O. (1980), Expected Species of Uranium, Neptunium and Plutonium in Neutral Aqueous Solutions, *J. inorg. nucl. chem.* 42, 1015

Bajo, C. (1982), Etude préliminaire des méthodes de dosage du Np pour des quantités inférieures à 1 µg, TM-42-82-16

Beall, G.W. and Allard, B. (1981), Sorption of Actinides from Aqueous Solution under Environmental Conditions, in: Adsorption from Aqueous Solutions, P.H. Tewari, Ed., Plenum Press.

Bidoglio, G., Tanet, G. and Chatt, A. (1985), Studies on Neptunium(V) Carbonate Complexes under Geologic Repository Conditions, *Radiochim. Acta* 38, 21

Bidoglio, G. and De Plano, A. (1986), Neptunium Migration in Salt Brine Aquifers, *Nucl. Techn.* 74, 307

Cauchetier, Ph. (1979), Determination of Microamounts of Neptunium by Differential Pulse Polarography, *J. Radioanal. Chem.* 51(2), 225

Cleveland, J.M., Rees, T.F. and Nash, K.L. (1985), Plutonium, Americium, and Neptunium Speciation in Selected Groundwaters, *Nucl. Techn.* 69, 380

Cross, J.E., Crossley, D., Edwards, J.W., Ewart, F.T., Liezers, M., McMillan, J.W., Pollard, P.M. and Turner, S. (1989), Actinide Speciation: Further Development and Application of Laser Induced Photoacoustic Spectroscopy and Voltammetry, Harwell, AERE-R-13299

Fahey, J.A. (1986), Neptunium, in: *The Chemistry of the Actinide Elements*, Katz, J.J., Seaborg, G.T. and Morss, L.R., Eds, Chapman and Hall, 2nd. Ed., Vol.1, pp.443-498

Foti, S.C. and Freiling, E.C. (1964), The Determination of the Oxidation States of Tracer Uranium, Neptunium and Plutonium in Aqueous Media, *Talanta*, 11, 385

Grenthe, I., Robouch, P. and Vitorge, P. (1986a), Chemical Equilibria in Actinide Carbonate Systems, *J. Less-Common Metals* 122, 225

- Grenthe, I., Riglet, C. and Vitorge, P. (1986b), Studies of Metal-Carbonate Complexes. 14. Composition and Equilibria of Trinuclear Neptunium(VI)- and Plutonium(VI)-Carbonate Complexes, *Inorg. Chem.* 25, 1679
- Inoue, Y. and Tochiyama, O. (1977), Determination of the Oxidation States of Neptunium at Tracer Concentrations by Adsorption on Silica Gel and Barium Sulfate, *J. inorg. nucl. Chem.* 39, 1443
- Jové, J., Cousson, A., Abazli, H., Tabuteau, A., Thévenin, T. and Pagès, M. (1988), Systematic Trends in the $^{237}\text{Neptunium}$ Mössbauer Isomer Shift: Overlap of IV, V and VI Neptunium Oxidation States and Correlation Between Isomer Shift and Crystal Structure, *Hyperfine Interactions* 39, 1
- Kim, J.I. (1986), Chemical Behavior of Transuranic Elements in Natural Aquatic Systems, pp. 413 ff. in: *Handbook on the Physics and Chemistry of the Actinides*, edited by A.J. Freeman and C. Keller, Elsevier Science Publishers
- Lierse, Ch., Treiber, W. and Kim, J.I. (1985), Hydrolysis Reactions of Neptunium(V), *Radiochim. Acta* 38, 27
- Lieser, K.H., Mühlenweg, U. and Sipos-Galiba, I. (1985), Dissolution of Neptunium Dioxide in Aqueous Solutions under Various Conditions, *Radiochim. Acta* 39, 35
- Lieser, K.H. and Mühlenweg, U. (1988), Neptunium in the Hydrosphere and in the Geosphere; I. Chemistry of Neptunium in the Hydrosphere and Sorption of Neptunium from Groundwaters on Sediments under Aerobic and Anaerobic Conditions, *Radiochim. Acta* 43, 27
- Maya, L. (1983) Hydrolysis and Carbonate Complexation of Dioxoneptunium(V) in 1.0 M NaClO_4 at 25°C, *Inorg. Chem.* 22, 2093
- Maya, L. (1984), Carbonate Complexation of Dioxoneptunium(VI) at 25 °C: Its Effect on the Np(V)/Np(VI) Potential, *Inorg. Chem.* 23, 3926
- Meyer, R.E., Arnold, W.D. and Case, F.I. (1984), Valence Effects on the Sorption of Nuclides on Rocks and Minerals, NUREG/CR-3389, ORNL-5978
- Moskvin, A.I. (1971), Hydrolytic Behavior of Neptunium (IV, V, VI), *Sov. Radiochem.* 13, 700

Newton, T.W. (1975), The Kinetics of the Oxidation-Reduction Reactions of Uranium, Neptunium, Plutonium and Americium in Aqueous Solutions, TID-26506

Niese, U. (1990), On the Occasion of the Fiftieth Anniversary of Neptunium Discovery, *Isotopenpraxis* 26, 352

Nilsson, K. and Carlsen, L. (1989), The Migration Chemistry of Neptunium, Risoe-M-2792

Patil, S.K., Ramakrishna, V.V. and Ramaniah, M.V. (1976), Aqueous Coordination Complexes of Neptunium, Bhabha Atomic Research Center, Bombay, India, B.A.R.C. 907

Patil, S.K., Ramakrishna, V.V. and Ramaniah, M.V. (1978), Aqueous Coordination Complexes of Neptunium, *Coord. Chem. Rev.* 25, 133

Phillips, S.L., Hale, F.V., Silvester, L.F. and Siegel, M.D. (1988), Thermodynamic Tables for Nuclear Waste Isolation, NUREG/CR-4864, Vol. 1

Riglet, Ch., Robouch, P. and Vitorge, P. (1989), Standard Potentials of the ($\text{MO}_2^{2+}/\text{MO}_2^+$) and ($\text{M}^{4+}/\text{M}^{3+}$) Redox Systems for Neptunium and Plutonium, *Radiochim. Acta* 46, 85

Savvin, S.B. (1964), Analytical Applications of Arsenazo III-II. Determination of Thorium, Uranium, Protactinium, Neptunium, Hafnium and Scandium, *Talanta*, 11, 1

Sevost'yanova, E.P. and Khalturin, G.V. (1976), *Sov. Radiochem.* 18, 738

Sheppard, M.I., Beals, D.I., Thibault, D.H. and O'Connor, P. (1984), Soil Nuclide Distribution Coefficients and their Statistical Distributions, AECL-8364

Susak, N.J., Friedman, A., Fried, S. and Sullivan, J.C. (1983), The Reduction of Neptunium(VI) by Basalt and Olivine, *Nucl. Techn.* 63, 266

Török, G. and Ruf, H. (1982), Determination of the Distribution of Neptunium at Tracer Concentrations Among its Oxidation States in Aqueous Nitric Acid Media, *Radiochim. Acta* 30, 223