Katholieke Universiteit Leuven
Faculteit Bio-ingenieurswetenschappen
Departement Microbiële en Moleculaire Systemen
Centrum voor Oppervlaktechemie en Katalyse

DISSERTATIONES DE AGRICULTURA

Doctoraatsproefschrift nr. 746 aan de faculteit Bio-ingenieurswetenschappen van de K.U.Leuven

The interaction between technetium and Gorleben humic substances

Proefschrift voorgedragen tot het
behalen van de graad van
Doctor in de
Bio-ingenieurswetenschappen

door

Kathleen Geraedts

Mei 2007

Doctoraatsproefschrift nr. 746 aan de faculteit Bio-ingenieurswetenschappen van de K.U.Leuven

ISBN 978-90-8826-014-8
Wettelijk depot D/2007/11.109/14

Katholieke Universiteit Leuven
Faculteit Bio-ingenieurswetenschappen
Departement Microbiële en Moleculaire Systemen
Centrum voor Oppervlaktechemie en Katalyse

DISSERTATIONES DE AGRICULTURA

Doctoraatsproefschrift nr. 746 aan de faculteit Bio-ingenieurswetenschappen van de K.U.Leuven

The interaction between technetium and Gorleben humic substances

Promotor:
Prof. A. Maes, K.U.Leuven

Leden van de examencommissie:
Prof. G. Volckaert, voorzitter
Prof. R. Merckx, K.U.Leuven
Prof. R. Schoonheydt, K.U.Leuven
Dr. N. Maes, SCK-CEN
Prof. B. Grambow, Ecole des Mines, Nantes

Proefschrift voorgedragen tot het behalen van de graad van Doctor in de Bio-ingenieurswetenschappen

door

Kathleen Geraedts

Mei 2007

Dankwoord

Eindelijk is het zover! De laatste verbeteringen zijn uitgevoerd en nu moet ik enkel nog de meest gelezen pagina schrijven. Een niet te onderschatten opdracht want een werk zoals dit had nooit beëindigd kunnen worden zonder de hulp en de steun van velen en ik zou dan ook niemand willen vergeten.

Op de eerste plaats gaat mijn dank uit naar prof. André Maes. André, een oprecht dank je wel voor alle hulp, alle suggesties, alle leerrijke discussies en het nauwgezet nalezen van deze tekst. Het was in het begin zeker niet evident om met een achtergrond van mijnbouwingenieur in de wereld van de bodem- en waterchemie te komen, maar ik ben je zeer erkentelijk dat we er samen in geslaagd zijn om dit onderzoek tot een goed einde te brengen.

Verder gaat mijn dank ook uit naar de leden van de jury voor hun opmerkingen en suggesties tot het finaliseren van dit werk: prof. Merckx, prof. Schoonheydt, prof. Grambow en Dr. Maes.

Ook de collega's van het Laboratorium voor Colloidchemie hebben allen een grote bijdrage geleverd: Jacqueline, bedankt voor de hulp bij en het uitvoeren van de experimenten. Zonder jouw ervaring en kennis zou het onmogelijk geweest zijn om de talloze experimenten af te werken. Verder wil ik nog Christophe en Eric bedanken voor alle hulp en tips bij het verwerken van de data en het neerschrijven van deze tekst. Ook Steven, Mathias, Agnes, alle thesisstudenten en stagaires mogen niet ontbreken in deze dankbetuiging. Samen met de anderen van het labo hebben jullie altijd voor een fijne werksfeer gezorgd.

Een speciaal woordje van dank gaat naar de European Synchrotron Radiation Facility (Grenoble, Frankrijk) voor de EXAFS en XANES metingen en de hulp van André Rossberg en Christoph Hennig bij het verwerken van de EXAFS metingen. De Katholieke Universiteit Leuven wil ik bedanken voor de doctoraatsbeurs die het me mogelijk heeft gemaakt om dit werk uit te kunnen voeren.

Onrechtstreeks, maar zeker zo belangrijk voor dit werk is de invloed van familie en vrienden: mijn ouders, die altijd voor me klaar staan. Ma en pa, bedankt ! Verder wil ik ook Jo, Africa, mijn schoonouders, alle vrienden en vriendinnen van vroeger en nu, alle vorige en huidige collega's en de (voormalige) ploeggenootjes van de volleybal in deze dankbetuiging betrekken. Eindelijk kan ik nu volmondig beamen: mijn doctoraat is af! En bedankt voor alle fijne momenten.

En tenslotte, nog een woordje voor de drie belangrijkste mannen in mijn leven. Bart, zonder jouw steun en overtuiging dat het allemaal wel zou afgeraken, zou dit werk zeker niet mogelijk geweest zijn. Bedankt voor alles ! Ik draag dit werk op aan jou, Jasper en Arvid.

Leuven, 6 mei 2007

Contents

Contents i
Samenvatting iii
Summary vii
Abbreviations xi
List of Publications xiii

General Introduction
1. Background of the study 1
2. Objectives and outline of this study 4

Chapter 1. The (geo)chemical behaviour of the radionuclide technetium
1.1 Introduction 7
1.2 Origin and fate 7
1.3 Redox chemistry and speciation of technetium 7
1.4 Technetium speciation in radioactive waste and the near-field 14
1.5 The geochemical behaviour of technetium in aquifer systems 15
1.6 Conclusions 25

Chapter 2. The Gorleben aquifer system: characterisation and interaction with radionuclides
2.1 Introduction 27
2.2 The Gorleben Sampling site 28
2.3 The interaction between radionuclides and Gorleben humic substances 32
2.4 Conclusions 34

Chapter 3. Factors effecting the reduction of pertechnetate in the presence and absence of humic substances and the formation of technetium – humic substance species
3.1 Introduction 35
3.2 Experimental set-up 36
3.3 Results and discussion 40
3.4 Conclusions 53

Chapter 4. Evidence for the existence of Tc(IV)-humic substance species by X-ray Absorption Near – Edge Spectroscopy
4.1 Introduction 55
4.2 X-ray absorption spectroscopy: theoretical background 56
4.3 Experimental set-up 57
4.4 Results and discussion 58
4.5 Conclusions 64

Chapter 5. Evidence for the formation of technetium colloids in humic substances by X-ray Absorption Spectroscopy
5.1 Introduction 67
5.2 EXAFS methodology 67
5.3 Experimental set-up 68
5.4 Results 70
5.5 Discussion 79
5.6 Conclusions 82

Chapter 6. Determination of the conditional interaction constant between colloidal technetium(IV) and Gorleben humic substances
6.1 Introduction 83
6.2 Experimental set-up 84
6.3 Results and Discussion 86
6.4 Conclusions 95

Chapter 7. A new method for technetium(IV) speciation in humic rich natural Gorleben groundwater
7.1 Introduction 103
7.2 Experimental set-up 104
7.3 Results and discussion 107
7.4 Conclusions 113

Chapter 8. Quantification of the conditional interaction between technetium(IV) and Gorleben humic substances using the La-precipitation method
8.1 Introduction 119
8.2 Experimental set-up 119
8.3 Results and discussion 121
8.4 Conclusions 129

General Conclusions 135

References 143

Samenvatting

De discussie in België rond kernenergie en de uitstap uit kernenergie is een uiterst actueel onderwerp. Er is immers de kernuitstapwet van 2003, waardoor tegen 2015 begonnen moet worden met het sluiten van de oudste kerncentrales om zo tegen 2025 de productie van elektriciteit via kernenergie volledig stop te zetten. Tegenstanders van het sluiten van de kerncentrales voeren echter aan dat er geen concurrentiële alternatieven zijn, en daarom werd er recent door de Commissie "Energie 2030" het advies gegeven om terug te komen op de beslissing om te sluiten. De Belgische regering en de publieke opinie zijn het hier niet mee eens.

Een van de problemen inherent aan de productie van elektriciteit door middel van kernenergie is het radioactieve afval. Vooral voor het langlevende hoogradioactieve afval moet er een adequate oplossing gezocht worden. Eén van de mogelijke oplossingen is opslag in (quasi) ondoordringbare ondergrondse geologische lagen zoals klei, graniet of zout. Voorbeelden hiervan zijn de Boomse kleilaag in Mol en de Gorleben zoutdiapier in Duitsland. Er is al sinds de jaren 1970 grootschalig onderzoek gaande of de voorgenoemde mogelijke ondergrondse opslagplaatsen voldoende bescherming voor mens en omgeving kunnen bieden tegen radioactieve besmetting. Tot dusver zijn er in de meeste landen nog geen definitieve beslissingen genomen of de onderzochte opslagplaatsen ook daadwerkelijk in gebruik zullen genomen worden. Enkel in Finland en de V.S.A. is de bouw van ondergrondse opslagplaatsen al begonnen.

Technetium-99 is een langlevend splijtingsproduct van uranium-235 en plutonium-239 dat voorkomt in hoogradioactief afval. 6% van het radioactieve kernafval bestaat uit technetium-99. Tc-99m wordt ook veelvuldig gebruikt in de medische wereld als "tracer" in de radiodiagnostiek. Onder oxiderende omstandigheden, bestaat Tc als het erg oplosbare en mobiele pertechnetaat (Tc(VII)). Onder reducerende omstandigheden, zijnde de omstandigheden heersend in mogelijke opslagplaatsen, zal (hoogstwaarschijnlijk) het tetravalente Tc voorkomen met een beperkte oplosbaarheid. Tc(IV) kan ook reageren met de verschillende geochemische immobiele en mobiele componenten aanwezig in de opslagplaatsen en de omringende watervoerende lagen.

In potentiële opslagplaatsen en de omringende watervoerende lagen zijn vaak aanzienlijke hoeveelheden opgeloste organische stof aanwezig. Zij kunnen associëren met technetium en zo voor een verhoogde oplosbaarheid van technetium zorgen. Hierdoor is een verhoogde migratie mogelijk van technetium-99 vanuit de opslagplaats naar oppervlaktewateren, waardoor technetium schade zou kunnen berokkenen aan mens en milieu. Om te kunnen oordelen of een potentiële opslagplaats voldoende veilig is moeten de concentraties aan radionucliden die vrij kunnen komen voldoende laag liggen. Er is nood aan goede methodes om dit te kunnen kwantificeren.

In dit onderzoek werd de interactie onder reducerende omstandigheden tussen mobiele organische stof (Gorleben humussubstanties) en technetium-99 bestudeerd.

Gorleben humussubstanties werden gekozen omdat deze goed beschreven zijn in de literatuur en er reeds veel onderzoek werd gedaan naar de interactie tussen deze humussubstanties en andere radionucliden.

Door middel van batch experimenten in een handschoenkast (met een gasmengsel van 95% N_2 en 5% H_2) werd het gedrag van technetium (onder de vorm van pertechnetaat) onder reducerende omstandigheden onderzocht in aan- en afwezigheid van Gorleben organische stof. De reductie van pertechnetaat bleek kinetisch gecontroleerd te zijn en kan enkel plaatsvinden in aanwezigheid van een reducerend oppervlak (zoals bv. het ijzer(II)houdend magnetiet). Dergelijke oppervlakken zullen courant aanwezig zijn als "backfill" in de opslagplaatsen, maar ook in de watervoerende lagen. Er werd in de bestudeerde tijdspanne geen interactie tussen Tc(VII) en humussubstanties gevonden.

Pertechnetaat werd vervolgens gereduceerd met behulp van reducerende oppervlakken zoals magnetiet en pyriet in aan- en afwezigheid van humussubstanties. Hierbij werd de concentratie aan Tc gevolgd als functie van de tijd. Bij evenwicht was de concentratie aan Tc in oplossing gedaald en verdeelde Tc zich dus tussen de vaste en de vloeibare fase, waardoor verondersteld kon worden dat pertechnetaat gereduceerd was. Maar zowel in aan- als in afwezigheid van humussubstanties (HS) werden verhoogde Tc concentraties gevonden t.o.v. de oplosbaarheid van het amorfe precipitaat $TcO_2.nH_2O$ dat theoretisch gezien gevormd zou zijn op de vaste fase. De bekomen Tc concentratie in aanwezigheid van organische stof lag zelfs een factor 100 hoger dan in afwezigheid van organische stof en werd verklaard door de vorming van Tc-humussubstantie species. Via gel permeatie chromatografie konden deze colloïdale Tc-HS species ook aangetoond worden. Ook in afwezigheid van humus substanties werden op de chromatogrammen grotere anorganische Tc species gevonden. Een verklaring voor de verhoogde oplosbaarheden (zowel in aan- als in afwezigheid van organische stof) lag dus in de vorming van gereduceerde colloïdale Tc species.

Met behulp van XANES spectroscopie werd voor de eerste maal bewezen dat de oxidatietrap van Tc in Tc-humussubstanties vierwaardig was. Door de gevormde Tc(IV) species op zowel het oppervlak als in de humus substantie met EXAFS spectroscopie te onderzoeken, werden de vormen van de Tc species bepaald. Alle bekomen EXAFS spectra konden gefit worden met een vorm analoog aan het amorfe $TcO_2.nH_2O$ precipitaat. De gevormde Tc(IV) species zowel op de vaste fase als in oplossing zijn bijgevolg mono-, di- of polynucleaire $(TcO(OH)_2)_n$ species. Hierdoor werd er besloten dat de interactie tussen Tc(IV) en humussubstanties bestaat als een colloïdale inclusie van tetravalente technetiumspecies in de humussubstanties. Dit is een ongewoon interactiemechanisme voor de reactie tussen radionucliden en humussubstanties.

In een volgende stap werd het gedrag van technetium onderzocht onder variabele geochemische omstandigheden. Pertechnetaat werd gereduceerd met behulp van magnetiet in aan- en afwezigheid van organische stof. Zowel de pH, de technetium concentratie, de organische stof concentratie, als de hoeveelheid magnetiet werden gevarieerd en de bekomen verdeling van technetium tussen de vaste en vloeibare fase werd bestudeerd als functie van de verschillende parameters. Hieruit bleek dat zowel in aan- als in afwezigheid van organische stof de verdeling van technetium tussen de vaste en vloeibare fase kon beschreven worden met een lineaire sorptie-isotherm. Dit

leidde tot de vaststelling dat de interactie tussen mono-, di- of polynucleaire $(TcO(OH)_2)_n$ species en humussubstanties kon gekwantificeerd worden via een (aangepaste) Schubert methode. Concentratiequotiënten gelijk aan 2.9 (± 0.3) (gebruik maken van de EQ3/6 database) of 3.0 (± 0.3) (NEA database) werden bekomen. De bekomen Log K^{HS} waarde bleek onafhankelijk te zijn van de pH en de bedekking van Tc op de humussubstanties. Deze twee feiten waren ongewoon voor een "normaal" metaal-humussubstantie interactiemechanisme (zoals complexatie) maar vormden een bijkomend bewijs voor het voorgestelde interactiemechanisme voor Tc(IV) en HS.

Voor de toepassing van de aangepaste Schubert methode werd de verdeling van Tc tussen een vaste en vloeibare fase gemeten. Maar om eenvoudig de interactie van Tc en humussubstanties onder diverse omstandigheden te kunnen kwantificeren, werd een nieuwe en simpele methode – de La-precipitatie methode – ontwikkeld. Deze methode is gebaseerd op het feit dat trivalente kationen zoals La^{3+} in staat zijn om opgeloste humussubstanties neer te slaan. Hierdoor konden de gebonden Tc-HS species fysiek gescheiden worden van de vrije ongebonden Tc species. De methode werd voldoende accuraat gevonden voor een kwantificatie van de vrije en gebonden Tc(IV) species in oplossing. Dit leidde in een volgende stap tot een bepaling van de concentratiequotiënt Log K^{HS} gelijk aan 2.6 (± 0.3) bepaald op experimentele resultaten waarbij Tc-HS species gevormd werden onder diverse omstandigheden (veranderingen in pH, Tc en HS concentratie, hoeveelheid reducerende fase). Naast magnetiet, werd als reducerende oppervlak voor pertechnetaat ook pyriet gebruikt. Bijkomend werden *in situ* omstandigheden nagebootst door pertechnetaat te reduceren in een Gorleben zand / Gorleben water mengsel. De gebruikte reducerende fase bleek geen invloed te hebben op de interactie tussen Tc en HS en was bijgevolg enkel een elektronenleverancier voor de reductie van pertechnetaat.

De gevonden waarde was iets lager dan de "Schubert waarde", maar de grote experimentele afwijkingen op de bekomen resultaten konden grotendeels dit verschil verklaren. De La-precipitatie methode kon bijgevolg gebruikt worden voor een vlugge en ruwe berekening van de concentratiequotiënt voor de Tc(IV)-humussubstantie species gevormd onder diverse omstandigheden. Analoog als bij de Schubert methode was de bekomen K^{HS} waarde onafhankelijk van pH en de Tc – HS bedekking.

De La-precipitatie methode kan ook gebruikt worden voor de studie van het gedrag van andere radionucliden in aanwezigheid van humussubstanties, doch enkel wanneer deze radionucliden een gelijkaardig gedrag vertonen als technetium. Voorbeelden hiervan zijn thorium en neptunium.

Om te kunnen oordelen over het gedrag en de stabiliteit van technetium-humussubstanties op lange termijn zou er bijkomend nog spectroscopisch onderzoek uitgevoerd moeten worden op de Tc-HS species. De relatieve hoeveelheden van de verschillende mono-, di- of polynucleaire $(TcO(OH)_2)_n$ species zouden bepaald moeten kunnen worden, waardoor de bekomen Log K^{HS} waarde verfijnd en verbeterd zou kunnen worden. Het al dan niet reversibele karakter van de gevormde Tc-HS species zou onderzocht moeten worden in batch desorptie-experimenten en kolomexperimenten, waarbij het dynamisch gedrag van de Tc-HS species gevolgd wordt, bijdragen tot een nog beter begrip van deze species.

Summary

In Belgium, the discussion on nuclear energy and the withdrawal from it are hot topics. In 2003, the federal government decided to start in 2015 with a gradual shutdown of the oldest nuclear power plants in order to have a complete halt of production of electricity through nuclear energy by the year 2025. Opponents of the closure of nuclear power plants state that there are no competitive alternatives, and therefore, it was recently advised by the Commission "Energie 2030" to reconsider the decision of 2003. However, the Belgian government and the public opinion very much disagree.

One of the major problems regarding production of electricity through nuclear energy is the radioactive waste. Especially, the long-living high-level radioactive waste needs a proper solution. A possible solution is disposal in a impermeable geologic layer such as clay, granite or salt. Examples of such are the Boom clay in Mol (Belgium) and the Gorleben salt diapyr in Germany. Since the years 1970 many studies are performed to investigate if the latter disposal sites offer sufficient protection against radioactive pollution for man and environment. Until now, most countries did not take a final decision whether the investigated sites will be used for future disposal. Only in Finland and the U.S.A., the building of geological disposal sites have started.

Technetium-99 is a long-lived ($t_{1/2} = 2.14 \times 10^5$ y) fission product of uranium-235 and plutonium-239. 6% of all fission products consists of technetium-99. The short-lived isomer technetium-99m is one of the most widely used radionuclides in nuclear medicine. Its geochemistry is dominated by a soluble, non-retarded oxyanion, $Tc(VII)O_4^-$, which is stable under oxidising conditions, and (most probably) a insoluble $Tc(IV)O_2.nH_2O$ phase, which is stable under anoxic conditions (*i.e.* conditions relevant for geologic disposal). Reduced Tc(IV) species can interact with mobile and immobile geochemical components of disposal sites and the surrounding aquifers.

In potential geological disposal sites and natural aquifers, dissolved organic matter is ubiquitous. An association between these species and technetium is possible, resulting in an enhanced solubility of Tc. Consequently, an enhanced migration of technetium-99 is possible from the disposal site to superficial waters where the radionuclide could damage man and environment. One of the fundamental questions whether a repository will remain safe or not is whether the concentrations of radionuclides that may enter the surrounding aquifers, will remain extremely low over geological periods of time. This necessitates the need for proper quantification methods.

This work focuses on the interaction under reducing conditions between the radionuclide technetium-99 and Gorleben humic substances. Gorleben humic substances were chosen because they are well described in literature and already many investigations were performed on the interaction between these humic substances and other radionuclides.

Through batch experiments in a glove box (mixture of 95% N_2 and 5% H_2), the behaviour of technetium (as the pertechnetate species) under reducing conditions was investigated in the presence and absence of Gorleben humic substances. The reduction of pertechnetate was found being kinetically controlled and only possible in the presence of a reducing solid surface (eg. the iron(II)containing Magnetite). Such surfaces are commonly present in the backfill of natural repositories and aquifer systems. No interaction between pertechnetate and humic substances occurred in the studied time period.

In a next step, pertechnetate was reduced with the aid of reducing surfaces such as Magnetite and Pyrite in the presence and absence of humic substances. The concentration of Tc was followed as a function of time. At equilibrium, the Tc concentration in solution was decreased and therefore Tc was distributed between the solid and the liquid phase; hence, a reduction of pertechnetate had occurred. However, both in the presence and absence of humic substances, enhanced Tc concentrations were observed compared to the theoretical solubility of the amorphous $TcO_2.nH_2O$ precipitate which (theoretically) must have been formed on the solid phase. The observed Tc concentration in the presence of humic substances was even 100 times higher than in the absence of humic substances, which was explained by the formation of Tc-humic substances species. Through gel permeation chromatography the presence of these Tc-humic substance species was proven. The chromatograms showed also in the absence of humic substances, Tc species of larger hydrodynamic size. The enhanced Tc solubilities (both in the absence and presence of humic substances) can thus be explained by the formation of reduced colloidal Tc species.

In this work, it was demonstrated for the first time by XANES spectroscopy that tetravalent Tc species are associated with humic. Investigation of the Tc(IV) species both on the solid surface as on the humic substances through EXAFS spectroscopy revealed the nature of the formed Tc species. All measured samples show similar EXAFS spectra for Tc which could be fitted by a hydrated $TcO_2.xH_2O$ phase. These hydrated $TcO_2.xH_2O$ phase are considered to be mono-, di- and polynuclear (or colloidal) Tc(IV) species. From the latter results, it was concluded that the association of Tc(IV) species and humic substances occurs by way of a colloidal inclusion of mono-, di- and polynuclear (or colloidal) Tc(IV) species within the humic substances. This latter type of interaction seriously differs from the generally accepted metal-humate complexation.

Further on, the behaviour of technetium under variable geochemical circumstances was investigated. Pertechnetate was reduced with the aid of Magnetite in the presence and absence of humic substances. The distribution of technetium between the solid and the liquid phase was studied as a function of pH, technetium and humic substance concentration and the amount of Magnetite. From all experimental results, it was observed that both in the presence and the absence of humic substances, the distribution of technetium between the solid and liquid phase could be described with a linear sorption isotherm. Therefore, the interaction between the mono-, di- and polynuclear (or colloidal) $(TcO(OH)_2)_n$ species and humic substances could be quantified using a modified Schubert approach. Conditional interaction constants Log K^{HS} were found equal to 2.9 (± 0.3) (when using the EQ3/6 database) and 3.0 (± 0.3) (NEA database).

This interaction constant Log K^{HS} was found independent of pH and Tc loading on humic substances. These two facts are unusual for a normal metal – humic substance interaction (as complexation) but are a further proof for the previously proposed interaction mechanism between Tc(IV) and HS.

In the aforementioned Schubert method, only the Tc distribution between the solid and the liquid phase is measured. However, in order to determine directly the interaction of Tc(IV) with humic substances in a variety of conditions, it is necessary to have a method for the direct determination of the individual solution concentrations of Tc(IV) associated with HS and the "free" Tc(IV). A method for quick speciation in solution was therefore developed that was called the La-precipitation method. The addition of a sufficient excess concentration of La^{3+} in humic substance containing solutions allows to precipitate all the humic colloids. This lead to a quantitative separation of Tc bound to HS and the free Tc species. The method was being found sufficiently accurate for the quantification of the free and bound Tc(IV) species. In a next step, the La-precipitation method was used to calculate a conditional interaction constant K^{HS} equal to 2.6 (± 0.3) for the interaction between Tc(IV) and humic substances for a large number of Tc-HS supernatant solutions obtained under various experimental conditions (varying pH, Tc and HS concentrations and amount of reducing solid phase). Besides Magnetite, also Pyrite was used for the reduction of pertechnetate. In addition, to mimic *in situ* circumstances, pertechnetate was reduced in a Gorleben sand / Gorleben groundwater mixture. The used type of reducing surface had no influence on the association between Tc and humic substances and acted only as a electron donor in the overall redox and association reaction.

The obtained Log K^{HS} value from the La precipitation method is slightly lower than the value obtained through the Schubert approach. Differences between the two values are probably explained by the large experimental scatter on the data used in both methods. Nevertheless, the La precipitation method is useful for a quick and rough determination of the conditional interaction constant of the interaction between Tc(IV) species and humic substances. Similar as with the Schubert method, the found K^{HS} value was found being independent of pH and Tc-HS loading.

The La precipitation method can be used when studying the behaviour of other radionuclides in the presence of humic substances, when they are expected to behave in a similar way as technetium. Examples of such are thorium and neptunium.

A better judgement on the behaviour and stability of technetium-humic substance species at a long time scale, necessitates additional spectroscopic studies. In order to refine the calculated interaction constant K^{HS}, the relative abundance of the different mono-, di- or polynuclear $(TcO(OH)_2)_n$ species must be determined. Whether the interaction between Tc(IV) and HS is reversible or not, should be investigated by desorption experiments. In addition, for a more detailed understanding of the Tc-HS species, it is recommended to perform column experiments where the dynamic behaviour of Tc(IV)-HS species of different ages is followed.

Abbreviations

A	Side reaction coefficient
CHESS	Chemical Equilibrium of Species and Surfaces
CN	Coordination Number
cpm	Counts per minute
DOC	Dissolved Organic Carbon
EXAFS	Extended X-ray Absorption Fine Spectrum
FA	Fulvic Acid
FT	Fourier Transform
GoHy	Gorleben Hydrological Sample
GPC	Gel permeation Chromatography
GS	Gorleben Sand
GW	Natural Gorleben (ground)Water
HA	Humic Acid
HS	Humic Substances
K_d	Distribution coefficient (presence of humic substances)
K_d°	Distribution coefficient (absence of humic substances)
K^{HS}	Conditional interaction constant for the interaction between Tc and humic substances
LSC	Liquid Scintillation Counting
NEA	Nuclear Energy Agency
R	Bond length
σ^2	Debye-Waller factor
SGW	Synthetic Gorleben (ground)Water
$[Tc]_{initial}$	Initial pertechnetate dose
$[Tc]_{equilibrium}$	Concentration of Tc in solution at equilibrium
$[Tc]_{La}$	Concentration of Tc in solution after La precipitation of the humic substances
$[Tc\text{-}HS]_{La}$	Concentration of Tc bound to humic substances
UV	Ultraviolet Light
Vis	Visible Light
XANES	X-ray Absorption Near-Edge Spectroscopy
XAS	X-ray Absorption Spectroscopy

List of Publications

Geraedts K., Bruggeman C., Maes A., Van Loon L.R., Rossberg A., Reich T., Evidence for the existence of Tc(IV) - humic substance species by X-ray absorption near-edge spectroscopy. Radiochimica Acta 90: 879-884 (2002)

Maes A., Bruggeman C., Geraedts K., Vancluysen J., Quantification of the interaction of Tc with dissolved boom clay humic substances. Environmental Science and Technology 37: 747-753 (2003)

Artinger R., Buckau G., Zeh P., Geraedts K., Vancluysen J., Maes A., Kim J. I., Humic colloid mediated transport of tetravalent actinides and technetium. Radiochimica Acta 91: 743-750 (2003)

Maes A., Geraedts K., Bruggeman C., Vancluysen J., Rossberg A., Hennig C., Evidence for the interaction of technetium colloids with humic substances by X-ray absorption spectroscopy. Environmental Science and Technology 38: 2044-2051 (2004)

GENERAL INTRODUCTION

1. Background of the study

Every human activity generates waste. Radioactive waste arises from the production of electricity in nuclear power plants through the fission of uranium fuel, from the decommissioning of nuclear facilities, and from the use of radioactive materials in medicine, agriculture, industry and research. Radioactive waste includes spent nuclear fuel, which has become highly radioactive after being used in a nuclear reactor. Spent fuel contains unburned uranium as well as plutonium, which are generated as a by-product of the fission process. These elements are extracted by reprocessing, thereby enabling them to be used again.

Most radioactive waste is very similar to domestic and industrial waste. It comprises a wide range of materials, tools, equipment, pipes, dismantled facilities and protective clothing that cannot be re-used and must be disposed of. There is one major difference compared with domestic waste: radioactive waste contains substances (radionuclides) that emit ionizing radiation. This is a particularly high-energy form of radiation, which can alter the structure of the matter into which it penetrates. Ionizing radiation can therefore damage living tissue and can be dangerous for people and the environment. Radioactivity diminishes over time, but until the radioactivity in this type of waste has decreased to a level that is acceptable for public health (which can take thousands or even millions of years) rigorous measures must be taken to ensure that the radiation cannot cause any harm to people or the environment. Many radioactive elements are harmful, even at extremely low levels when taken up directly into the body.

Although most countries have presently decided to reduce or quit the nuclear energy production, the question of "what to do with the high-level radioactive waste?" remains. Many alternatives were proposed during the last decades (figure 1), but the geological repository option remains the only scientifically credible, long-term solution for safely isolating waste without having to rely on active management. In a deep disposal repository, radioactive waste is stored in such a way that no active intervention by future generations would be required without, however, preventing such an intervention if these generations thought it would be useful. Although there are still some significant technical challenges, the broad consensus within the scientific and technical communities is that enough is known to move forward with geological disposal.

In May 2001, Finland became the first country to approve plans for a geologic repository and building the repository will start in 2010. Other countries were not far behind, and in February 2002, the United States, set the light on green for geological disposal at the Yucca Mountain in Nevada. In Belgium, the final decision is not yet taken, but ONDRAF/NIRAS[1] carries out many studies in co-operation with the Studiecentrum voor Kernenergie (CEN-SCK) and various engineering consultancies

[1] ONDRAS/NIRAS: the Belgian Agency for Radioactive Waste and Enriched Fissile Materials

and universities, to verify whether final disposal in deep clay layers can guarantee the protection of man and the environment in the long term. These studies have been going on for over 25 years. The work has focused on the Boom clay in the Mol-Dessel region and, to a lesser extent, on the Ypresian clays in the Doel region. The outcome of the research has reinforced the confidence in clay as a natural barrier, and confirms that deep disposal in poorly indurated clay (such as the Boom clay), remains a conceivable option. In Germany, underground exploration of a salt dome at Gorleben began in 1986. The Gorleben site had been studied since 1979 as a potential permanent radioactive waste repository. After the 1999 parliamentary election, study of the Gorleben salt dome was temporarily stopped, pending further study of other types of geologic environments and to clarify conceptual and safety issues. A new site will be selected based on comparison with Gorleben, which may yet be an interim storage site.

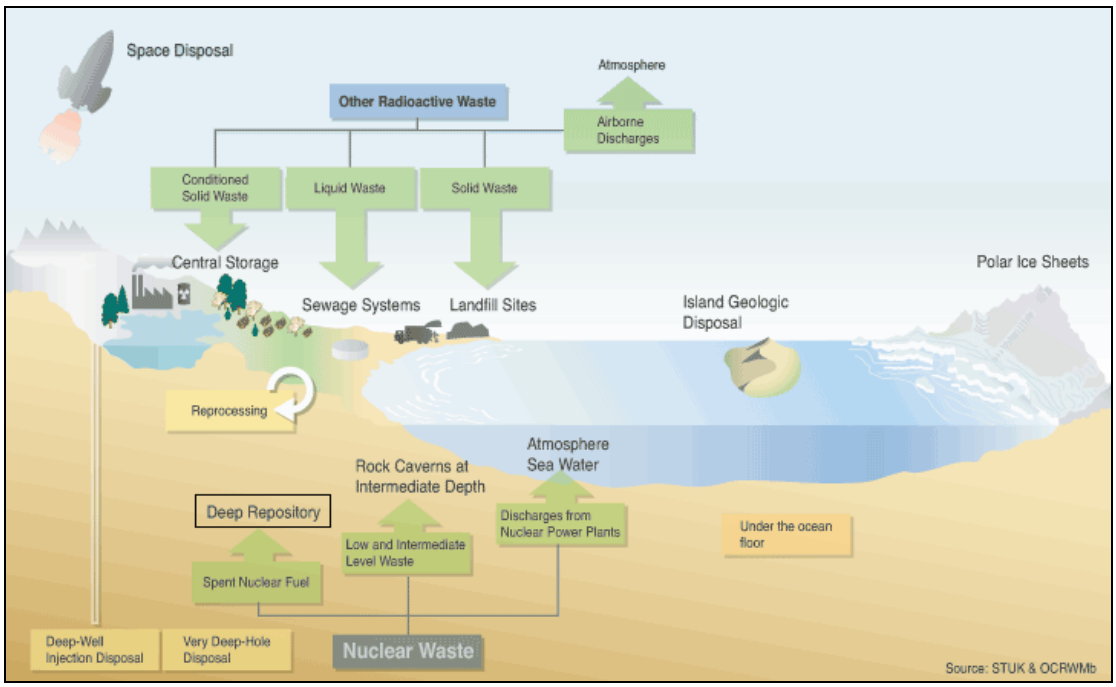

Figure 1. Proposed radioactive waste disposals [2]

The requirements for a selected disposal site are severe: (i) no tectonic activity must be possible in the area, and (ii) groundwater penetration must be inhibited. However, in most selected disposal sites, some infiltration of groundwater is unavoidable and prevention of migration or leaching of hazardous components either as dissolved species or as suspended or colloidal[3] material to surrounding aquifers cannot be fully guaranteed. Given the limitations of the engineered repository barrier, one of the fundamental questions in performance assessment studies[4] or deciding whether a repository will remain safe or not is whether the geochemical reactions, between the waste, the host rock, and the fluids present will keep concentrations of radionuclides

[2] From: http://www.grid.unep.ch/waste/html_file/40-41_radioactive.html
[3] Arbitrarily, colloids have a size between 0.001 and 1 µm (Stevenson, 1982).
[4] Performance assessment is a very broad risk analysing considering all involved processes when selecting possible sites for geological disposal of high-level radioactive waste.

in the surrounding aquifers extremely low over geological periods of time. It is further essential to understand, to model, and to predict the reactions that will occur between the hazardous waste components and the groundwater, between the hazardous waste components and the container in which they were initially enclosed, and between the waste components and the surrounding geological material. This will allow making estimations of the amounts of the hazardous components being transported away from the repository.

The concentration of the radionuclides in groundwater depends on a number of reactions between the fluid, the minerals present, and the gases dissolved in the fluid. In particular the role of oxygen, mobile and immobile organic matter, complex ion formation, and ionic strength are of special interest.

In natural aquifers, mobile and immobile organic matter are ubiquitous and take part in the geochemical solid-water interface reactions. The distribution of radionuclides between the solid and liquid phase is mainly governed by the distribution of organic matter, as organic matter is very well known to form complexes with metals and radionuclides (Bertha and Choppin, 1978, Stevenson, 1982, Kim 1993, Hummel, 1997,…). These organic colloids are therefore considered as particularly important because they can be present in aquifers near potential candidate storage sites. For example, the Boom clay formation in Belgium contains between 120 and 200 mg natural organic matter pro dm^3 in the aqueous solution (Henrion, 1985, De Craen *et al.*, 2004). The aquifers overlying the salt dome in Gorleben contain dissolved organic carbon concentrations from 0.1 to 200 mgC/L (Kim *et al.*, 1990, Buckau, 1991).

Natural organic matter consists of a wide variety of compounds, from which the humic substances (humic and fulvic acids) are the most important. Humic substances are widely distributed in soil, water and fossil organic resources and represent the greatest reservoir of organic carbon on the surface of the Earth. They play an important role in the mobilisation of metal ions in soils and aquatic environments, and affect the availability and toxicity of these metal ions. It is very important to realise that neither the humic nor fulvic acid, despite having a specific name, are made up of one single pure compound. Each humic substance is a heterogeneous mixture of organic substances connected with each other via an organic aliphatic or aromatic matrix. In humic substances, different structural entities (or functional groups) can be distinguished. In other words, humic substances are organic “macromolecules” which have a poly-functional character (figure 2). However until today, scientists specialised in humic substance research, can still not agree on the correct chemical structure and origin or formation pathways of humic substances (Stevenson, 1982, Clapp and Hayes, 1999).

The research concerned with the burial of radioactive waste focuses on humic substances as a possible complexing agent or potential carrier of radionuclides in the geo- and biosphere. Hence, colloidal organic material charged with radionuclides and formed in the near field (near the waste storage), could migrate to the far field (away from the waste storage) (Côme, 1988). This viewpoint was enforced by field examples of radionuclide migration: radioactive cobalt and uranium complexed by organic matter was found in the groundwater near the burial site from Oak Ridge National Laboratory (Means *et al.*, 1978). Radioactive plutonium and americium associated with organic colloids were transported over a distance of 3.4 km away

from the laboratories of Los Alamos (U.S.A.), although laboratory experiments predicted only a few meters of migration (Penrose *et al.*, 1990). Additionally, studies for a salt repository in New Mexico (U.S.A.) indicated that, of all waste radionuclides released in this repository, radioactive carbon, technetium and iodine may reach the surface before they have decayed. Again this transport was associated with organic colloids (Choppin *et al.*, 2001). A thorough comprehension and a quantification of the possible interaction between radionuclides and humic substances are therefore of primary importance for performance assessment studies.

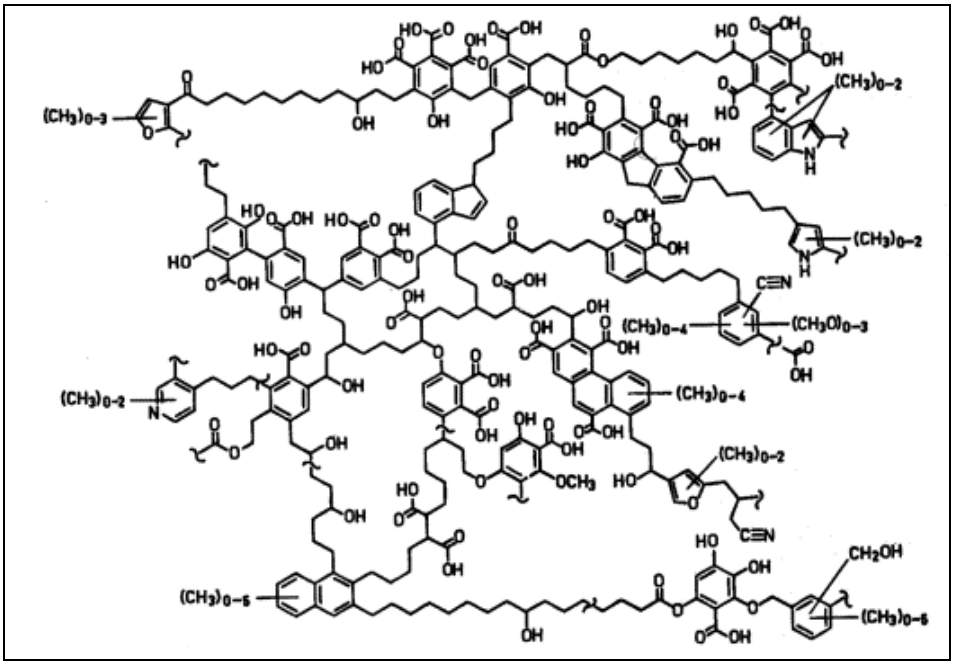

Figure 2. Humic acid structure proposed by Schulten (1994) and Schnitzer (1994).

2. Objectives and outline of this study

This work focuses on the interaction between the radionuclide technetium-99, a fission product of uranium-235 and plutonium-239, and Gorleben humic substances. Gorleben humic substances were chosen because they are well described in literature and the Gorleben salt dome in Germany has been investigated for many years as a potential storage site. In addition, these humic substances are easily available in groundwater of the aquifers overlaying the salt dome.

The main objectives of this Ph. D work are:

(i) studying the behaviour of technetium both in the absence and presence of (Gorleben) humic substances,

(ii) determining the valence state of technetium in "technetium-humic substance species",

(iii) determining the nature of technetium species in the technetium-humic substance species, and

(iv) determining an interaction constant for the interaction between technetium and Gorleben humic substances.

The outline of this work is given in the following:

In Chapter 1, an overview of the (geo)chemistry of the radionuclide technetium and its interaction with geochemical substrata is given.

In Chapter 2, the Gorleben case is emphasised more in detail; this chapter describes further the origin and properties of Gorleben humic substances and gives a short overview of literature references on the interaction of Gorleben humic substances and different radionuclides.

In Chapter 3, suitable circumstances are sought for the preparation of Tc-humic substance species via reduction of pertechnetate in presence of reducing solid phases and humic substances (synthetic and lab scale natural systems). Special attention is given at the behaviour of technetium in lab scale natural systems, where the Gorleben aquifer was mimicked.

In Chapter 4, the valence state of technetium-humic substance species in synthetic and lab scale natural systems was determined by X-ray Absorption Near-Edge Spectroscopy.

In Chapter 5, the nature of the Tc(IV) species within the humic substances is investigated by Extended X-ray Absorption Fine Structure Spectroscopy.

In Chapter 6, the interaction between Tc(IV) and humic substances was investigated more in detail via a Schubert approach for systems where Tc(IV) was distributed between the solid Magnetite and the liquid humic containing phase. Some important system parameters (Tc concentration, humic substance concentration and pH) are varied and their influence was studied. Further on, the interaction was quantified and a conditional interaction constant was obtained.

In Chapter 7, due to the fact that the aforementioned Schubert method was only applicable for systems where Tc(IV) was distributed between the solid Magnetite and the liquid humic containing phase, a new and quick method – called the La precipitation method – was developed for easy quantification of the concentration of technetium associated with humic substances and the free inorganic Tc(IV) concentration in solution.

In Chapter 8, a conditional interaction constant for the interaction between technetium and humic substances under a variety of experimental circumstances was obtained using the newly developed method. The interaction constants found with this method and the Schubert method are compared.

In a final chapter, an overview is given of the general conclusions on the geochemical behaviour of technetium under reducing conditions in presence and absence of humic substances and the observed interaction mechanism between Tc and humic substances. Future research needs are briefly discussed.

CHAPTER 1

THE (GEO)CHEMICAL BEHAVIOUR OF THE RADIONUCLIDE TECHNETIUM

1.1 Introduction

In this chapter, a literature survey regarding the origin, properties, redox chemistry and geochemical behaviour of technetium, element 43 of the periodic table of Mendelejev, is presented. Technetium is found in group VIIb of the periodic table and its chemical properties resembles more or less those of the homologous and neighbouring elements manganese, rhenium, and molybdenum, ruthenium, respectively. Therefore, a pronounced tendency for hydrolysis, complex formation with organic and inorganic ligands and binding to solids and colloids, both organic and inorganic, can be expected.

1.2 Origin and fate

In 1869 Dmitri Ivanovich Mendelejev reported his periodic table in a reasonably complete form, which provided a systematic ordering of the elements based on their molar masses. However, the table showed some gaps, among them element 43. Mendelejev predicted that this gap would be filled by a heavier analogue of manganese, which he named *eka*-manganese (*eka*, from the Sanskrit word for one), and that its atomic weight would be approximately 100.

Several scientists claimed its discovery and various names were given to element 43: Kern (1877), Barrière (1896), Ogawa (1908) and Noddack *et al.* (1925) who named it respectively davyum, lucium, nipponium and masurium. However, the majority of the claims was erroneous, and usually resulted from mixtures of several elements being misidentified as being a single element.

The merit of the discovery of element 43 has gone to C. Perrier and E. Segré (1937), who found a new element upon bombarding molybdenum (element 42) by deuterons in a cyclotron at Berkeley University (California). Perrier and Segré proved that the bombardment left one proton in the molybdenum and formed a new element. Technetium was "born".

Technetium was the first element to be produced artificially. Only very small quantities are produced naturally by spontaneous atomic fission in uranium ore bodies (Kenna and Kuroda, 1961, Dixon *et al.*, 1997, Curtis *et al.*, 1999). Hence, the name technetium, after the Greek τεχνικός (which means artificial) is an obvious choice. Technetium is now obtained in large quantities as a by-product from atomic fission in

nuclear reactor power plants. Nuclear reactors (with a power of 3500 MW_{th}) produce about 100 g technetium per day (Schwochau, 2000).

Technetium has twenty-one isotopes, with mass numbers from ^{90}Tc to ^{110}Tc, along with seven isomers: ^{93m}Tc, ^{94m}Tc, ^{95m}Tc, ^{96m}Tc, ^{97m}Tc, ^{99m}Tc, and ^{102m}Tc. However, in several cases the identifications of the isotopes are tentative. All isotopes of technetium are radioactive. The majority of these isotopes have half-lives ranging from 0.82 seconds (^{110}Tc) to 61.2 days (^{97m}Tc). There are three long-lived isotopes ^{97}Tc ($T_{1/2} = 2.6x10^6$ y), ^{98}Tc ($T_{1/2} = 4.2x10^6$ y) and ^{99}Tc ($T_{1/2} = 2.14x10^5$ y). Two of these isotopes are prepared by irradiation of molybdenum with deuterons or protons. The third of these long-lived isotopes, ^{99}Tc, is the most important one for nuclear waste disposal since several tonnes are produced each year as fission products of ^{235}U and ^{239}Pu in nuclear reactors. Actually, 6% of all fission products consists of technetium-99 (Lieser and Bauscher, 1987). It has a specific activity of 650 $MBq.g^{-1}$ and decays by emission of β^--particles with E_{max} of 300 keV to the stable isotope ruthenium-99.

One very important application for technetium lies in the field of nuclear medicine. The short-lived isomer technetium-99m is one of the most widely used radionuclides in nuclear medicine, because of its many favourable properties: short half-live (6.0 h), low radiation dose (99.996% IT; E_γ = 142 keV), and the γ-radiation is measurable with good yield. Other applications are the use of technetium compounds and alloys in the prevention of corrosion (Cartledge, 1955) and superconduction - Tc becomes a superconductor when the temperature drops to 11.2 K or below - (Shankland, 1955). But, due to the fact that all technetium isotopes are radioactive, its use in these last mentioned applications is of course very limited.

Nowadays, technetium-99 has been released into the environment during global fallout from nuclear tests, releases from nuclear reprocessing plants, dumping of radioactive material in the sea and the disposal of low- and intermediate-level wastes. As a result of these activities, technetium-99 has been found in groundwater at sites where nuclear wastes have been reprocessed or stored (McCullough *et al.*, 1999), and it remains a significant contaminant in effluents from nuclear fuel reprocessing plants currently in operation (Macaskie, 1991, Kershaw *et al.*, 1999, Schwochau, 2000). In future, when disposal of high-level radioactive waste will be made in deep geological repositories, it is eventually expected that technetium will enter the deep groundwater and will migrate up to superficial groundlevels. However, to what extent this can or will occur is yet unknown. Studies for a salt repository in New Mexico (U.S.A.) indicate that, of all radionuclides released in this repository, carbon-14, technetium-99 and iodine-129 may reach the surface before they have decayed (Choppin *et al.*, 2001). The knowledge of the behaviour of technetium under various environmental circumstances plays therefore an essential role in the risk evaluation (or performance assessment) of potential repositories.

1.3 Redox chemistry and speciation of technetium

1.3.1 Introduction

The redox chemistry of technetium is crucial in governing its mobility in the geosphere. Technetium has a [Kr] $4d^5\ 5s^2$ electronic configuration and the seven electrons occupying the outer orbits make valence states between 0 and +7 possible. In addition, also technetium in valence state -1 has been noticed (Rard, 1983). In view of the numerous oxidation states, an extensive oxidation-reduction chemistry of technetium is expected. For each valence state, different chemical forms (or species) of Tc have been identified (Rard, 1983, Rard *et al.*, 1999, Schwochau, 2000, Rard, 2005). The speciation of Tc in each valence state is determined by typical reactions, such as hydrolysis and association with organic and/or inorganic ligands.

It is generally accepted that the most stable occurring valence states of Tc in aqueous solutions (in the absence of complexing agents) under oxidising and reducing conditions are respectively Tc(VII) - (TcO_4^-), and Tc(IV) (*e.g.* TcO^{2+}, $TcO(OH)^+$, $TcO(OH)_2$) species. At low pH and under reducing conditions, also Tc(III) species can occur. Figure 1-1 shows an Eh-pH diagram for Tc species in the absence of complexing ligands.

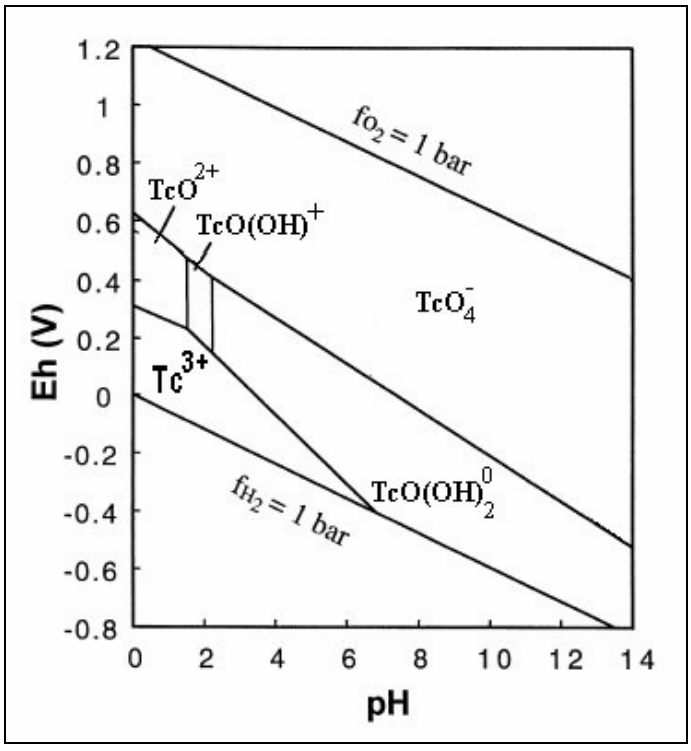

Figure 1-1. Eh-pH diagram for Tc (adapted from Lieser and Bauscher, 1987)

Species of the other valence states are considered to be unstable in the absence of complexing ligands and disproportionate into the +7 and/or +4 valence states. However, in the presence of complexing ligands, Tc species of all valence states

could be prepared and stabilised in aqueous solutions (as being frequently done in the nuclear medicine) (Schwochau, 2000).

1.3.2 Technetium(VII): pertechnetate reduction

The most stable oxidation state in contact with air in the entire pH range is Tc(VII), which exist as the highly soluble anionic species pertechnetate (TcO_4^-). The pertechnetate ion has a tetrahedral structure similar to the permanganate ion, but is less readily reduced.

However, under (suitable) reducing conditions, the most important reduction reaction of pertechnetate involves the reduction to Tc(IV), according to the following reaction:

$$TcO_4^- + 3\ e^- + 6\ H^+ \rightarrow TcO^{2+} + 3\ H_2O \qquad \text{(Rard, 1983)} \qquad (1\text{-}1)$$

Also other reaction pathways (or reaction products) are mentioned in literature:

$$TcO_4^- + 3\ e^- + 4\ H^+ \rightarrow TcO(OH)_2 + H_2O \qquad \text{(Rard } \textit{et al.}\text{, 1999)} \qquad (1\text{-}2)$$

$$TcO_4^- + 3\ e^- + 4\ H^+ \rightarrow TcO_2.nH_2O + (2\text{- n})\ H_2O \qquad \text{(Rard } \textit{et al.}\text{, 1999)} \qquad (1\text{-}3)$$

The reduction of pertechnetate is of course not solely restricted to the formation of Tc(IV) species. As already mentioned in the previous section, technetium can exist in valence states +7 to -1; hence, 1 e^- till 8 e^- reduction reactions must be possible. The reducing agent together with the solution pH and the solution composition all have a profound impact on the reaction mechanism and the resulting technetium species. Table 1-1 gives an overview of some reduction reactions involving pertechnetate and their corresponding standard electrode potentials (Rard, 1983, Rard *et al.*, 1999).

Reaction	valence state	E° (V)
$TcO_4^- + e^- \rightarrow Tc\,O_4^{2-}$	VI	-0.610
$TcO_4^- + 2\ e^- \rightarrow Tc\,O_4^{3-}$	V	-0.600
$2\ TcO_4^- + 6\ H^+ + 4\ e^- \rightarrow Tc_2O_5 + 3\ H_2O$	V	-
$TcO_4^- + 4\ H^+ + 3\ e^- \rightarrow TcO_2.nH_2O + (2 - n)\ H_2O$	IV	+0.660
$TcO_4^- + 5\ H^+ + 3\ e^- \rightarrow TcO(OH)^+ + 2\ H_2O$	IV	+0.638
$TcO_4^- + 4\ H^+ + 3\ e^- \rightarrow TcO(OH)_2 + H_2O$	IV	+0.595
$TcO_4^- + 3\ H_2O + 3\ e^- \rightarrow TcO^{2+} + 6\ OH^-$	IV	-0.995
$TcO_4^- + 3\ H_2O + 3\ e^- \rightarrow TcO(OH)^+ + 5\ OH^-$	IV	-0.742
$TcO_4^- + 3\ H_2O + 3\ e^- \rightarrow TcO(OH)_2 + 4\ OH^-$	IV	-0.509
$TcO_4^- + 4\ H_2O + 4\ e^- \rightarrow Tc^{3+} + 8\ OH^-$	III	-1.080
$TcO_4^- + 8\ H^+ + 7\ e^- \rightarrow Tc + 4\ H_2O$	0	+0.485

Table 1-1. Possible reduction reactions of pertechnetate and corresponding E° values (Rard, 1983, Rard *et al.*, 1999)

The reduction of Tc(VII) to lower valence states can be obtained by using one of the following methods: 1) reduction in solution by using (strong) reducing agents such as borohydride, stannous ions, hydrazine, ascorbic acid, thiourea, zinc and iron (Vilcek *et al.*, 1981, Spitsyn *et al.*, 1983, Stalmans, 1986, Potapova *et al.* 1989, Kopunec and Blaszek, 1994), 2) electrochemical methods (Lawson *et al.*, 1984, Walton *et al.*, 1985, Maslennikov *et al.*, 1997), 3) catalytic thermal methods (Lieser *et al.*, 1987, Burnett *et al.*, 1995, Bernard *et al.*, 2001), 4) reduction by use of reducing bacteria (Stalmans, 1986, Henrot, 1989, Lloyd *et al.*, 2000, Abdelouas *et al.*, 2002) and 5) reduction by "electron donating" surfaces such as magnetite (Fe_3O_4), pyrite (FeS_2) and ironsulphide (Lee and Bondietti, 1983, Cui and Eriksen, 1996a, 1996b, Wharton *et al.*, 2000).

1.3.3 Technetium(IV)

a. TcO^{2+} and its (mono/dinuclear) hydrolysis species

Under appropriate reducing conditions, the predominant reduced form of technetium is the TcO^{2+} ion, which hydrolyses at pH values above 2 (figure 1-1). In reducing aqueous solutions, the following hydrolysis equilibria (reactions 1-4 – 1-9) are expected according to the EQ3/6 (Wolery, 1992) or NEA (Wanner, 1988) databases[5]:

EQ3/6 database:

$TcO^{2+} + H_2O \rightleftharpoons TcO(OH)^+ + H^+$ LogK= -1.1355 (1-4)

$TcO^{2+} + 2\ H_2O \rightleftharpoons \mathbf{TcO(OH)_2(aq)} + 2\ H^+$ LogK= -3.3221 (1-5)

$2\ TcO^{2+} + 4\ H_2O \rightleftharpoons \mathbf{(TcO(OH)_2)_2(aq)} + 4H^+$ LogK= -0.1271 (1-6)

NEA database:

$TcO^{2+} + H_2O \rightleftharpoons TcO(OH)^+ + H^+$ LogK= -1.50037 (1-7)

$TcO^{2+} + 2\ H_2O \rightleftharpoons \mathbf{TcO(OH)_2(aq)} + 2\ H^+$ LogK= -4.00099 (1-8)

$TcO^{2+} + 3\ H_2O \rightleftharpoons TcO(OH)_3^- + 3\ H^+$ LogK= -14.9036 (1-9)

The species in bold are predominant in a pH range between 3 and 10 and a redox potential varying between 0 en -250 mV when performing calculations with the two databases. The concentrations of the different species and the total solubility for both databases are shown in figure 1-2 and 1-3. Calculations were made using the CHESS computer code (van der Lee, 1993). The used CHESS version (JCHESS 2.0) contains the most recent updates for Tc in both used databases. Both figures demonstrate that the main species (> 99%) in the pH range 3 – 11 is the neutral $TcO(OH)_2$ species.

[5] The EQ3/6 and NEA databases tabulate all known geochemical reactions for radionuclides, besides the data for more ordinary elements abundantly present in geochemical substrata and groundwater. In literature, these databases are frequently used by geochemical modellers for calculations involving radionuclides and the environment.

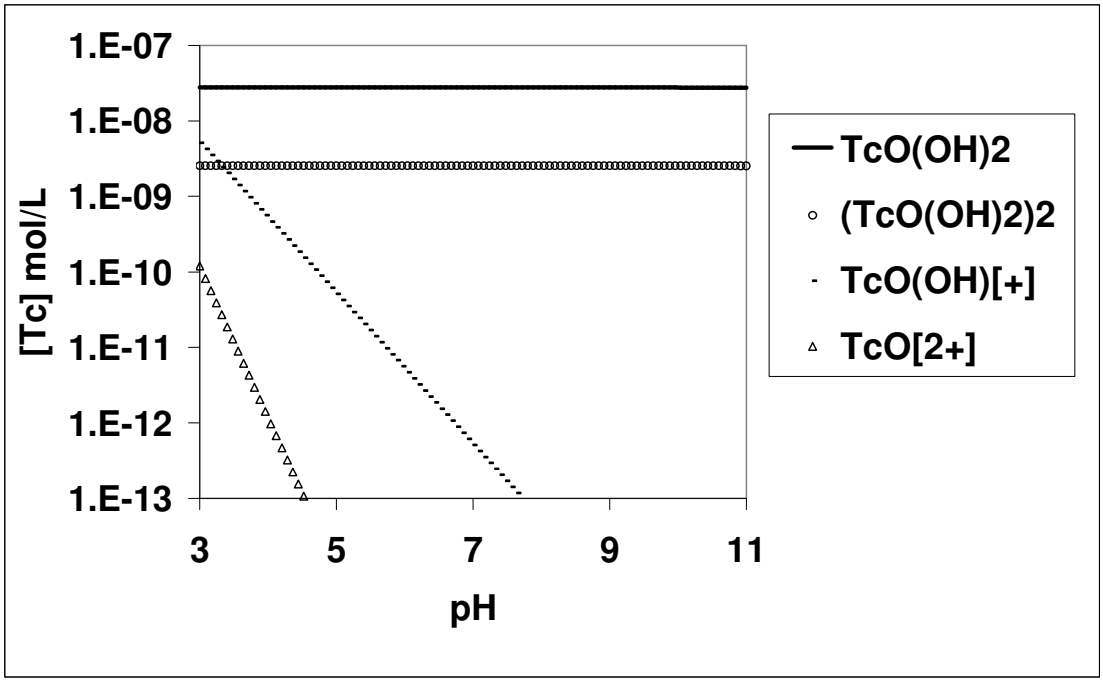

Figure 1-2. Change in technetium(IV) species concentration in the pH range 3-11 according to the EQ3/6 database (calculations made by CHESS at Eh = -250 mV)

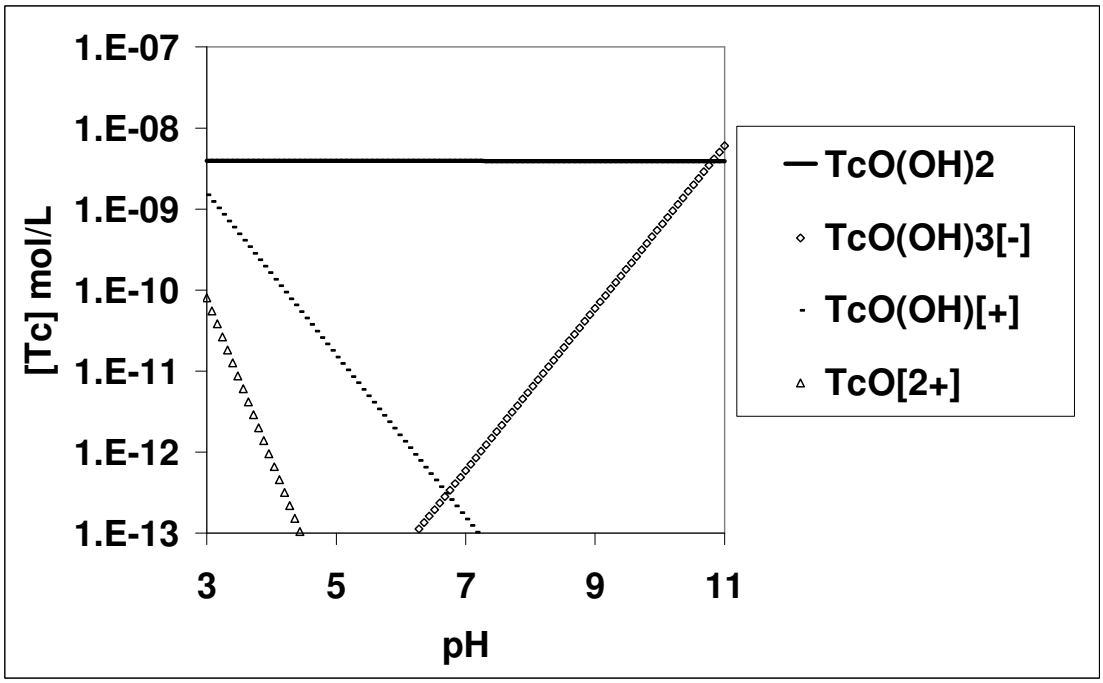

Figure 1-3. Change in technetium(IV) species concentration in the pH range 3-11 according to the NEA database (calculations made by CHESS at Eh = -250 mV)

b. Tc(IV) precipitates

Above a concentration of 3×10^{-8} mol/L or 3×10^{-9} mol/L, CHESS proposed respectively the formation of amorphous precipitates $TcO_2.2H_2O$ (EQ3/6 database) or $TcO_2.1.6H_2O$ (NEA database) according to the following reactions:

$$TcO^{2+} + 3\ H_2O \rightleftharpoons \mathbf{TcO_2.2H_2O(am)} + 2\ H^+ \qquad \text{LogK= 4.2319} \qquad (1\text{-}10)$$

$$TcO^{2+} + 2.6\ H_2O \rightleftharpoons \mathbf{TcO_2.1.6H_2O} + 2\ H^+ \qquad \text{LogK= 4.4012} \qquad (1\text{-}11)$$

However, several researchers experimentally observed solubilities of Tc(IV)-oxides in (acidic) aqueous solutions in the range of 10^{-10} to 10^{-6} mol/L, thus below and above the expected solubility of 10^{-8} - 10^{-9} mol/L (Hanke *et al.*, 1986, Meyer *et al.*, 1991, Burnett *et al.*, 1995 and Schwochau, 2000).

Under natural reducing conditions and high enough technetium concentrations, an amorphous Tc(IV) precipitate will be the most important Tc species formed. Via thermal decomposition of NH_4TcO_4 crystalline TcO_2 precipitates can be prepared with a very low solubility (probably less than 10^{-10} mol/L) (Meyer *et al.*, 1991). The study of their structure and properties can be useful for comparison with the amorphous precipitates (see chapter 5).

c. Polynuclear or colloidal Tc(IV) species

Several explanations were proposed for the discrepancies between the reported solubilities of the amorphous Tc(IV)-oxide. One explanation assumed that the reported solubilities do not refer to a well-defined solid phase but to hydrated oxohydroxide $TcO_2.nH_2O$ with $0\leq n\leq 2$, depending on the preparation method, pre-treatment, alteration and temperature (Burnett *et al.*, 1995).

Another possible explanation for the measured high $TcO_2.nH_2O$ solubilities, is the formation of polynuclear or colloidal Tc(IV) species after reduction of pertechnetate. Further investigation of the supernatant solutions by (ultra)filtration (and other) techniques proved indeed the presence of real Tc(IV) colloids (Rard, 1983, Hanke *et al.*, 1986, Meyer *et al.*,1991, Naito *et al.*, 1998, Sekine *et al.*, 1998, 2002, 2004, Schwochau, 2000, Vichot *et al.*, 2002, Fattahi *et al.*, 2005 and Poineau *et al.*, 2006). It appears that the initial Tc concentration is a further important factor in solubility experiments on Tc(IV) oxides. When the initial concentration is above 10^{-5} mol/L, polymeric and/or colloidal forms of technetium may be present (Meyer *et al.*, 1991).

Hanke *et al.* (1986) proposed the existence of colloidal Tc species being dependent on the pertechnetate reduction method used to prepare the Tc(IV) oxohydroxide. They claimed that upon pertechnetate reduction i) with strong reducing agents (such as Zn/HCl, Sn^{2+} or hydrazine) or ii) via electrochemical reduction, colloidal Tc species appear, in contrast with the standard method based on thermal decomposition of NH_4TcO_4.

When pertechnetate was reduced with stannous ions, Naito *et al.*, (1998) and Sekine *et al.* (1998, 2002, 2004) observed the presence of stable Tc(IV) colloids.

Concentrations of Tc(IV) colloids in solution up to 4×10^{-5} mol/L were observed. During 3 months no sedimentation of Tc(IV) colloids occurred. When ionic strength increases, a gradual sedimentation of technetium was observed. TEM analysis showed the existence of spherical particles with a diameter ranging from 30 to 50 nm.

Vichot *et al.* (2002) observed via XAS polymeric Tc species in mixed sulphate / chloride media. They proposed a general formulation of these species as $Tc_nO_p^{(4n-2p)+}(H_2O)_q$, being a precursor for the solid $TcO_2.nH_2O$ precipitates.

Lukens *et al.* (2002) performed EXAFS spectroscopy on alkaline solutions (2 mol/L NAOH) containing Tc species after electrochemical reduction and radiolysis of pertechnetate (in the absence of complexing ligands). The results showed the presence of colloidal $TcO_2.nH_2O$ species in solution.

Poineau *et al.* (2006) studied the condensation mechanisms of tetravalent technetium in chloride media in the pH range 0 – 1.5 and discovered a new dimer complex of Tc(IV): $Tc_2OCl_{10}^{4-}$. After increasing the pH, UV-visible measurements showed a cyclization of this species into polymeric Tc(IV) species leading finally to the precipitation of $TcO_2.nH_2O$.

1.4 Technetium speciation in radioactive waste and the near-field

Fission products including technetium-99 are separated from uranium during reprocessing and are solidified in liquid tanks by calcination or glassification. It is expected that technetium occurs mainly in valence states +IV or +VII after solidification (Schwochau, 2000, Lukens *et al.*, 2002).

Upon disposal of the radioactive waste containing tanks in a geological barrier, the containment is assumed to resist corrosion by aqueous solutions no longer than about one hundred years. Thereafter, the radioactive waste is subject to water leaching, and silicates formed by glassification will be exposed to hydrolysis. The backfill and geological barrier show reducing properties; hence, any oxidised Tc species present could be reduced to Tc(IV) when appropriate conditions are present.

It must be mentioned that besides the aforementioned two main Tc species, pertechnetate and (colloidal) $TcO_2.nH_2O$ species, also other Tc species can be formed in the near-field depending on the composition of the groundwater solutions and the back-fill. Back-fill material is selected according to their specific sorption properties towards the different radionuclides present in nuclear waste. A review of published literature indicated that various minerals and synthetic adsorbent materials such as oxides, hydroxides, natural and modified alumino-silicates, sulphides, carbonates, phosphates, carbon, and functionalised novel sorbents have been tested for their "getter" properties for technetium, existing as either Tc(VII) or Tc(IV) (Strickert *et al.*, 1980, Palmer and Meyer, 1981, Lee and Bondietti, 1983, Shade *et al.*, 1984, Walton *et al.*, 1985, Haines *et al.*, 1987, Lieser and Bauscher, 1987, 1988, Ito and Kanno, 1988, Winkler *et al.*, 1988, Zhuang et al., 1988, Ito and Akiba, 1991, Byegard *et al.*, 1992, Del Cul *et al.*, 1993, Zhuang *et al.*, 1995, Cui and Eriksen, 1996a, 1996b,

Kang *et al.*, 1996, Kunze *et al.*, 1996, Liang *et al.*, 1996, Balsley *et al.*, 1997, 1998, Kang *et al.*, 1999, Wharton *et al.*, 2000, Zhang et al., 2000, Mattigod *et al.*, 2003, Pepper *et al.*, 2003,…).

The interaction between technetium and these possible back-fill materials can lead to the formation of different new types of Tc species. Reduced Tc species have a pronounced tendency for complex formation with organic and inorganic ligands such as EDTA, humic substances, carbonates,… (Seifert *et al.*, 1982, Noll *et al.*, 1983, Stalmans, 1986, Van Loon *et al.*, 1986, Hashimoto *et al.*, 1993, Roβler *et al.*, 2000, Tkac *et al.*, 2000, Wildung *et al.*, 2000,…) and binding to solids and colloids, both organic and inorganic, such as natural organic matter, (iron)oxyhydroxides, sulphides and carbonates … (Lee and Bondietti, 1983, Stalmans, 1986, Cui and Eriksen, 1996a, 1996b, Wildung *et al.*, 2000, …). The question of which different Tc species prevails in the near-field on a longer time scale and which soluble or colloidal Tc species could enter the far field (the aquifer systems) is, however, not yet resolved.

1.5 The geochemical behaviour of technetium in aquifer systems

In order to determine and quantify the reactions playing between a radionuclide and all the components of a complex system, such as an aquifer system, it is instructive to investigate each individual reaction. In the next few sections, the interaction between some selected technetium species and components possibly present in an aquifer system are described from literature sources. In this Ph. D. work, it is implicitly assumed that when technetium enters an aquifer system, it will be the pertechnetate species or the unbound Tc(IV) species such as soluble $TcO(OH)_2$, TcO^{2+} or colloidal $TcO_2.nH_2O$. Therefore, the reactions between

(i) technetium (pertechnetate and reduced Tc species) and (reducing) solid phases,
(ii) technetium (pertechnetate and reduced Tc species) and components present in natural groundwater (other than humic substances), and
(iii) technetium and humic substances

will be described more in detail in the following paragraphs.

It must be emphasised that in the following overview, only those aspects are highlighted that are relevant for this Ph. D. research. Therefore, the interaction between other types of Tc species, formed after contact with specific back-fill materials in the disposal site and the aquifer system are not described. And, although the uptake of technetium in plants, micro-organisms and animals is also important in the overall (bio)geochemical behaviour of technetium, this will not be discussed in this overview nor in the further chapters of this work. The interested reader is referred to more specialised work on this matter (*eg.* Murphy and Johnson, 1993, Echevarria *et al.* ,1997, Schwochau, 2000, Bennet and Willey, 2003, Thorne, 2003, Asworth and Show, 2005, …).

1.5.1 The interaction between pertechnetate and (reducing) solid phases

Under oxidising conditions, the pertechnetate ion will not likely be sorbed in significant amounts by soils and suspended bottom sediments of predominantly negative charge, but will be highly mobile in soils and waters and thus available for uptake in biota. However, most research on the geochemical behaviour of technetium in soils or sediments under oxidising conditions, was still concentrated on the possible sorption behaviour of pertechnetate on these soils and sediments and consequently, distribution coefficients are calculated (Routson *et al.*, 1977, Gee and Campbell, 1980, Lieser and Bauscher, 1987, Serne *et al.*, 1993 and Kaplan and Serne, 1998).

Distribution coefficients (K_d) between Tc and the different sediments are calculated as follows: $K_d = \frac{(A_{initial} - A_{final}) \times V}{A_{final} \times M_{sed}}$ with V is the volume of the Tc-amended solution added to the sediment (mL), $A_{initial}$ and A_{final} are the Tc activities respectively before and after contact of the solution with the sediment and M_{sed} is the sediment mass (g).

Most researchers obtain K_d values ranging from -0.18 to +0.11 mL/g. Essentially all soils in temperate climates have a net negative charge. Hence, negative distribution coefficients are a consequence of anion exclusion (due to repulsion between pertechnetate and the negatively charged sediments). This lead to increased activity coefficients for technetium in the bulk solution and consequently to negative distribution coefficients.

These very low or even negative distribution coefficients between TcO_4^- and sediments implies that under normal oxidising conditions TcO_4^- will not sorb on soils, sediments; hence, under oxidising conditions pertechnetate is very mobile in soils and sediments.

Lee and Bondietti (1983) investigated the behaviour of technetium under reducing conditions in the presence of sulphide, iron and ferrous sulphide solutions and removed pertechnetate from solution (at an elevated pH) by (co-)precipitation with iron and/or sulphide minerals. Their conclusions were: 1) in the absence of S^{2-}, pertechnetate was reduced by Fe(II) and lost from solution by hydrolysis, 2) in the presence of S^{2-} alone, pertechnetate was not reduced and a Tc_2S_7 precipitate was formed. (However, this last reaction has only been noticed in strong acid solutions and formation of such a compound under environmental conditions has not been reported yet), and finally, 3) in the presence of both Fe(II) and S^{2-}, Tc was reduced and co-precipitated with FeS.

Vandergraaf *et al.* (1984) observed "sorption" of technetium (added to the systems as pertechnetate) under reducing conditions only on iron-oxide inclusions in ferrous-iron-containing minerals and on iron-oxide coatings in micro fractures in granite, but not on the ferrous-iron minerals within the granite themselves. Subsequent static sorption tests with crushed magnetite showed that sorption is a function of the composition of the solution and of the radionuclide concentration, and only occurred in the absence of oxygen. The authors concluded that technetium is reduced and removed from solution by iron(II)-oxides, and not by minerals containing ferrous iron not as an integral part of their crystal lattice. Reduction of technetium occurs close to

the mineral surface, and not in the bulk of the solution by dissolved ferrous ions. The authors assumed that Tc(IV) is formed after reduction of pertechnetate, however, they did not have direct evidence for this.

Haines *et al.* (1987) showed by a Fourier transform infrared (FTIR) study that the reaction between TcO_4^- and magnetite (Fe_3O_4) occurs via surface-mediated reduction of TcO_4^- to Tc(IV) and by precipitation of $TcO_2.nH_2O$ on the Fe_3O_4 surface.

Cui and Eriksen (1996a and 1996b) investigated under reducing conditions 1) the reduction of pertechnetate by ferrous iron in solution, 2) the influence of sorbed and precipitated Fe(II), and 3) the (surface-mediated) reduction of pertechnetate in solution by Fe(II)-bearing fracture filling material from a natural fracture in granite, hornblende and magnetite. The authors concluded that the three-electron reduction process of pertechnetate in slightly acid to basic solutions containing Fe(II), although thermodynamically feasible, was found to be kinetically hindered and a highly improbable process. However, Fe(II) sorbed on the wall of untreated reaction vessels, precipitated as $Fe(OH)_2(s)$ or $FeCO_3(s)$, and Fe(II) containing minerals were all found to reduce TcO_4^-.

One of the most important reduction reactions used throughout this research is the reduction of pertechnetate by magnetite. Therefore, this reaction is discussed in more detail in the next paragraphs.

The reduction of pertechnetate to Tc(IV) by magnetite can be described by the following half-cell redox reactions for Tc(VII) coupled with magnetite (Fe_3O_4) oxidation to maghemite (γ-Fe_2O_3) (Pourbaix, 1966):

$$TcO_4^- + 4\,H^+ + 3e^- \rightarrow TcO_2.nH_2O + (2 - n)\,H_2O$$
$$(\,3\,[Fe^{2+}Fe_2^{3+}]O_4 \rightarrow 4\,\gamma\text{-}[Fe_2^{3+}]O_3 + Fe^{2+} + 2e^-\,) \times 1.5$$

$$TcO_4^- + 4.5\,[Fe^{2+}Fe_2^{3+}]O_4 + 4\,H^+ \rightarrow TcO_2.nH_2O + 6\,\gamma\text{-}[Fe_2^{3+}]O_3 + 1.5\,Fe^{2+} + (2 - n)\,H_2O \qquad (1\text{-}12)$$

with an equilibrium cell potential at 25°C of
$E = 0.835\ V + 0.020\ Log[TcO_4^-] - 0.079\ pH - 0.03\ Log[Fe^{2+}]$

For pH, pertechnetate and ferrous iron concentrations of trace level, the cell potential for this reaction is positive, and thus reduction of pertechnetate by magnetite is thermodynamically favourable. The foregoing equation predicts that pertechnetate reduction decreases with increasing pH.

Cui and Eriksen (1996b) proposed a theory about the surface-mediated pertechnetate reduction, which explains also the pH dependency of the reduction reaction. They postulated that the reduction of pertechnetate is kinetically controlled and occurs in a first step via adsorption of pertechnetate anions to a magnetite surface by a ligand exchange mechanism of replacement of the surface hydroxyl groups by pertechnetate (the rate-determining step) and in a next step pertechnetate is reduced. The reduction rates will be pH-dependent, due to the fact that for an oxide surface, the charge of the surface functional groups is pH-dependent. This implies that with increasing pH, the hydroxylated surface becomes more and more negatively charged; hence, there will

be less available sites for pertechnetate anion sorption and consequently a lower reduction rate. Hence, the point of maximal pertechnetate reduction coincides with the point of zero charge of the magnetite surface (6.5). However, it is worth noticing that at lower pH, two mechanisms can act together: adsorption of the pertechnetate by an electrostatic mechanism (surface functional groups are positively charged) and the aforementioned ligand exchange of hydroxyl functional groups by the pertechnetate anion.

Pepper *et al.* (2003) investigated the interaction between pertechnetate and green rusts (layered hydrous oxides containing both Fe(II) and Fe(III) and with interlayer sulfate or carbonate anions) under reducing conditions. Green rusts concentrated over 99.8% of the Tc, present as TcO_4^-, from aqueous solution. The mechanism of removal from solution was proposed to be reduction of pertechnetate by reaction with both sulphate- and carbonate-form green rusts and formation of strong Tc(IV) surface complexes. X-ray absorption spectroscopy showed that the reduced Tc species were present as a TcO_2-like environment.

1.5.2 The interaction between reduced Tc species and solid phases

The behaviour of technetium under reducing conditions is in most cases described as a reduction of pertechnetate due to the presence of reducing solid phases as pyrite or magnetite to irreversible formation of sparingly soluble species of Tc(IV) *e.g.* $TcO_2.nH_2O$. However, sparse knowledge is present on the behaviour of $TcO_2.nH_2O$ in the presence of natural sediments.

Lieser and Bauscher (1987) were amongst the first to investigate the behaviour of technetium under reducing environmental conditions. They represented the behaviour of technetium under reducing conditions as a sorption ratio R_s which corresponded to a distribution between the solid and the liquid phase. The sorption ratio is proposed to be the amount of Tc(IV) that has been precipitated in form of $TcO_2.nH_2O$, respectively to the residual concentration of Tc species in solution. High sorption ratios of the order of 10^3 ml/g were reported for the sorption of technetium on 5 sediments consisting mainly of quartz and some silicates taken a various depths from the layers covering the salt dome at Gorleben.

Walton *et al.* (1985) prepared soluble Tc(IV) by electrochemical reduction of pertechnetate in bicarbonate solutions and contacted them with Fe(III) oxyhydroxides. They reported that soluble Tc(IV) was rapidly removed from bicarbonate solutions by Fe(III) oxyhydroxides. A chemisorption mechanism, rather than an electrostatic mechanism was proposed, because at the pH in their experiments, the Fe(III) oxyhydroxide surface as well as the Tc(IV) bicarbonate complexes were negatively charged.

Pepper *et al.* (2003) observed that the concentration of Tc remaining in solution after reaction with green rusts increased with the total amount of pertechnetate added at circumneutral pH. They suggested that the reaction between Tc(IV) and green rust occurs by way of a surface complexation represented by the following reaction:

$$=Fe–O^- + TcO^{2+} \rightarrow =Fe–OTcO^+ \qquad LogK = 20.8 \qquad (1\text{-}13)$$

Zachara *et al.* (2007) investigated the nature of the solid phase redox products after reduction of pertechnetate by aqueous Fe(II) in pH 6-8 solutions. Beyond a pH = 7 pertechnetate was reduced and a Tc(IV)/Fe(II)/Fe(III)-containing precipitate was formed. According to Tc-EXAFS measurements and structural modelling, its molecular environment was found consistent with an octahedral Tc(IV) dimer bound in bidentate edge-sharing mode to octahedral Fe(III) associated with surface of vacancy sites in the formed solid phase.

1.5.3 The interaction between pertechnetate and dissolved ferrous iron

The interaction between pertechnetate and dissolved ferrous iron is a direct reduction in solution of TcO_4^- to Tc(IV) as reported by several research groups (Stalmans, 1986, Lieser and Bauscher, 1987, Byegard *et al.*, 1992). However, the presence of, added or unintentionally formed, Fe(II)-containing solid phases in the systems studied does not make the interpretation of the experimental data straightforward and it cannot be concluded from these studies that the reduction of pertechnetate by dissolved ferrous iron is possible.

1.5.4 The interaction between pertechnetate and dissolved sulphide ions

In acid solutions and at elevated sulphur concentrations, Tc_2S_7 will precipitate according to the following reaction (Rulfs and Meinke, 1952, Lee and Bondietti, 1983):

$$2\ TcO_4^- + 7\ HS^- + 9\ H^+ \rightleftharpoons Tc_2S_7\downarrow + 8\ H_2O \qquad \text{LogK} = 230.241 \qquad (1\text{-}14)$$

1.5.5 The interaction between reduced Tc species and (in)organic ligands (besides humic substances)

Under reducing conditions, reduced technetium species can form stable complexes with organic and inorganic ligands. It is generally accepted that technetium is present as Tc(IV) under such circumstances, but in most cases no experimental evidence was given for this proposition.

Technetium was observed to form stable complexes with inorganic anions such as chloride (Dalziel *et al.*, 1958, Kawashima *et al.*, 1976, Flint and Lang, 1986, Fattahi *et al.*, 2005, Liu *et al.*, 2005, Poineau *et al.*, 2006), bromide (Flint and Lang, 1986, Abram and Kirmse, 1993), sulphate (Spitsyn *et al.*, 1976, Vichot *et al.*, 2003), and carbonate (Wildung *et al.*, 2000, Keith-Roach *et al.*, 2003). Wildung *et al.* identified, through a combination of high-resolution transmission electron microscopy, X-ray absorption spectroscopy, and thermodynamic calculations, soluble Tc carbonates as a reaction product in pure culture experiments with Shewanella putrefaciens, and suggested that soluble Tc carbonates may be a significant transport pathway for reduced Tc species in anaerobic subsurface environments. Keith-Roach *et al.* (2003) investigated the distribution of technetium in sediments of Needle's Eye (UK) and Mariager Fjord (Denmark) via a sequential extraction procedure. A large part of Tc found at these sites was found in the fraction associated with carbonate.

The synthesis of reduced Tc-organic ligand complexes usually involves three components: pertechnetate, a reducing agent and an organic ligand. Complex formation can occur with organic ligands that contain generally one or a combination of two of the following functional groups: amino, hydroxyl, carboxyl and sulphydryl. These complexing agents can be subdivided into four main groups (Münze and Abram, 1991, Schwochau, 2000):

- hydroxycarboxylates: citrate, malate, tartrate, …
- aminocarboxylates: such as EDTA, DTPA, NTA, …
- polyamines: such as ethyldiamine
- sulphydryl amino acids: such as methionine, cysteine and derivatives

With the exception of polyamines, stable configurations between technetium and complexing ligands are only achieved when the coordinative binding involves different functional groups (Schwochau, 2000). Quantitative data on the oxidation state of technetium within these complexes is however scarce. The general consensus is that Tc is in the +IV state. However, +III and +V have been claimed, the lower valencies being more likely to occur in strongly stabilizing ligands.

1.5.6 The interaction between technetium and humic substances

a. The reduction of pertechnetate by humic substances

Humic substances are formed by the decay of dead plants, microbes and animals and are ubiquitous in soils, sediments and natural groundwaters. No interaction between Tc(VII) and (dissolved) humic substances was described in literature (Lieser and Bauscher, 1987, Sheppard and Thibault, 1992, Tkac *et al*., 2000).

A few research groups (Wolfrum and Bunzl, 1986, Liescher and Bauscher, 1987, Stalmans, 1986, Stalmans *et al.*, 1986) pointed to the involvement of humic substances in pertechnetate reduction by stating that the possible high sorption of Tc on solid humic substances, could be directly related to the reduction of Tc(VII) to lower valence states (and less soluble Tc species) by the humic substances themselves. However, the used solid humic substances (peat) in the study of Wolfrum and Bunzl were not purified before use; hence, small (Fe(II))-reducing surfaces could also be present and be involved in the reduction of pertechnetate. Stalmans (1986) investigated in his Ph. D. research the reductive properties of Boom Clay groundwater (containing a high amount of humic subtances) and observed that a 99% reductive yield was achieved within 5 to 8 days. However, again it must be mentioned, that it was not verified whether Fe(II) oxides (colloidal or not) were present or were unintentionally formed.

Stalmans also investigated the behaviour of technetium-99 in a Boom Clay suspension environment (at a pH = 8.3) and concludes that Boom clay is a suitable environment for direct pertechnetate reduction. The pyrite particles present in Boom clay together with humic substances were suggested to be responsible for the pertechnetate reduction.

b. The interaction between reduced technetium species and humic substances

In view of the composition of humic substances, it is expected that humic substances, or soil organic matter in general, are able to stabilise Tc in reduced forms. In general, the immobilization of technetium is more pronounced in soils containing high levels of solid organic matter (Wildung *et al.*, 1979, Sheppard *et al.*, 1983, Wolfrum and Bunzl, 1986, Sheppard *et al.*, 1990, Tagami and Uchida, 1996, 1997, Tkac *et al.*, 2000, Keith-Roach *et al.*, 2003, Abdelouas *et al.*, 2005,…). In the studies by Keith-Roach *et al.* and Abdelouas *et al.*, technetium binding to soils and sediments was investigated by a sequential extraction procedure. In both studies, the majority of the Tc uptake was found in the natural organic matter part.

The synthesis of Tc-HS species and direct interaction between Tc and (both solid as dissolved) humic substances was only investigated by few researchers (Stalmans, 1986, Van Loon *et al.*, 1986, Sekine *et al.* 1993, 1997, Röβler *et al.*, 2000 and Tkac and Kopunec, 2003a and 2003b). Stalmans (1986) proposed the formation of a TcO^{2+}-complex and thus assumed the Tc(IV) valence state. The proof of existence of dissolved Tc-humic substance complexes was given by gel permeation chromatography. Van Loon *et al.* (1986) proposed from the oxidation behaviour of Tc-humic substance complexes, that in order to explain the non-linearity of the first-order rate plot for the oxidative decay of Tc-humic substance complexes, that it is likely that a variety of Tc-complexes occur in humic substances, depending on the particular combination of functional groups involved in coordinative binding.

Although, it is expected that for technetium only the valence states VII and IV are stable under environmental conditions, due to the reducing/oxidising, and complexing properties of humic substances, the presence of different valence states for technetium within the humic substances could be possible. Sekine *et al.* (1993) concluded by an indirect measurement that in presence of humic acids, Tc(III) species are formed and associate with the humic acids. But these experiments were done at low pH and in absence of HCO_3^-. Speciation calculations with the CHESS computer code (based on EQ3/6 database), predicts the Tc^{3+} species as the dominant species at low pH, sufficiently low redox potential and in absence of humic substances. At higher pH (higher than 4), Tc(IV) species are becoming more dominant. Hence, in neutral and alkaline environment, associations between Tc(IV) species and humic substances are more likely to occur. But experimental evidence for this species is lacking and will be presented in this thesis.

In most aforementioned studies the Tc - humic substance species were made under experimental conditions not relevant for environmental circumstances, hence the properties of these formed species can differ from those formed under environmental circumstances. Indeed, as already stated by Münze (1981) and further acknowledged by Schwochau (2000), one of the disturbing features in the synthesis of Tc complexes is that the nature of the reaction products may be quite variable, depending on the experimental procedure. Complexes expected to be identical, as prepared by ligand exchange or reduction-complexation procedures may be quite different. Hence, one must be vary careful when drawing conclusions on the possible interaction mechanism for Tc and organic ligands when trying to compare results obtained under different circumstances.

c. Quantification of the interaction of Tc with boom clay humic substances

In order to elucidate the Tc geochemical behaviour in reducing environments rich in humic substances, Maes *et al.* (2003) determined for the first time a conditional interaction constant for Tc with Boom clay humic substances. The interaction of Tc with dissolved HS from Boom Clay was studied using a modification of the method for the determination of the interaction of Cd with dissolved Boom Clay HS (Maes *et al.*, 1992b). The trace Cd-HS conditional complexation constant was determined from Cd and HS distribution measurements at different Boom Clay solid/liquid ratios under *in situ* reducing conditions of solid- and liquid-phase composition. The new method consisted in measuring the Tc distribution in different successive extracts taken at different Boom Clay solid/liquid ratios, and for different Tc occupancies of the solid phase. The solid phase was able to sorb Tc(IV) to a very large extent ($LogK_d \approx 2.5$ to 4.0), and two sorption sinks (one of which is humic substances) on the Boom clay were detected. The interaction constant between Tc and HS was then determined from the competition for Tc between the dissolved HS and the Boom Clay solid via a Schubert-like approach. The following equation which is based on the Schubert approach (Schubert, 1948) is therefore valid :

$$Log(K_d^0/K_d - 1) = LogK^{HS} + Log[HS] - LogA \qquad (1\text{-}15)$$

K_d^0 and K_d respectively stand for the distribution coefficient of Tc in the absence and in the presence of dissolved HS. $LogK^{HS}$ stands for the interaction constant of Tc with dissolved HS and A is the side reaction coefficient which corrects for the presence of other inorganic Tc(IV) species in solution (see further on). The HS concentration was given in moles of charge/L.

A value for K_d^0 was not experimentally available but as demonstrated by Maes *et al.* (1992b) the K_d^0 and K^{HS} (or K^{HS}/A) values could be obtained by fitting the data to

$$LogK_d = LogK_d^0 - Log(1 + K^{HS} \times [HS]/A) \qquad (1\text{-}16)$$

which is simply a modification of equation (1-15). This latter (more rigorous) approach is made in figure 1-4 which shows the log K_d (in kg/L) versus the log [HS] (in moles of charge/L) curves, per initial Tc concentration. The values for K_d^0 and log K^{HS}/A, which are used to calculate the various solid or broken lines, are given on the figure. It was observed that all the data can be fitted with one single K^{HS}/A value ($LogK^{HS}/A = 5.30$) and different K_d^0 values (one K_d^0 per Tc occupancy).

The use of the ratio K^{HS}/A is due to the fact that thus far no concrete Tc(IV) reaction mechanism with dissolved HS has been proposed. In order to achieve this, and hence allowing discrimination between K^{HS} and the side reaction coefficient, the theoretical Tc(IV) speciation in Boom Clay environments in the absence of HS was considered.

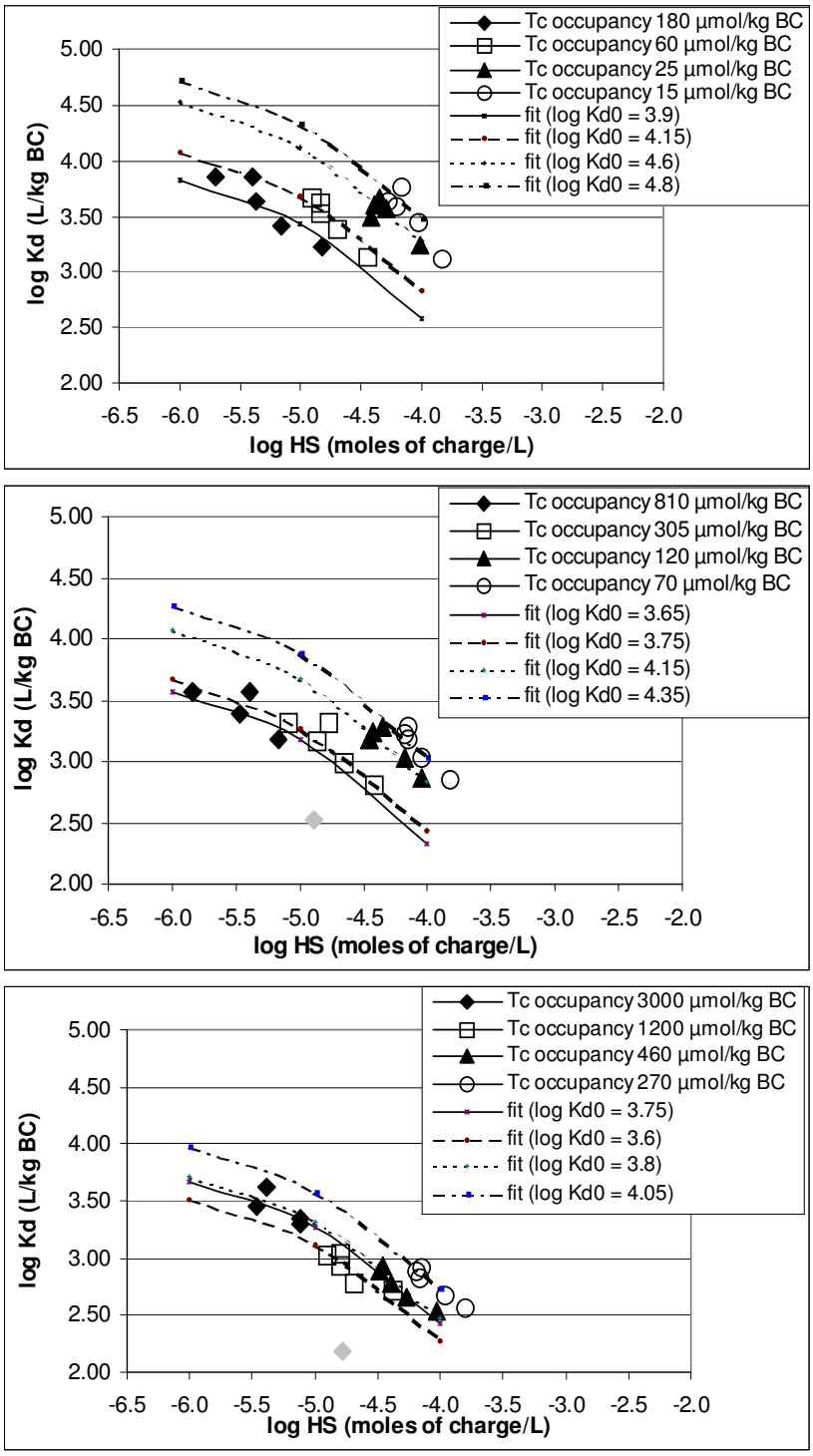

Figure 1-4. Experimental log K_D (L/kg Boom Clay) values versus log HS (moles of charge/L), identified per solid/liquid (S/L) ratio (in kg/L) and Tc occupancy (in µmol/kg Boom Clay). Displayed lines are fitted theoretical K_D vs. log HS relationships derived from the Schubert equation. Fitting parameters were log K^{HS}/A = 5.30 and log K_D^0 (L/kg Boom Clay) values as given in the figure keys. Each plot represents one initial Tc concentration : 3.5×10^{-6} M (top), 1.8×10^{-5} M (middle), 7.1×10^{-5} M (down).

The concentrations of Tc(IV) species in solution in the absence of humic substances are governed by the hydrolysis equilibria and formation of carbonate complexes. Depending on the database used (EQ3/6 or NEA) the concentrations of the different Tc(IV) species may change. For the pH and HCO_3^- concentration of the experiment (pH = 8.3; $[HCO_3^-]$ = 0.014 mol/L) and assuming that no TcO_2 precipitate will form the percentage species concentration was predicted:

1) following NEA database: $TcO(OH)_2$ (85.46%) $TcCO_3(OH)_3^-$ (5.87%), $TcCO_3(OH)_2$ (5.43%), $TcO(OH)_3^-$ (0.24%) , $TcO(OH)^+$(1.52×10^{-4}%), TcO^{2+} (3.03×10^{-11}%).

2) Following the EQ3/6 database for a total Tc concentration of 10^{-7} M : $TcO(OH)_2$ (68.68%), $(TcO(OH)_2)_2$ (31.32%), $TcO(OH)^+$(6.39×10^{-5}%), TcO^{2+} (7.52×10^{-12}%).

The concentrations for the species are dependent on the total Tc concentration due to the fact that polynuclear complexes of $TcO(OH)_2$ were incorporated. However, for all Tc concentrations considered in this experiment, the neutral Tc(IV) species are by far the major species present in solution.

The Schubert plot obtained by combining the experimental K_d values and the extrapolated K_d^0 values gave a slope close to unity indicating that a rather simple reaction mechanism can be written. Since no extra information on the nature of the complexes formed was known, it was proposed to discuss two widely different interaction mechanisms and their corresponding K^{HS} values:

1) It was assumed that TcO^{2+} complexes are formed with the dissolved humic substances according to the following reaction and corresponding K^{TcO2+} value:

$$TcO^{2+} + HS \Leftrightarrow TcO^{2+}\text{-}HS \qquad (1\text{-}17)$$

The side reaction coefficient A is then $10^{13.316}$ (EQ3/6) and $10^{12.675}$ (NEA) respectively.

2) Since the overwhelming fraction of Tc species in solution (especially when the EQ3/6 database is followed) consists of the neutral species $TcO(OH)_2$ and $(TcO(OH)_2)_2$, an interaction mechanism of these species with dissolved humic substances was also considered. The equilibrium constant $K^{TcO(OH)2}$ refers to the reaction equilibrium:

$$Tc(neutral) + HS \Leftrightarrow Tc(neutral)\text{-}HS \quad (EQ3/6) \qquad (1\text{-}18)$$
$$TcO(OH)_2 + HS \Leftrightarrow TcO(OH)_2\text{-}HS \quad (NEA) \qquad (1\text{-}19)$$

which in fact corresponds more to a hydrophobic sorption mechanism[6]. The value of the side reaction coefficient to be introduced into equations (1-15 – 1-16) then equals $10^{0.000}$ (EQ3/6 – irrespective of the Tc concentration since all neutral Tc(IV) species are included) and $10^{0.076}$ (NEA) respectively.

[6] Due to the low solubility of $TcO_2.nH_2O$ and the neutral species involved in the interaction between technetium and humic substances, the name "hydrophobic" sorption mechanism was chosen in analogy with the sorption of hydrophobic species such as Polyaromatic Hydrocarbons on humic substances.

The mean values for $LogK^{TcO2+}$ are 18.6 (±0.3) and 18.0 (±0.3) for the EQ3/6 and NEA database respectively, and for $LogK^{TcO(OH)2}$ the mean values are 5.3 (±0.3) (EQ3/6) and 5.4 (±0.3) (NEA). The data clearly demonstrated that within less than one order of magnitude the obtained K^{TcO2+} and $K^{TcO(OH)2}$ values were independent of the concentration of dissolved HS, or of the total Tc concentration in solution or at the surface.

Both K^{HS} values described the interaction of inorganic Tc(IV) species with dissolved humic substances in the equilibrium solution. In order to find out which of both reactions is actually occurring, more information (e.g. spectroscopic, kinetic) is necessary. However, it was shown that the K^{TcO2+} constant remained independent of the Tc loading of the dissolved HS, which is unusual for humic substances, especially in the wide loading range considered in these experiments (10^{-11} – 10^{-6} mol Tc/g HS). Indeed, due to the heterogeneity of the functional groups in humic substances, metal complexation reactions are typically known to depend on the loading (Hummel, 1997 and 1999) especially in the low loading range studied here. The constancy of the $K^{TcO(OH)2}$ value describing the hydrophobic sorption mechanism is expected for sorption of hydrophobic compounds. It was therefore concluded and suggested that the hydrophobic sorption reaction ($K^{TcO(OH)2}$) is governing the distribution of Tc(IV) between Tc(IV)-HS associations and inorganic Tc(IV) species in solution. Seen the proposed hydrophobic interaction mechanism, the HS concentration is better given in g/L, which then corresponds to a $LogK^{HS}$ value equal to 2.6 (±0.3).

A question remains about the reversibility of the observed processes. Since the series of successive extracts were taken at different total equilibration times ranging from 1-6 weeks and since all Tc distributions lead to the same unique description of the data it was concluded that equilibrium must have been installed after one week of (intermittent) equilibration.

1.6 Conclusions

In order to perform calculations for performance assessment studies for a geological disposal site and/or the overlaying aquifers, the knowledge of the thermodynamic stabilities, solubilities and (geo)chemical behaviour under variable geochemical conditions of all the radionuclides present in radioactive waste, is very important. For most of these radioactive elements, their properties and behaviour under various conditions have been studied intensively over the last 25 years, but even until today their (geo)chemical behaviour has not been understood in sufficient detail. Especially, in the case of technetium, great gaps on the knowledge of its geochemical behaviour are to be filled. It is the intention of this Ph. D. Work to provide some answers by investigating the behaviour of technetium both in the absence and presence of (Gorleben) humic substances, by determining the valence state of technetium and the nature of technetium species in “technetium-humic substance species” and by quantification of a conditional interaction constant for the interaction between technetium and Gorleben humic substances.

From the literature overview given in this chapter, some general conclusions that are relevant for the understanding of the further chapters of this Ph. D. work can be drawn:

1) Under environmental oxidising conditions, technetium exist as Tc(VII).
2) Under environmental suitable reducing conditions, Tc(IV) species prevail.
3) Suitable reducing conditions for the reduction of pertechnetate include the presence of a reducing solid phase with Fe^{2+} as an integral part of the crystal lattice. However, some studies where Tc(VII) was reduced by dissolved Fe(II) are also reported. In terms of suitable reducing agents for pertechnetate reduction, humic rich aquifer systems must be able to ensure a suitable reducing environment to obtain reduced Tc substance species, considering the fact that such a system should contain both solid and dissolved components having reducing functionalities.
4) After reduction of pertechnetate, an amorphous precipitate $TcO_2.nH_2O$ is formed. The solubility of this amorphous precipitate seems to depend on the experimental preparation method.
5) When the initial pertechnetate concentration is too high, after reduction polymeric and/or colloidal forms of technetium may be present.
6) Reduced Tc species are able to form complexes or to associate with inorganic ligands and solid or dissolved humic substances, presumably present in natural aquifer systems.
7) In the case of the interaction between reduced Tc species and humic substances, neither the correct interaction mechanism nor the valence state of Tc within these complexes has been clarified. The interaction between reduced Tc species and the reducing solid phases presumably present in aquifer systems, has also not been investigated or quantified in relation with the presence of humic substances. Only, a conditional interaction constant for the interaction between Tc and Boom clay humic substances has been reported. It was proposed that the interaction between Tc and HS occurred by way of a hydrophobic interaction mechanism.

CHAPTER 2

THE GORLEBEN AQUIFER SYSTEM: CHARACTERISATION AND INTERACTION WITH RADIONUCLIDES

2.1 Introduction

For a high-level radioactive waste disposal in a geological formation, natural barriers isolating the waste from the biosphere, are the host formation and the overlaying strata. At the Gorleben site (Lower Saxony, Germany, see figure 2-1), the host rock is a Permian salt dome with an overlaying strata consisting of sedimentary rock with a complex aquifer system. The most important scenario for radionuclides moving from the repository to the biosphere is transport with groundwater. At the Gorleben site sandy sediments of high permeability are found from the surface down to the top of the salt dome. The Gorleben groundwaters contain relatively high amounts of soluble and mobile humic substances (up to 400 mg/L), which can act as potential carriers for radionuclides such as technetium.

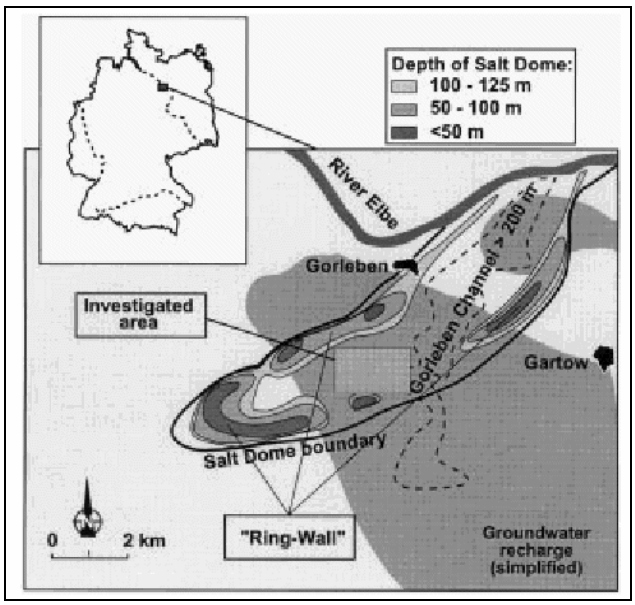

Figure 2-1. Overview of the Gorleben site (from Buckau *et al.*, 2000)

A tremendous amount of data on geology, hydrology and geochemistry of the investigated area at Gorleben (indicated in figure 2-1) are available (Buckau *et al.*, 2000). In 2000, the German authorities have postponed their decision to use the Gorleben site as a "final" disposal site for high radioactive waste and they are

searching for alternative sites and/or alternative solutions for the high radioactive waste problem. Nevertheless, further investigation of the behaviour of radionuclides in the Gorleben site and the overlaying aquifers are still very useful for comparison with other case studies where also high amounts of humic substances are present.

In this chapter, an overview is given of the Gorleben sampling site and the origin, composition and main properties of Gorleben humic substances. Also a short review is given on the available literature data concerning the interaction between several radionuclides and Gorleben humic substances.

2.2 The Gorleben sampling site

2.2.1 Geological background of the Gorleben sampling site

The aquifer sites at Gorleben, from which groundwaters are sampled, are situated between 150 and 300 metre depth of glacial sand, silt, marl and clay overlying a salt dome with a volume of approximately 8×10^{10} m^3. The salt dome consists of evaporites deposited during the uppermost Permian (Zechstein) about 230 million years (MY) ago. The Zechstein deposits are dominated by rock salts with stratigraphic intercalations of potassium salts, anhydrite and clay. The uplift of the salt depositions took place from the Upper Triassic (200 MY) to the lower Cretaceous (100 MY) when the salt dome probably was unroofed (Buckau *et al.*, 2000). The uplift rate during the Tertiary is estimated at 0.01 to 0.02 mm per year. The elevation of the diapir caused rupturing and folding of the overlying and surrounding Miocene "brown-coal" sand and clay. Two main aquifers within the Miocene and Pleistocene sands and silts are locally subdivided into four aquifers. The age of the lowermost groundwater is probably of the order of 10^4 years.

2.2.2 Origin and mobility of humic colloids in the Gorleben aquifer system

In the investigated area of the Gorleben aquifer system, fresh water is found in the upper 50 m and saturated salt brines are found below approximately 230 m close to the underlaying salt dome. Groundwater of varying salinity is found at intermediate depths, partly with high-elevated dissolved organic carbon (DOC) concentrations. DOC concentrations up to 200 mgC/L are found (Kim *et al.*, 1990, Buckau, 1991). These high DOC concentrations are the result of in situ generation in conjunction with mineralisation of sedimentary organic carbon. In the Gorleben aquifer, this process is favoured by the combination of dissolution of sulphate from the cap-rock of the salt dome and Miocene brown coal and Pleistocene peat deposits. Considerable vertical groundwater exchanges occur over the entire depth of the investigated groundwaters. There is no indication of sorption or decomposition of DOC. Due to the rapid mixing of groundwater, the migration of humic colloids cannot be precisely monitored. Within this aquifer system, humic colloids are ubiquitous and below 50 m depth they are continuously generated in situ. These in situ generated humic colloids are presumably transported into the upper 50 m fresh water region. However, they are dispersed and diluted to concentrations below approximately 5 mgC/L due to the rapid groundwater flow (Buckau *et al.*, 2000).

2.2.3 Sampling site

Boreholes and their associated sediment cores carry individual identification numbers. Figure 2-2 gives details on the position of the boreholes of the investigated area (area is indicated in figure 2-1). From these drillings, sediment cores have been analysed and wells for groundwater samples at different depth have been constructed. The investigated area is approximately 1.5 × 2 km. The groundwaters are selected in view of the highly varying DOC concentrations (1 to 80 mgC/L) and considering the predominance of groundwater flow through highly permeable sandy sediments and the corresponding importance for the potential radionuclide migration, the groundwaters are selected from such sediments. Water samples carry the designation: "GoHy-(Gorleben hydrological sample) followed by the borehole number. The groundwater used in this Ph. D. research is the GoHy-2227, and will be called "natural Gorleben groundwater" further on.

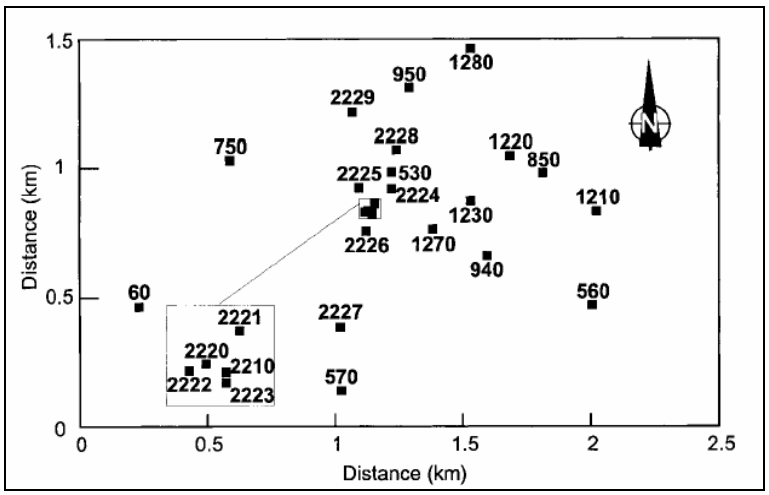

Figure 2-2. Location of boreholes for sediment core and groundwater sampling in the investigated area. The location of this area is shown in figure 2-1.

2.2.4 Natural Gorleben groundwater

a) Groundwater sampling and field analysis

The chemical and physico-chemical parameters from field-analysis from the Gorleben groundwater are shown in table 2-1.

b) Laboratory analysis

- inorganic composition

Inorganic groundwater components were determined by ICP-AES, ICP-MS, HPLC and titration (Artinger *et al.*, 1998a). The results are summarised in table 2-2:

Water temperature / (°C)	14.8
pH	7.7
Redoxpotential / (mV)	-123
Electr. conductivity / (µS/cm)	4600
O_2 (free) / (mg/L)	<0.1
CO_2 (free) / (mg/L)	12.7
H_2S / (mg/L)	present (*)
HCO_3^- / (mg/L)	488.2

Table 2-1. Chemical and physico-chemical parameters from field-analysis of the sampled groundwater GoHy-2227 (Artinger *et al.*, 1998a).

(*) quantification not possible, but remarkable smell of H_2S

Element	mmol/L	Anion	mmol/l
Na	40.5304	Cl^-	33.6732
K	0.1798	F^-	0.2053
Mg	0.1934	HCO_3^-	8.0033
Ca	0.6681	NO_3^{2-}	<0.0001
Sr	0.0024	PO_4^{3-}	0.0358
Ba	0.0002	SO_4^{2-}	0.2820
Al	0.0041		
Si	0.0221		
Fe	0.0059		
Mn	0.0005		
Ti	0.0058	Ionic	44×10^{-3}
B	0.0315	strength	

Table 2-2. Inorganic composition and ionic strength of the sampled Gorleben groundwater (Artinger *et al.*, 1998a)

- Dissolved organic carbon

For the sampled GoHy-2227 groundwater, the DOC concentration is 81.9 mgC/L, which is distributed between 79% humic acids, 8% fulvic acids and 13% hydrophilic acids as was determined with the standard XAD-8 method (Aiken, 1985).

The size distribution of the DOC was determined by ultrafiltration at different pore sizes and subsequent DOC measurements of the filtrates. The hydrodynamic size of DOC is less than 300 kDa for this groundwater, corresponding to a hydrodynamic diameter of less than 15 nm (Buckau, 1991).

Via the standard procedure using a XAD-8 resin, Gorleben humic and fulvic acids were isolated from the natural Gorleben groundwater (Artinger *et al.*, 1998a). These isolated humic and fulvic acids were further characterised for their 1) elemental composition, 2) major inorganic components using ICP-AES and ICP-MS, and 3) functional group content using different procedures (barium exchange capacity, calcium exchange capacity and direct titration). In tables 2-3 – 2-5, an overview of the results is given. The obtained results are in agreement with literature values for humic and fulvic acids (Kononova, 1966, Stevenson, 1982).

	Gorleben HA	Gorleben FA
Element		
C	56.3	57.2
H	4.5	4.9
N	1.7	1.1
S	1.7	1.4
O	35.8	35.4
Atom ratio		
H/C	0.98	1.02
O/C	0.46	0.46

Table 2-3. Elemental composition (%) and H/C and O/C atom ratios for Gorleben humic and fulvic acids (Buckau, 1998)

	Gorleben HA	Gorleben FA
Na	19.0	2196
Ca	22.6	437
Mg	4.0	44
Al	39.3	-
Si	68	1196
Fe	277	52.9
Co	2.5	0.24
Ce	1.1	0.1
Eu	0.05	0.01
Th	7.4	0.23
U	2.2	-

Table 2-4. Inorganic impurities (in µg/g) for Gorleben humic and fulvic acid determined by ICP-AES and ICP-MS (Buckau, 1998)

Determination method	Humic substance	Σ –COOH + Phenolic OH	–COOH	Phenolic OH
BaEC	Gorleben HA	6.6 ± 0.3		
CaEC	Gorleben HA		4.8 ± 0.3	1.9 ± 0.4
Direct Titration	Gorleben HA		5.4 ± 0.4	
	Gorleben FA		5.70 ± 0.09	

Table 2-5. Content of proton exchanging functional groups (in mEq/g) in Gorleben humic and fulvic acids determined by barium exchange capacity (BaEC) at high pH, calcium exchange capacity (CaEC) in acetate buffered medium, and "Direct Titration" (Buckau, 1998)

- bacteria

Experiments were conducted to verify whether any aerobic or anaerobic bacteria are present within the sampled natural Gorleben groundwater. A culture medium was inoculated with the groundwater but after 24 hours no bacterial colonies were detected.

2.2.5 Gorleben sand

The Gorleben Sand used at the research centre F.Z.K. (Germany) and in the experiments in this Ph. D. work, is representative for various sandy sediments at different depths in the Gorleben aquifer system. The sand has been sampled from near the aquifer surface. The aeolian fine sand (d_{10}=0.12 mm and d_{50}=0.18 mm, unconformity[7] U=1.7) is related to the transition from the younger Weichsel cold age to the Holocene (≈20.000 to 10.000a).

According to X-ray diffraction analysis and X-ray fluorescence spectroscopy, the sand consists of about 85% quartz, 10 to 15% feldspar (albite and microcline) and <5% other minerals (e.g. haematite, mica). The grain size analysis showed that the silt part was about 0.25% and clay <0.1%. The organic carbon content of the Gorleben sand can be estimated to <0.5%. This was done by carbon analysis of gas released upon sample combustion. The presence of organic carbon is confirmed by black charcoal like particles with a carbon content of 55% and an ash content of 10%. The larger of these particles have a specific surface area 10 m^2/g as determined by nitrogen gas adsorption according to Brunauer, Emmet and Teller (BET method, Brunauer *et al.*, 1938). The origin of these particles is yet not clear, however, lignite particles from reworked older sediments appears improbable, because the sampled Gorleben sand has a Pleistocene eolian origin and was not covered by glaciers in the Weichsel cold age (Artinger *et al.*, 1998a).

The cation exchange capacity (CEC) of the sand was determined according to Mechlich with barium chloride, and a mean value of 1.02 (± 0.02) meq/100 g was obtained. The specific surface, determined by the BET method had a mean value of 1.10 (± 0.09) m^2/g. Potentiometric titration of the solid phase was used to determine the point of zero charge; a pH value 4.6 was obtained (Artinger *et al.*, 1998a). Because pure quartz has pH_{pzc} of about 2, the value of 4.6 indicates the presence of considerable amounts of other proton exchanging substances. This could be the organic substances (charcoal like particles) or the minerals, such as alkali feldspars and/or iron hydroxides like haematite, found on the quartz surface.

2.3 The interaction between radionuclides and Gorleben humic substances

During the last decade, the choice of the Gorleben salt dome as a potential host for high level radio-active waste disposal induced a huge interest for studies of the behaviour of radionuclides in the surrounding (humic rich) aquifer system. It is

[7] In particle size analyses of soil samples the unconformity (or uniformity coefficient) is a measure of the slope of a grading curve and gives therefore the uniformity of the soil. It is calculated as the ratio d_{60}/d_{10}. Samples with values less than 2 are rated uniform.

expected, that besides sorption on solid phases present in the Gorleben sand, their behaviour is mostly governed by complexation or association with the dissolved humic substances present in the groundwater. This would of course cause an enhanced solubility and mobility of these elements.

Tri- and tetravalent radionuclides and analogues such as europium (Carlsen, 1990, Maes *et al.*, 1991, Kim *et al.*, 1994, Benes *et al.*, 2002, Geckeis *et al.*, 2002), uranium (Dearlove *et al.*, 1991, Zeh *et al.*, 1997, Geckeis *et al.*, 2002), americium (Kim *et al.*, 1991a, 1993, Buckau *et al.*, 1992), protactinium (Kim *et al.*, 1991a, 1994), thorium (Geckeis *et al.*, 2002), terbium (Bidoglio *et al.*, 1991) curium (Kim *et al.*, 1991b, 1993, Buckau *et al.*, 1992, Shin *et al.*, 1995), neptunium (Kim and Sekine, 1991, Kim *et al.*, 1994, Zeh *et al.*, 1997, Marquardt and Kim, 1998) and technetium (Sekine *et al.*, 1993, 1997) were all found to form complexes with dissolved Gorleben humic and fulvic acids and for some of the aforementioned interactions, complexation constants were determined via various methods (table 2-6). A total detailed description of the interaction between these elements and dissolved Gorleben humic substances is beyond the scope of this Ph D. Research; the interested reader is referred to the given literature references.

R.N.	HS	pH	Method	Log β	Unit	Reference
Eu(III)	HA	6	IE	5.00 – 5.21	L/g	Carlsen, 1990
	HA	6	IE	7.93 – 8.22	L/Eq.H^+	Maes *et al.*, 1991
	HA	9	IE	12.86 – 13.04	L/Eq.H^+	Maes *et al.*, 1991
U(IV)	HA	1-10	UF - IE	14.7 ± 0.5	L/mol	Zeh *et al.*, 1997
Am(III)	HA	4	UV	6.02	L/mol	Kim *et al.*, 1993
	HA	4	UF	6.10	L/mol	Kim *et al.*, 1993
	HA	5	UV	6.40	L/mol	Kim *et al.*, 1993
	HA	5	UF	6.28	L/mol	Kim *et al.*, 1993
	HA	5	TRLFS	6.07 ± 0.07	L/mol	Kim *et al.*, 1993
	FA	6.0	UV	5.78 ± 0.07	L/mol	Buckau *et al.*, 1992
Tb(III)	HA	8.5	TRLIF	6.70 ± 0.20	L/mol	Bidoglio *et al.*, 1991
Cm(III)	HA	5	TRFLS	6.07	L/mol	Kim *et al.*, 1993
	HA	6	TRFLS	6.22 ± 0.07	L/mol	Kim *et al.*, 1991b
	FA	6	TRFLS	5.90 ± 0.11	L/mol	Buckau *et al.*, 1992
Np(V)	HA	7 – 9	UV-Vis	3.58 ± 0.05	L/mol	Marquardt and Kim, 1998a
	HA	6	UV-Vis	2.28 ± 0.06	L/mol	Kim and Sekine, 1991
	HA	7	UV-Vis	2.45 ± 0.03	L/mol	
	HA	8	UV-Vis	2.71 ± 0.09	L/mol	
	HA	9	UV-Vis	3.10 ± 0.07	L/mol	

Table 2-6. Conditional complexation constants (Log β) for the interaction between radionuclides and Gorleben humic substances (HA or FA), determined at an ionic strength = 0.1 and at various pH values.

It is further worth noticing, that in laboratory experiments the Gorleben sand/Gorleben groundwater system as a whole becomes gradually reducing with time and was able to reduce Np(V) to Np(IV) (Zeh *et al.*, 1997, Marquardt *et al.*, 1999). After reduction, Np(IV)-Gorleben humic substance species were formed. The kinetics

of the reduction reaction was found pH dependent, but a sound explanation for this behaviour was not given. Difficulties arised from the fact that on the one hand, probably different reducing groups of the humic substances could reduce the Np(V), but on the other hand also other components (such as ferrous ions) present in the groundwater or the Gorleben sand might reduce the neptunium.

Artinger *et al.* (1998b, 2002a) investigated the transport behaviour of Am in a Gorleben sand/Gorleben groundwater system through laboratory column experiments. It was observed that as the contact time between Am and humic colloids prior to introduction into a column is increased, the mobility of colloid-borne Am is enhanced and hence the recovery of Am in the effluent increased. On the other hand, an increase of the migration time and residence time in the column, respectively, reduced the Am recovery. Similar results were reported for the transport behaviour of uranium (Artinger *et al.*, 2002b) and tetravalent actinides and technetium (Artinger *et al.*, 2003). A kinetic behaviour of the trace metal ion interaction was observed, *i.e.* with increasing contact time between the radionuclide-HS, slow dissociation modes are progressively populated resulting in an enhanced radionuclide transport.

For technetium, however, no thorough study was yet performed on its behaviour in the Gorleben aquifer system and its interaction with dissolved Gorleben humic substances. Only, Tc(III) species were found to form complexes with dissolved Gorleben humic substances (Sekine *et al.*, 1993, 1997). But, as already stated in chapter 1, these species were prepared at low pH and their relevancy for environmental conditions can be questioned.

2.4 Conclusions

A tremendous amount of data on geology, hydrology and geochemistry are available for the Gorleben site. In addition, dissolved Gorleben humic substances were extensively studied. This makes them especially appropriate for investigations in relation with radionuclides present in (high level) nuclear waste.

Although many studies are reported on the interaction between various radionuclides and Gorleben humic substances, no thorough study has been performed on the interaction between technetium and Gorleben humic substances.

CHAPTER 3

FACTORS AFFECTING THE REDUCTION OF PERTECHNETATE IN THE PRESENCE AND ABSENCE OF HUMIC SUBSTANCES AND THE FORMATION OF TECHNETIUM – HUMIC SUBSTANCE SPECIES

3.1 Introduction

The purpose of this Ph. D. research is to examine, quantify and explain the interaction between technetium species and (Gorleben) humic substances under *in situ* reducing conditions. Although, theoretically, interactions between oxidised Tc species (pertechnetate) and humic substances could be possible, a direct association between these two species was not described in literature (*cfr.* Chapter 1). Tc - humic substance species were only found under reducing conditions and the valence state of Tc within these species was supposed to be below +7.

It is the intention of this chapter to find suitable pathways for pertechnetate reduction and Tc-HS formation under conditions relevant for environmental reducing conditions. Most known methods for pertechnetate reduction are not related to *in situ* behaviour, and could induce formation of "new Tc species", which otherwise would not have been formed under normal *in situ* conditions (Shilov *et al.*, 1996, Rard *et al.*, 1999). Potentially the interaction of such "new Tc species" with humic substances could lead to irrelevant results. For this research, the attention is focussed on the reduction of pertechnetate catalysed by Fe(II)-containing minerals, sulphur containing minerals, Fe(II) containing solutions or humic substances; hence "electron donating" natural compounds which are (or could be) present in possible burial sites and their surrounding aquifers.

Lee and Bondietti (1983) investigated the behaviour of technetium in the presence of sulphide, iron and ferrous sulphide solutions and removed pertechnetate from solution (at an elevated pH) by (co-)precipitation with iron and/or sulphide minerals. The degree of Tc removal in solution for the aforementioned reactions, depended on the concentration of ferrous iron and/or sulphide at constant pertechnetate concentrations. Cui and Eriksen (1996a, 1996b) investigated 1) the reduction of pertechnetate by ferrous iron in solution, 2) the influence of sorbed and precipitated Fe(II), and 3) the (surface-mediated) reduction of pertechnetate in solution by Fe(II)-bearing fracture filling material from a natural fracture in granite, hornblende and magnetite. Magnetite was found to be the most efficient reductant.

In Chapter 1, it was concluded that in terms of suitable reducing agents for pertechnetate reduction, humic rich aquifer systems could be able to ensure a suitable reducing environment to obtain reduced Tc substance species, considering the fact that such a system should contain both solid and dissolved components having reducing functionalities. But an ambiguity remained as to whether pertechnetate can be reduced by ferrous iron in solution and/or humic substances (both solid or dissolved). It was also concluded that the presence of a reducing solid phase (such as magnetite) is necessary for the reduction of pertechnetate, considering the fact that presumably a three-electron reduction occurs.

3.2 Experimental set-up

All experiments were carried out at ambient temperature (22°C) in a controlled atmosphere glove box flushed with a mixture of N_2 (95%) and H_2 (5%) to minimise the intrusion of oxygen into the reaction vessels. The box atmosphere was circulated over a catalytic converter (Pt) in order to remove excessive oxygen. The mean concentration of O_2 in the glove box throughout the experiments was below 2 ppm.

All chemicals used were of analytical grade and the water used was deionized, filtered by a Water Purification System (Milli-Q) and finally boiled out to obtain oxygen-free water. Technetium-99 (0.1 mol/L) was purchased from Amersham in a 0.1 mol/L NH_4OH aqueous soluton. Pertechnetate solutions were prepared by diluting aliquots of the stock solution.

Gorleben groundwater (GoHy-2227 - GW) containing 165 mg/l organic matter and Gorleben sand (GS) from the potential disposal site at Gorleben (Germany) were used as supplied by Forschungszentrum Karlsruhe (Germany). The water was stored in a closed bottle covered with Al foil to avoid light inside the glove box. Synthetic Gorleben groundwater (SGW) was prepared as a mixture of 3.2×10^{-2} mol/L NaCl and 8×10^{-3} mol/L $NaHCO_3$, and was taken as representative for the inorganic composition of the natural Gorleben groundwater (Artinger *et al.*, 1998a).

Tc-99 in solution was measured by Liquid Scintillation Counting (Packard 1600 CA Liquid Scintillation Analyser) using Packard Ultima Gold as the scintillation cocktail. Via counting reference samples with known Tc-99 concentrations, the unknown Tc-99 concentration within the studied supernatant solution can be determined. The collected counts correspond to less than 2% error at 2σ level. The presence of humic substances can influence the obtained counts by a process called chemical quenching, which reduces the obtained counts for Tc compared to the actually present in the sample. The quenching was monitored by the transformed Spectral Index of the External standard (tSIE), which is calculated from the Compton spectrum induced in the scintillation cocktail by an external Ba-133 source. Via a so-called "quenching curve" (a relationship between the efficiency of the obtained Tc counts and the ln(tSIE)), the obtained Tc counts are corrected. The quenching curve was determined by liquid scintillation counting of samples containing various dissolved humic substance concentrations and the same Tc concentration. It was observed that the obtained quenching curve is independent on the kind of humic substances used, but dependent on the Tc concentration present. Therefore, polypropylene vials are filled with 19 ml of diluted natural Gorleben groundwater in SGW, resulting in a humic

substance concentration range between 16.4 and 164 mg/L and 1 ml of the different pertechnetate solutions, resulting in a total Tc concentration in solution between 10^{-8} and 10^{-3} mol/L. Systems containing high humic substance concentrations (between 150 and 400 mg/L) were made by dissolving Aldrich humic acids in SGW in different polypropylene vials and adding the same aforementioned pertechnetate solutions. For each Tc concentration used, the obtained quenching curve is not linear, but the curve can be approached by two linear relationships, which intersects at a tSIE value of 155. For each Tc concentration used, a specific quenching curve was determined.

Total Fe(II)-concentration in solution was determined by a colorimetric method at 508 nm using o-phenantroline and sodiumacetate.

The pH measurements were made by a Portatest 655 and a WTW SenTix 50 glass electrode. The redox potentials were monitored by a combined redox Toledo Mettler P14805-DXK-S8/120 electrode connected to the Portatest 655. The humic substances concentration was obtained from Absorbance measurements at 280 nm (LKB spectrophotometer). Diluted solutions of the natural Gorleben groundwater (165 mg/L) were taken as standard solutions.

Gel permeation chromatography was performed on the supernatant solutions of nearly all experiments to verify the presence of Tc-HS, inorganic Tc(IV) species and/or pertechnetate species. The analysis was carried out by eluting a 1 ml sample aliquot over a glass column (30x1 cm), filled with Superdex 30 Prep Grade gel (Pharmacia Biotech). The eluent was a 0.15 mol/L NaCl solution containing 0.002% NaN_3 to prevent microbial growth. The U.V.-absorbance (280 nm) was measured continuously and the collected fractions (1.5 ml) were analysed for Tc by Liquid Scintillation Counting. This method allowed only to determine Tc qualitatively because a part of the humic substances and reduced Tc species are retained at the top of the column.

Pertechnetate reduction in the absence of humic substances

a. Reduction of pertechnetate by Fe^{2+} in solution

The behaviour of pertechnetate in the presence of Fe^{2+} in solution was investigated as a function of time, by preparing different polypropylene vials containing 19 ml of a Fe^{2+} solution and 1 ml of a pertechnetate solution in SGW. The Fe^{2+} solution was made by dissolving $FeCl_2.4H_2O$ in MQ-water in the glove box. The final Tc and Fe^{2+} concentrations were respectively 2.5×10^{-6} and 5×10^{-5} mol/L. The initial pH was equal to 8.2. The vials were turned slowly head over head.

In a second experiment, a series of identical mixed solutions as before were prepared but the pH was raised to 9.5 by adding a small volume of 0.1 mol/L NaOH in order to induce a freshly precipitated $Fe(OH)_2$ surface. The reaction was followed as a function of time. Finally, the influence of pH was studied more in detail by preparing polypropylene vials containing a final concentration of 2×10^{-2} mol/L Fe^{2+} and 2.5×10^{-6} mol/L pertechnetate in a pH range of 7 to 10 (by adding small volumes of 0.1 mol/L NaOH). The vials were analysed after 24h.

All samples were centrifuged (Beckman Centrifuge J2-21, rotor JA-20) for 30 min at 39191×g and the supernatant was analysed for total Tc, total Fe(II)-concentration, pH and Eh.

b. Reduction of pertechnetate by reducing solid surfaces

Experiments were conducted in SGW in presence of different iron(II)-containing minerals: illite, Fe^{2+}-saturated illite, glauconite, Fe^{2+}-saturated glauconite, phlogopite, Fe^{2+}-saturated phlogopite, synthetic iron(II) sulphide, magnetite, siderite and pyrite. Small sized fractions of these minerals were obtained by crushing the solids in the glovebox using an Agate mortar and pestle, and sieving to < 200 µm fractions. In addition for pyrite and ironsulphide, fractions < 100 µm were collected. The Fe^{2+}-saturated minerals (- illite, - glauconite and - phlogopite) were prepared in dialyis membranes by repeated equilibration with solutions of 2×10^{-2} mol/L $FeCl_2.4H_2O$.

The reaction is followed as a function of time by preparing multiple polypropylene vials, containing 100 mg of all the aforementioned mineral fractions and 20 ml of a 2.5×10^{-6} mol/L pertechnetate solution in SGW. The influence of the amount of reducing surface on the extent of reduction was studied with 20, 50 and 100 mg of Pyrite (< 0.1 µm). The vials were turned slowly head over head to ensure good mixing. All samples were centrifuged for 30 min at 39191×g and the supernatant solutions were analysed for total Tc concentration, pH and Eh.

The behaviour of pertechnetate in the presence of dissolved humic substances

Pertechnetate solutions (concentrations ranging between 10^{-6} and 10^{-4} mol/L) in Synthetic Gorleben groundwater (SGW) were prepared by diluting aliquots of the stock solution. In polypropylene vials, 19 ml of Natural Gorleben groundwater, Kranichsee humic and - fulvic acid solutions and Aldrich humic acid solutions were spiked in duplo with 1 ml of the different pertechnetate concentrations, resulting in Tc starting concentrations ranging between 5×10^{-8} and 5×10^{-6} mol/L.

The vials were turned slowly head over head and after centrifugation (30 min, 39191×g), the supernatant solution was analysed after 3 and 26 days, for total Tc concentration, pH and Eh. To verify the presence or absence of pertechnetate species at equilibrium, gel permeation chromatography was performed on the supernatant solutions.

Pertechnetate reduction in the presence of humic substances and a reducing solid phase

Two different types of systems were investigated:

1) Synthetic reducing systems
   Experiments were conducted in the presence of a reducing solid phase and dissolved humic substances. To allow the follow up of the reaction with time a sufficient number of these lab scale synthetic reducing systems were prepared in different polypropylene vials which contained 50 mg of the minerals Magnetite, Pyrite, Siderite and synthetic Iron(II)sulphide and 19 ml of natural Gorleben water. A similar set of experiments was made with 50 mg of magnetite mixed with 19 ml of different synthetic groundwater solutions

containing 150 mg/L Kranichsee humic acids, Kranichsee fulvic acids or Aldrich humic acids. After a pre-equilibrium period of three days, 1 ml of a pertechnetate solution (in SGW) was added. Duplicate systems of Magnetite, Pyrite and FeS mixed with 19 ml natural Gorleben Groundwater were prepared but 1 ml pertechnetate was only added after 3, 7, 14 and 50 days preequilibation. The final Tc concentration was 2.5×10^{-6} mol/L.

The vials were turned slowly head over head to ensure good mixing. Sampling was made at regular time intervals. After centrifugation for 30 min at 39191×g, the supernatant was analysed for total Tc, pH, Eh. In addition, to verify the presence or absence of pertechnetate, gel permeation chromatography was performed on selected supernatant solutions.

2) Lab scale natural reducing systems
To mimic a natural reducing environment, in the second type, experiments were conducted in the presence of 10 g Gorleben sand and 19 ml natural Gorleben water. After an appropriate pre-equilibrium period, 1 ml of a pertechnetate solution (in SGW) was added. The final Tc concentration was 2.5×10^{-6} mol/L.

The vials were turned slowly head over head to ensure good mixing. The reaction is followed as a function of time and all samples were centrifuged for 15 min at 5927×g. The supernatant was analysed for total Tc, pH, Eh. The presence or absence of pertechnetate was checked by gel permeation chromatography.

The reducing components within a lab scale natural system

In order to identify the reducing components of the lab scale natural systems. The behaviour of pertechnetate in the presence of charcoal (manually collected from the Gorleben sand) was investigated. Experiments were conducted in the presence of 50 mg charcoal particles and 19 ml natural Gorleben water or synthetic Gorleben groundwater. After a pre-equilibrium period of four weeks, sufficient to meet appropriate Eh conditions, 1 ml of a pertechnetate solution (in SGW) was added. The initial Tc concentration was 2.5×10^{-6} mol/L.

The vials were turned slowly head over head to ensure good mixing. The reaction is followed as a function of time and all samples were centrifuged for 30 min at 39191×g. The supernatant was analysed for total Tc, pH, Eh and the presence of TcO_4^- by GPC.

The reverse equilibrium approach

A Tc precipitate was first prepared using a methodology already described in a previous: sufficient polypropylene vials, containing 100 mg Magnetite and 20 ml of a 2.5×10^{-6} mol/L pertechnetate solution in SGW, were prepared. The vials were turned slowly head over head to ensure good mixing. All samples were centrifuged for 30 min at 39191×g and the supernatant solutions were analysed for total Tc

concentration, pH and Eh. The reduction reaction was followed as a function of time. When equilibrium was reached the supernatant solution was replaced with natural Gorleben groundwater. Subsequently, total Tc concentration, HS concentration, pH, Eh and the presence or absence of TcO_4^- and Tc-HS species were followed during 300 days.

3.3 Results and discussion

3.3.1 Pertechnetate reduction in the absence of humic substances

Whether pertechnetate is reduced or not, can be verified by observing a decreasing or a constant Tc(VII) concentration in solution when using Tc(VII) concentrations above the solubility level of an amorphous precipitate. This precipitate is considered to be $TcO_2.nH_2O$ and is the most important (directly formed) Tc species under natural reducing conditions and in the absence of a sufficient amount of complexing (dissolved or solid) ligands (see chapter 1). However, no unique solubility was observed for $TcO_2.nH_2O$, but rather a range of concentrations (between 10^{-8} and 10^{-6} mol/L). This solubility range was explained by the presence of Tc(IV) colloids in the supernatant solution.

a. The reduction of pertechnetate by Fe^{2+} in solution

Initially, experiments were conducted to verify whether, under environmental circumstances, the need for a reducing surface (according to Cui and Eriksen, 1996a) to reduce pertechnetate in alkaline solutions was really necessary. Experiments were conducted in synthetic groundwater solutions in the presence of free Fe(II). At different time intervals, the redox state was determined. Redox potential values (-240 to -310 mV) were always below those necessary for TcO_4^- reduction (see pH-Eh diagram, figure 1-1, Chapter 1). The initial Fe(II) concentration ($5x10^{-5}$ mol/L) decreased within a few days to a stable value of approximately $2.5x10^{-5}$ mol/L (see figure 3-1, before indicated addition of NaOH). The decrease in Fe(II) concentration was concurrent with a slight decrease in pH. However, it was observed that the initial Tc concentration of 2.5×10^{-6} mol/L remained constant within 10 days of investigation. Hence, no reduction occurred.

This result is in contrast with earlier observations made by Stalmans (1986), Vandergraaff (1988) and Lieser and Bauscher (1987), who concluded that reduction of pertechnetate by Fe^{2+} in solution was possible. However, these latter experiments were not checked thoroughly for pH, redox state and amount of remaining iron in solution. Probably, the pH was high enough and unintentially, $Fe(OH)_2$ or other iron(II)-containing minerals were formed and were able to reduce pertechnetate.

When the pH of the synthetic groundwater solutions containing pertechnetate and $FeCl_2$ (5×10^{-5} mol/L) was increased by adding NaOH to a pH of 9, 99% of the initial Tc concentration disappeared from solution within 5 hours (see figure 3-1, after addition of NaOH). The Tc concentration at equilibrium was equal to 2.5×10^{-8} mol/L. The Fe(II) concentration in solution also decreased to undetectable values (i.e. $<10^{-6}$ mol/L).

To look more into detail for the influence of pH in the previous experiment, another experiment was conducted with higher Fe^{2+} concentrations. The experimental conditions as well as the results are shown in table 3-1. The reduction of 2.5×10^{-6} mol/L pertechnetate was examined in the pH range from 4 to 10.25. Only in the case of a pH > 7.80 a significant reduction of pertechnetate was noticed after 24 hours. At these high pH's, the redox potential lowered to values -200 - -300 mV. Moreover beyond pH 7.8, only 5 % of the initial Fe-concentration remained in solution as free Fe^{2+}.

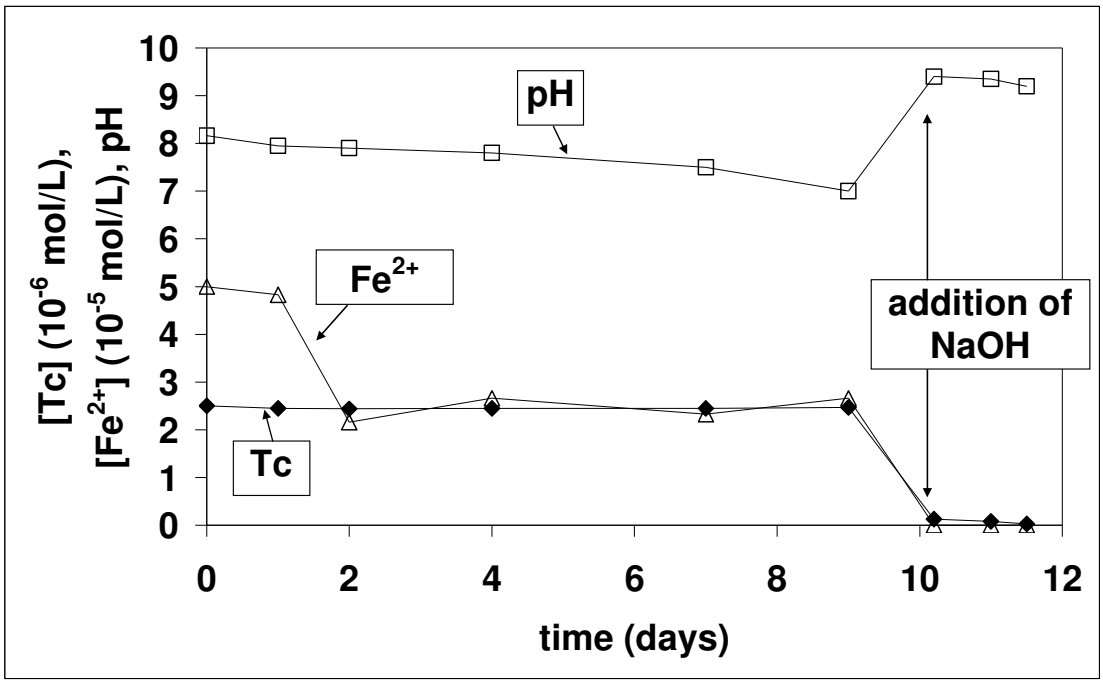

Figure 3-1. Reduction of pertechnetate in the presence of Fe(II). After 10 days NaOH was added (see arrows). Measurements of total Tc - and Fe solution concentration (mol/L), and pH as a function of time (days).

The results of these experiments are in agreement with Cui and Eriksen (1996a) and Zachara *et al.* (2007) and can be explained as follows. Fe(II) in solution is not reacting, or at least very slowly, with the pertechnetate anion. Upon addition of NaOH, Fe(II) was precipitated as $Fe(OH)_2$ according to:

$$Fe^{2+} + 2\ OH^- \rightleftharpoons Fe(OH)_2(s) \qquad K_{sp}=8.10^{-16} \qquad (3\text{-}1)$$

The reduction of pertechnetate is most probably caused by reaction with the 'active' precipitate $Fe(OH)_2$. A plausible mechanism for the disappearance of Tc from solution is sorption of TcO_4^- on the $Fe(OH)_2$ precipitate followed by a reduction of TcO_4^- to $TcO_2.nH_2O$ (Cui and Eriksen, 1996b). The found Tc solubility of 2.5×10^{-8} mol/L lies in the range of observed Tc solubilities for $TcO_2.nH_2O$.

Sample	pH	Eh (mV)	Fe^{2+}-conc. (mol/L)	[Tc] (mol/L)
1	4.05	+ 98	$\approx 10^{-3}$	2.32×10^{-6}
2	4.25	+ 63	$\approx 10^{-3}$	2.48×10^{-6}
3	4.32	+ 13	$\approx 10^{-3}$	2.25×10^{-6}
4	4.67	- 45	$\approx 10^{-3}$	2.35×10^{-6}
5	7.80	- 189	$\approx 10^{-4}$	1.5×10^{-7}
6	10.25	- 309	4×10^{-5}	$2.00\times^{-8}$

Table 3-1. Experimental conditions and results of pertechnetate reduction after 24 hours

b. The reduction of pertechnetate by reducing solid surfaces

To mimic a natural situation, further experiments were conducted in the presence of different solid phases. The experimental conditions and results summarised in table 3-2.

Amount sorbent (mg)	sorbent	Size sorbent (µm)	pH	Eh (mV)	Time for 99 % Tc removal	[Tc] (mol/L)
100	Illite	< 200	5.5 - 6	-	∞ *	2.5×10^{-6}
100	Fe^{2+}-illite	< 200	5.5 – 6	-140 - +35	∞ *	2.5×10^{-6}
100	Glauconite	< 200	6 - 6.5	-100 - -200	∞ *	2.5×10^{-6}
100	Fe^{2+}-glauconite	< 200	6 - 6.5	-	∞ *	2.5×10^{-6}
100	Phlogopite	< 200	6 - 6.5	-100 - -200	∞ *	2.5×10^{-6}
100	Fe^{2+}-phlogopite	< 200	6 - 6.5	-	∞ *	2.5×10^{-6}
100	FeS	< 200	8.2 – 8.9	-250	~ 24 h	8.5×10^{-9}
100	FeS	< 100	8.3	-250	< 3 h	6.8×10^{-9}
100	Magnetite	< 200	9.0	-200	< 3 h	9.7×10^{-9}
100	Siderite	< 200	7.2 – 7.3	-225 - -175	< 24 h	1.3×10^{-8}
100	Pyrite	< 200	7.8 – 9	-175 - -160	~ 24 h	1.1×10^{-8}
100	Pyrite	< 100	6.8	-275	< 2.5 h	9.8×10^{-8}
20	Pyrite	< 100	8.3	-276 - -158	~ 48 h	1.1×10^{-8}
50	Pyrite	< 100	8.3	-296 - -145	~ 24 h	9.8×10^{-9}
100	Pyrite	< 100	8.4	-301 - -225	~ 3.5 h	1.2×10^{-8}

Table 3-2. Experimental conditions (amount, kind of sorbent, size of sorbent, pH, Eh), time for 99% Tc removal and [Tc] solution concentration of experiments with Fe^{2+}-containing solid phases to study the reduction of 2.5×10^{-6} mol/L pertechnetate in SGW.
* No removal of Tc was detected after 14 days of reaction.

In all experiments with clay minerals, 100% of the added Tc was found back in the equilibrium solution after 14 days of contact. Even in presence of the Fe^{2+} saturated clay minerals, no reduction of technetium occurred. These findings are in contradiction with Cui and Eriksen (1996a), who stated that Fe^{2+} sorbed on a solid phase could reduce TcO_4^-.

Table 3-2 shows that those minerals in which Fe^{2+} constitutes a large part of the phramework (ironsulphide, siderite, magnetite and pyrite) were able to quickly remove pertechnetate from solution. Moreover, after reduction of 2.5×10^{-6} mol/L pertechnetate, the equilibrium Tc concentration lies in the commonly observed solubility range of amorphous $TcO_2.nH_2O$ based on literature data (see Chapter 1).

Clearly co-ordinatively bound Fe^{2+} is needed in sufficient amount at the mineral surface to obtain a quick reduction of Tc(IV) to $TcO_2.nH_2O$. Ion exchanged Fe^{2+} or free Fe^{2+} in solution do either not reduce pertechnetate at all or the reduction kinetics is very slow. Fe^{2+} present in small quantities in the phramework of illite, glauconite and phlogopite apparently present unsufficient surface Fe^{2+} to cause a measurable reduction (under the present experimental conditions).

In the cases of pyrite and ironsulphide, a relation between the particle size and the reaction kinetics can be observed. The redox reaction kinetics increases with decreasing particle size. The higher specific surface area of smaller particles can easily explain this.

The influence of the amount of sorbing and reducing surface on the removal of technetium is demonstrated for pyrite in figure 3-2. The data and experimental conditions from this experiment are also shown in table 3-2.

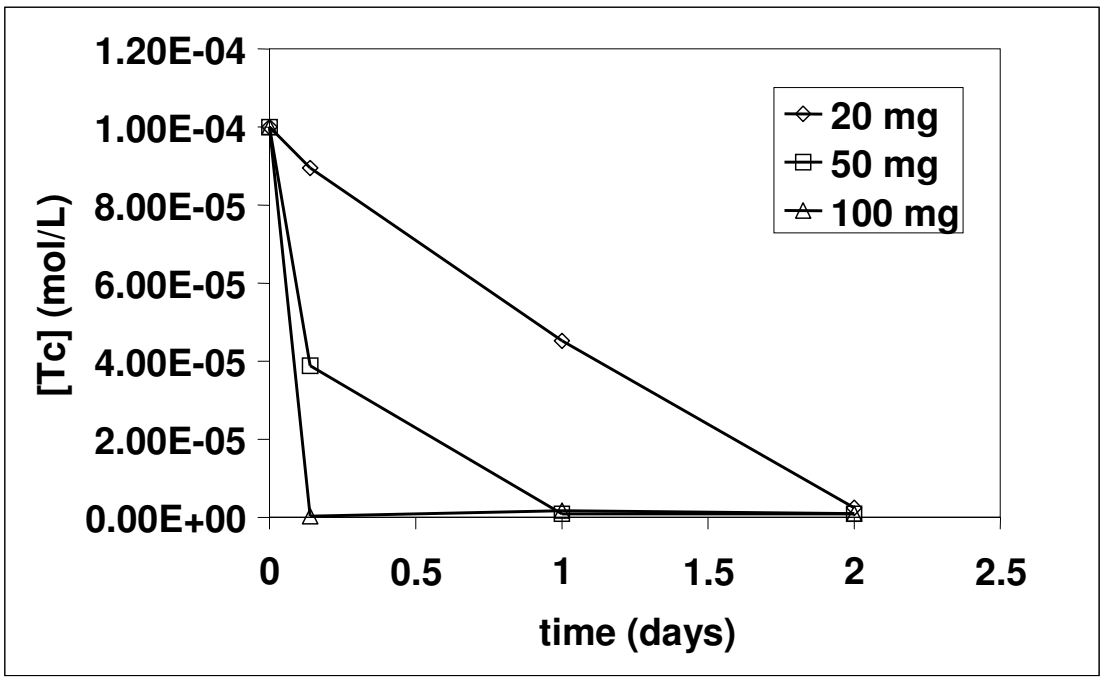

Figure 3-2. The supernatant solution concentration of technetium as a function of time upon reduction of 2.5×10^{-6} mol/L pertechnetate in synthetic Gorleben groundwater and in presence of various amounts of pyrite: 20 (◊), 50 (□) and 100 mg (Δ). pH = 8.3, Eh range = -301 - -145 mV.

The reaction kinetics clearly increases with the amount of reducing surface in the suspension. This observation is in general agreement with Byegard *et al.*, 1992 and Cui and Eriksen, 1996b.

Summarising, it was not possible to reduce pertechnetate in solution containing dissolved Fe^{2+} or via Fe^{2+}-containing clay minerals such as illite, glauconite and phlogopite, even in presence of additional ion exchanged Fe^{2+}. Reduction of pertechnetate was only possible using Fe^{2+}-containing minerals, such as pyrite and magnetite or freshly precipitated $Fe(OH)_2$, which all present coordinatively bound Fe^{2+} in sufficient surface concentrations. In view of the fact that the reduction of pertechnetate to $TcO_2.nH_2O$ requires three electrons, the density of Fe^{2+} on the solid surface is therefore likely to be an important, if not critical factor in controlling the reduction reaction.

As already described in Chapter 1, Cui and Eriksen (1996b) proposed a theory about the surface-mediated pertechnetate reduction by Magnetite. They postulated that the reduction of pertechnetate is kinetically controlled and occurs in a first step via adsorption of pertechnetate anions to the Magnetite surface by a ligand exchange mechanism of replacement of the surface hydroxyl groups by pertechnetate (the rate-determining step) and in a next step pertechnetate is reduced. The reduction rates will be pH-dependent, due to the fact that for an oxide surface, the charge of the surface functional groups is pH-dependent. This implies that with increasing pH, the hydroxylated surface becomes more and more negatively charged; hence, there will be less available sites for pertechnetate anion sorption and consequently a lower reduction rate. For the reduction of pertechnetate by other Fe(II) containing minerals, a similar reduction mechanism is expected.

The reduction of pertechnetate in solution by heterogeneous electron transfer from structurally bound Fe(II) in minerals is therefore a complex process involving sorption, electron transfer between the solid interface and pertechnetate, and solid-state electrochemical reactions. Magnetite, FeS and Pyrite have all (very) low band gaps, respectively 0.1, 0.1 and 0.95 eV (Xu and Schoonen, 2000) between the valence and conduction band and fast electron transfer can therefore easily occur, which explains their fast reduction rates for pertechnetate.

3.3.2 The behaviour of pertechnetate in the presence of dissolved humic substances

The behaviour of pertechnetate in the presence of different kinds of dissolved humic substances (Gorleben, Kranichsee and Aldrich) was investigated as a function of time (up to 26 days). The pH and redox potentials varied respectively between 7.9 and 8.1, and, between -150 and +20 mV and were sufficient for pertechnetate reduction (see figure 1-1, Chapter 1). In all systems, the initial Tc concentration (between 5×10^{-8} and 5×10^{-6} mol/L) remained in solution after 26 days of reaction, indicating that no precipitate has formed. However, one cannot conclude from this result alone that the pertechnetate has not been reduced because, it could be possible that all technetium is associated with the dissolved humic substances. However, after 26 days all GPC of supernatant solutions for all HS were similar to the example shown in figure 3-3, where it is shown that i) all technetium in solution remained as pertechnetate, and ii)

no interaction between technetium and humic substances occurred in the studied time period.

In contrast with the aforementioned results, Stalmans (1986) concluded that dissolved Boom clay humic substances were able to reduce pertechnetate. Most probably the Boom clay extract used in his experiments contained inorganic colloids (FeS_2, Fe-coated clay minerals) which enhance the reduction of pertechnetate.

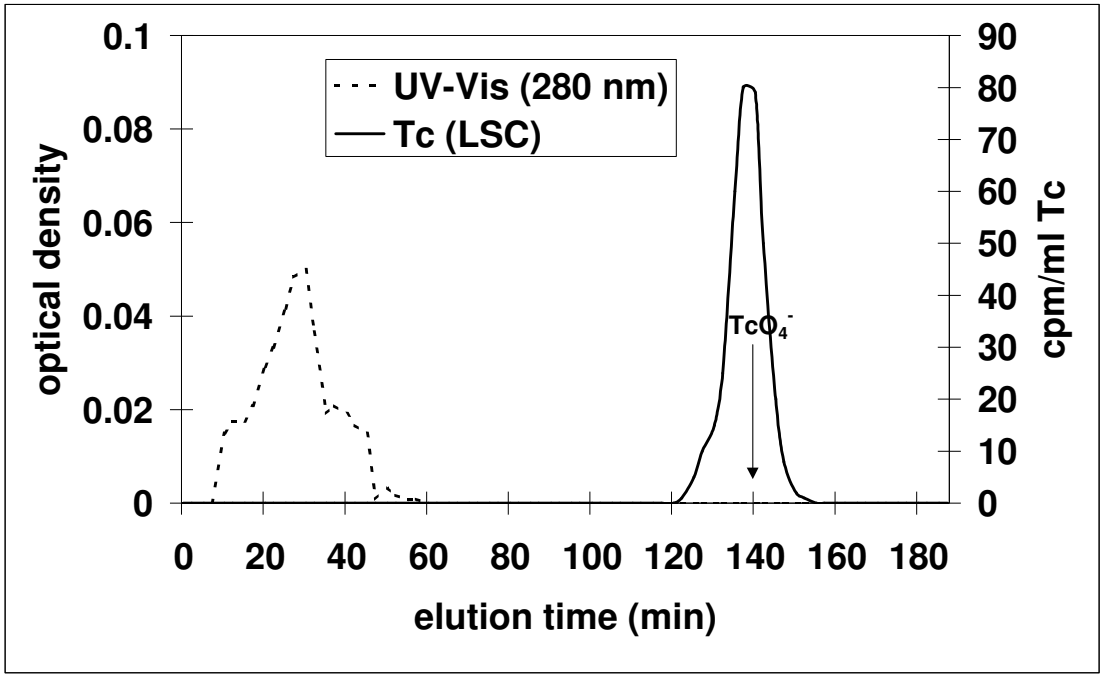

Figure 3-3. Gel permeation chromatogram of the supernatant solution of a system containing Tc and Gorleben humic substances after 26 days contact time. The elution time for pertechnetate is indicated. pH = 8.1, Eh = -125 mV.

3.3.3 The behaviour of pertechnetate in the presence of humic substances and a reducing solid phase

Batch systems as a function of time were studied for four different iron(II)-containing surfaces (synthetic iron(II)sulphide, pyrite, magnetite and siderite) in the presence of natural Gorleben groundwater and for an initial pertechnetate concentration of 2.5×10^{-6} mol/L.

The change of total Tc concentration in solution with time is shown in figure 3-4 for all systems. The pH was equal to 9 in all systems and redox potentials were all well below zero (around -150 à -250 mV); hence, favourable conditions for pertechnetate reduction were present. In all experiments, the humic substance content in the supernatant solution was around 164 mg/L, indicating that no substantial amount of humic substances was sorbed on the solid phases.

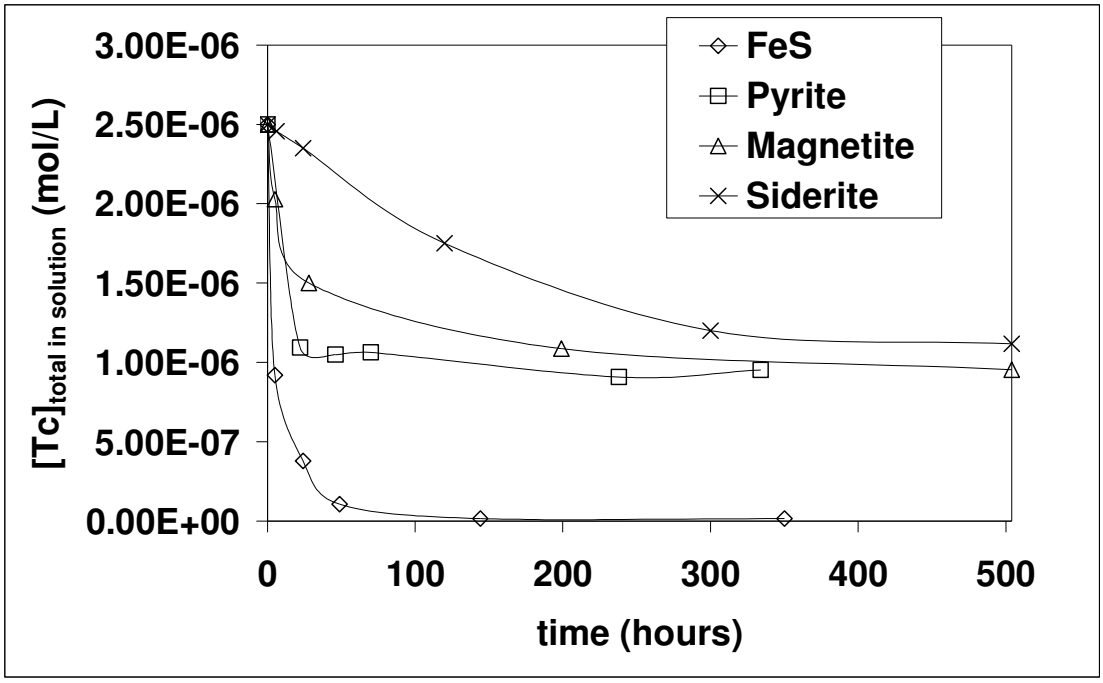

Figure 3-4. Total Tc concentration in the supernatant solution (mol/L) versus time (hours) for 4 different batch experiments: reduction of pertechnetate in presence of synthetic iron(II)sulphide (FeS) (◊), pyrite (□), magnetite (Δ), siderite (×) and natural Gorleben groundwater with $[Tc]_{initial} = 2.5\times10^{-6}$ mol/L.

In presence of humic substances the reduction kinetics is in general much slower than in absence of humic substances (table 3-2). It takes between 2 to 14 days for the humic containing synthetic reducing systems to reach equilibrium. The decreased Tc concentration in solution is interpreted as a reduction of pertechnetate to Tc species with a lower solubility, most probably the amorphous precipitate $TcO_2.nH_2O$.

In experiments where the pre-equilibrium time span of the reducing solid phases (magnetite, pyrite or FeS) and the natural Gorleben groundwater before addition of pertechnetate was varied between 3 and 50 days, no enhanced kinetics for pertechnetate reduction nor differences in the equilibrium solubility (data not shown).

The pertechnetate reduction for other types of humics was studied with 50 mg Fe_3O_4 and respectively Kranichsee HA, Kranichsee FA and Aldrich HA. Figure 3-5 shows the variation of total Tc in the supernatant solution with time for the three different solutions. In the systems containing the Kranichsee humic substances, the pH varied between 6.5 and 7. Redox potentials were all well below zero (around -50 à -150 mV). The systems containing Aldrich humic acids had pH and Eh values respectively equal to 9 and -150 mV. Hence, in all systems, favourable conditions for pertechnetate reduction were obtained.

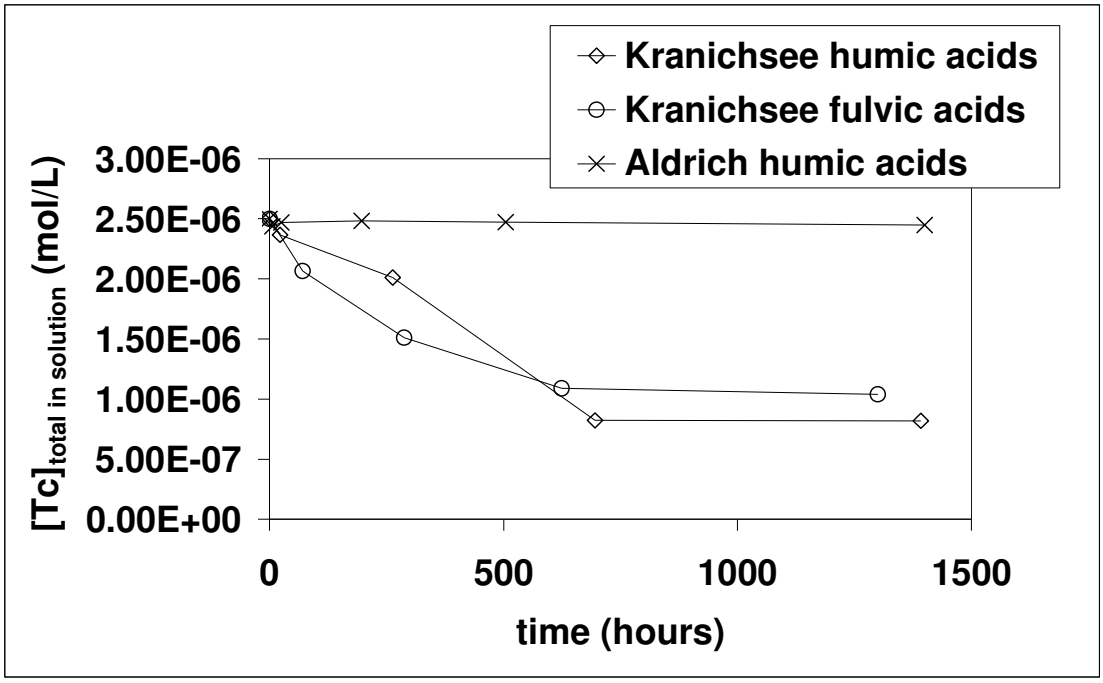

Figure 3-5. Total Tc concentration in supernatant solution (mol/L) versus time (hours) for three different batch experiments: reduction of pertechnetate in presence of magnetite and Kranichsee humic acids (◊), Kranichsee fulvic acids (o) and Aldrich humic acids (×).

The technetium reduction kinetics in presence of Kranichsee humic or - fulvic acid solutions and Magnetite were comparable to results obtained with natural Gorleben groundwater and Magnetite, indicating that the decreased Tc concentration in solution can be interpreted as a reduction to $TcO_2.nH_2O$. In the presence of Aldrich humic acids and Magnetite on the contrary, pertechnetate was not reduced as was proven by GPC. No sound explanation was found for this unexpected behaviour.

The observed Tc solubility after pertechnetate reduction with the aid of pyrite, magnetite and siderite, and in the presence of Gorleben HS (pyrite, magnetite, siderite systems in figure 3-4) and Kranichsee HS (magnetite system in figure 3-5) equals about 10^{-6} mol/L, which is a factor 100 higher compared with the results when no humic substances were present. The increased solubility is interpreted as an association between reduced Tc species and dissolved humic substances. The association between Tc and humic substances was already proven before by Stalmans (1986) using GPC. Therefore, gel permeation chromatography taken on supernatant solutions at equilibrium are also performed on the present systems. Figure 3-6 shows an example of such a chromatogram, where it is demonstrated that complete reduction occurred and that Tc and HS are eluted together. For all experiments in which pertechnetate was reduced in presence of a reducing solid phase combined with humic substances, comparable chromatograms were obtained for the equilibrium supernatant solutions.

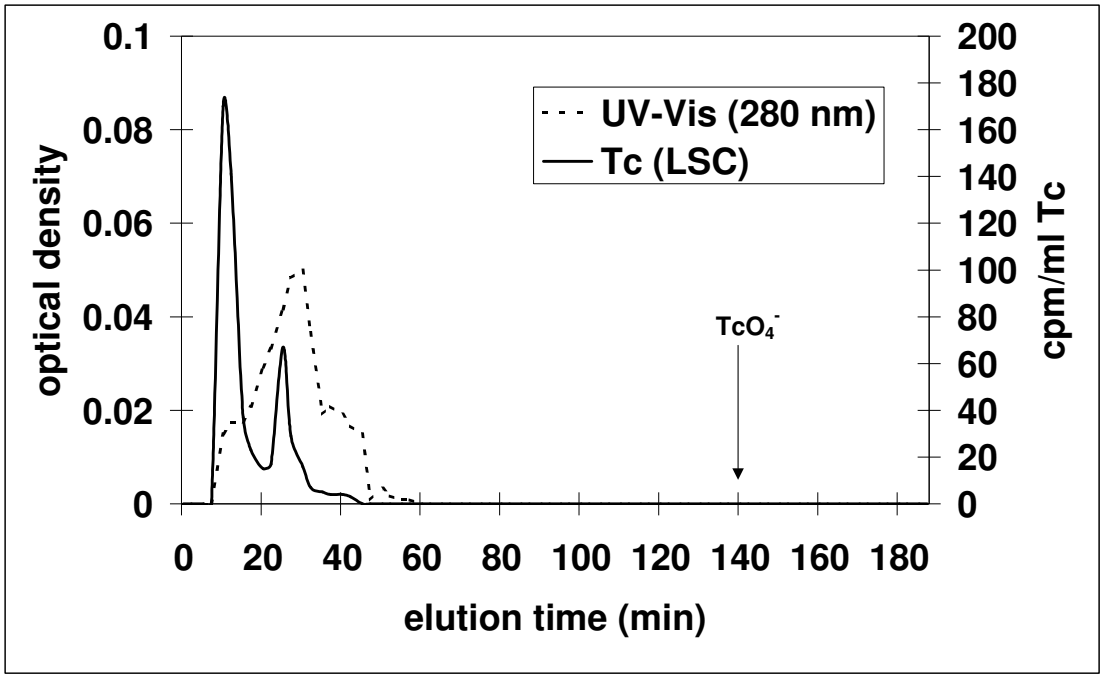

Figure 3-6. Gel permeation chromatogram of the supernatant solution at equilibrium of a system where pertechnetate was reduced in presence Gorleben humic substances and magnetite. The elution time for pertechnetate is indicated. pH = 8.5, Eh = -250 mV.

The above results demonstrate that the three surfaces - pyrite, siderite and magnetite - behave similarly with respect to the reduction of pertechnetate. Only the results in presence of synthetic iron(II)sulphide deviate from those obtained in presence of the three other surfaces. In the case of FeS a lower free Tc level and a significantly lower Tc solubility was observed. Probably an amorphous Tc-sulphide is formed with a low solubility. Allen *et al.* (1997) and Lee and Bondietti (1983) observed TcS_2-like phases via respectively EXAFS and XRD spectroscopic techniques in the presence of FeS minerals (but these experiments were performed in the absence of humic substances).

It was shown that pertechnetate reduction in the presence of humic substances only occurs in the presence of a reducing surface. The aim of the following experiments was therefore to verify whether these findings also apply for the case of Gorleben sand suspensions in Gorleben groundwater. It was shown in literature that the Gorleben sand/Gorleben groundwater system as a whole becomes gradually reducing with time and was able to reduce Np(V) to Np(IV) (Artinger *et al.*, 1998a).

In order to find suitable conditions for pertechnetate reduction in a Gorleben sand/Gorleben groundwater system, experiments were conducted in which the time of pre-equilibrium of the Gorleben sand (10 g) with Gorleben groundwater (19 ml) was varied before the addition of pertechnetate (1 ml 5×10^{-5} mol/L). In all systems the total Tc concentration in solution was determined after one day of reaction.

In contrast with synthetic systems, a significant dependence on the pre-equilibrium time span was noticeable, as is shown in figure 3-7. The initial Tc concentration in solution in all studied systems was equal to 2.5×10^{-6} mol/L. When the pre-equilibrium time span was increased, a lowering of total Tc in solution was observed. However,

after a certain threshold time span, the measured Tc concentration after one day of reaction, remained constant at 10^{-6} mol/L irrespective of the pre-equilibrium time span.

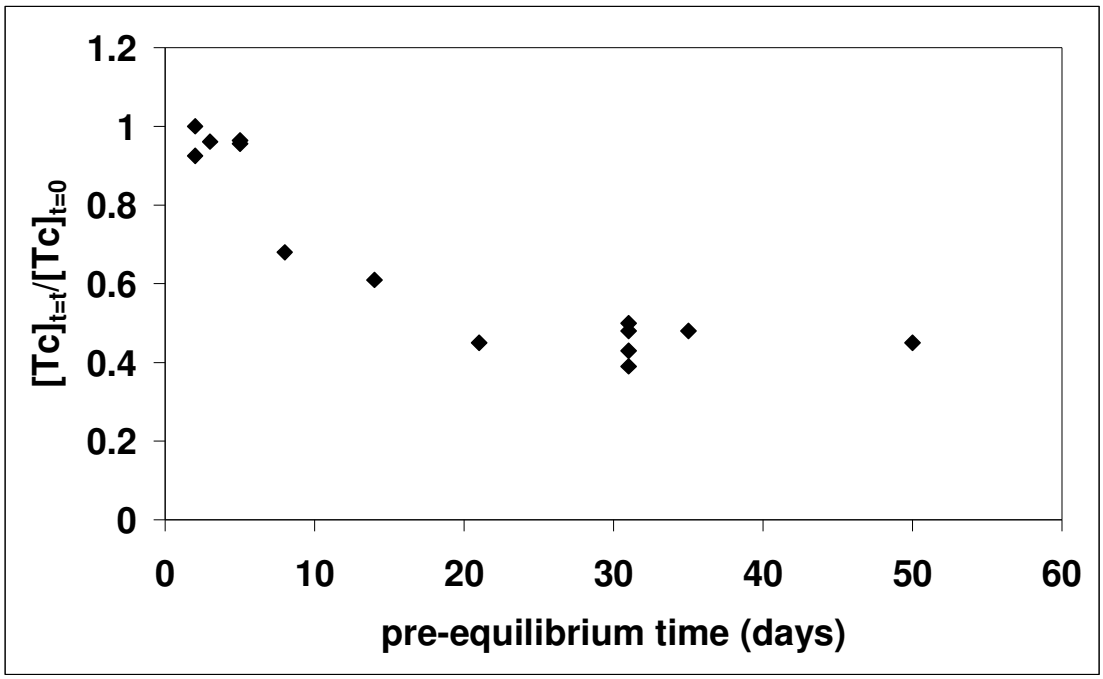

Figure 3-7. The Tc concentration ratio in solution after one day of reaction as a function of the pre-equilibrium time span (days) of the Gorleben sand/Gorleben groundwater suspension before addition of pertechnetate.

In the next series of experiments, these findings were studied in more detail by following the reaction of Tc as a function of time in 2 systems with respectively a short and long pre-equilibrium time span (figure 3-8). The following conclusions can be drawn:

- Systems with a long pre-equilibrium period (> 21 days) show immediate reduction to a constant soluble Tc concentration in time. The enhanced Tc solubilities in the supernatant solution are double the Tc concentration found in the (previously mentioned) synthetic systems (2×10^{-6} versus 10^{-6} mol/L).
- Systems with a short pre-equilibrium time (4 days) do not lead to the expected equilibrium on the basis of the results with long pre-equilibrium times, despite the fact that the total time span of the experiment (1500 hours) exceeded the long pre-equilibrium period of 336 hours. Indeed the total Tc concentration decreased with time, but no equilibrium was reached. Via gel permeation chromatography it was shown that even after 1000 hours of reaction, still pertechnetate was left in the system, in contrast with the systems with a long pre-equilibrium time, where already in the first analysis point no pertechnetate was found left in solution or at least the concentration of pertechnetate was below detection limit (10^{-9} mol/L).

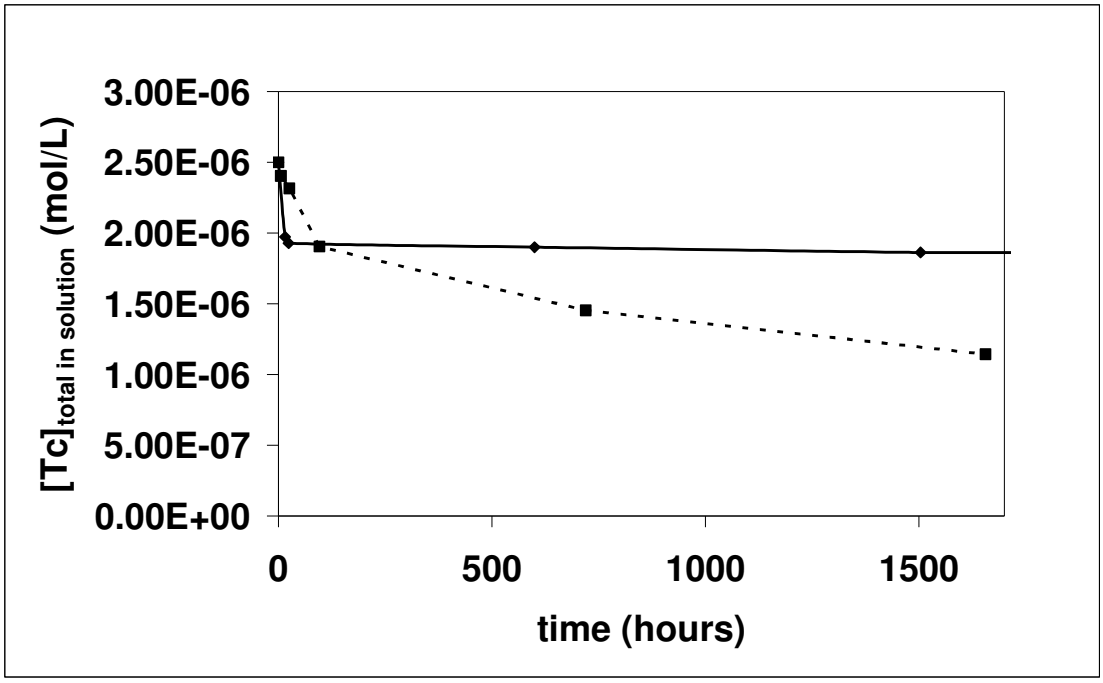

Figure 3-8. The solubility of technetium (mol/L) as a function of time (hours) for lab scale natural systems with a long (46 days) pre-equilibrium period (—) or short (3 days) pre-equilibrium period (---) before addition of pertechnetate.

From these experiments, it can be concluded that in order to have suitable reducing conditions in the Gorleben sand/Gorleben groundwater suspensions, that probably a time depending reaction is occurring within these systems. The sand was sampled at the (sub)surface of the Gorleben site (see chapter 2); hence, the reducing properties of the sand itself are minimal. However, when original Gorleben groundwater (always kept under nitrogen atmosphere) is brought in contact with the sand, after a certain period of time, the systems as a whole became reducing enough for pertechnetate reduction. A sound explanation for this behaviour is not yet found.

Therefore, it is recommended that to obtain a suitable reducing environment for the reduction of pertechnetate and consecutive association of reduced Tc species with dissolved humic substances, to apply a pre-equilibrium period of at least 3 weeks for the Gorleben sand/Gorleben groundwater suspensions, before the addition of pertechnetate. This recommendation corresponds best with the mimicking of the *in situ* situation.

3.3.4 Reducing components within a lab scale natural system

After centrifugation of the lab scale natural systems, three different phases could be distinguished in the polypropylene vials: 1) at the bottom, the light-coloured sand, 2) a second layer consisting of a black pasta of organic matter and 3) the liquid phase (containing dissolved humic substances). After separation and (qualitatively) Tc monitoring of the different layers, it was noticed that most (> 50%) of the technetium was associated with the second layer. This "black pasta" originates from a re-precipitation after solubilisation (or dispersion) of the charcoal particles.

In the next experiments, the particular role of the charcoal particles was investigated: in 3 different systems: 1) charcoal particles and synthetic groundwater, 2) original Gorleben sand and synthetic groundwater and, 3) charcoal particles and natural Gorleben groundwater. After a pre-equilibrium period of one month, a pertechnetate solution was added (resulting in an initial Tc concentration of 2.5×10^{-6} mol/L). The pH was equal to 8.5 in all systems and redox potentials were observed all well below zero (between -50 and -200 mV); hence, favourable conditions for pertechnetate reduction were present. Figure 3-9 shows the solubility of technetium as a function of time, within the different investigated systems.

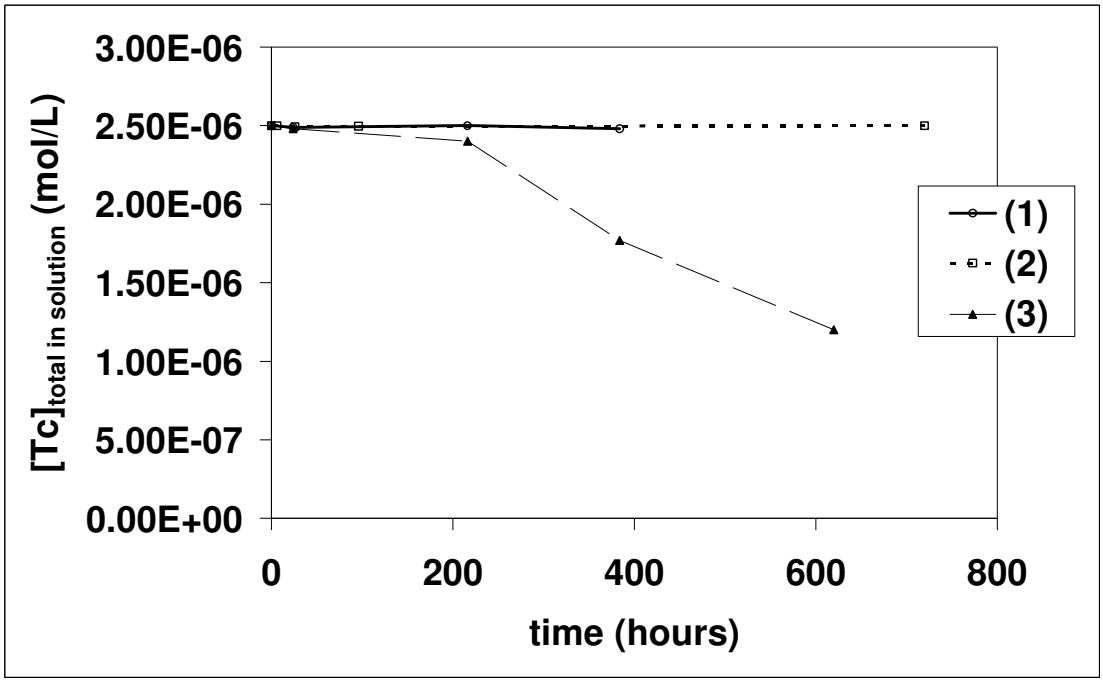

Figure 3-9. The solubility of technetium as a function of time in the following systems: (1) charcoal particles and synthetic groundwater, (2) Gorleben sand and synthetic groundwater, and (3) charcoal particles and natural Gorleben groundwater.

From this figure, it is obvious that neither the charcoal particles nor the Gorleben sand in synthetic groundwater are able to reduce pertechnetate. The GPC results for these cases show an (almost) complete recovery of all technetium as pertechnetate. Only the system containing both the charcoal particles and the natural Gorleben groundwater are able to slowly reduce the pertechnetate (as was verified by GPC).

In these systems, it was again observed that after centrifugation most insoluble Tc was associated with the black pasta (containing the charcoal particles). As it is demonstrated in the previous sections that the (presumably) three-electron reduction of pertechnetate only occurs near a suitable reducing surface and not in solution by the humic substances alone, it seems plausible that such a reducing surface is present or at least is (slowly) formed "near" the charcoal particles when contacting them with the natural Gorleben groundwater.

The reduction kinetics of pertechnetate in the charcoal/natural Gorleben groundwater systems is much slower compared to the lab scale natural systems, although, the systems containing the charcoal particles were pre-equilibrated for one month. The experiments with the charcoal particles were only performed with (rather) large charcoal particles and the fact that within the sand also numerous very small "black points" are visible, can easily explain the better reactivity for pertechnetate reduction of the lab scale natural systems.

3.3.5 The reverse equilibrium approach

Figure 3-10 shows the results of the "reverse equilibrium approach", when natural Gorleben water was added to the precipitated (or sorbed) Tc species on a magnetite phase and the total Tc concentration was followed as a function of time.

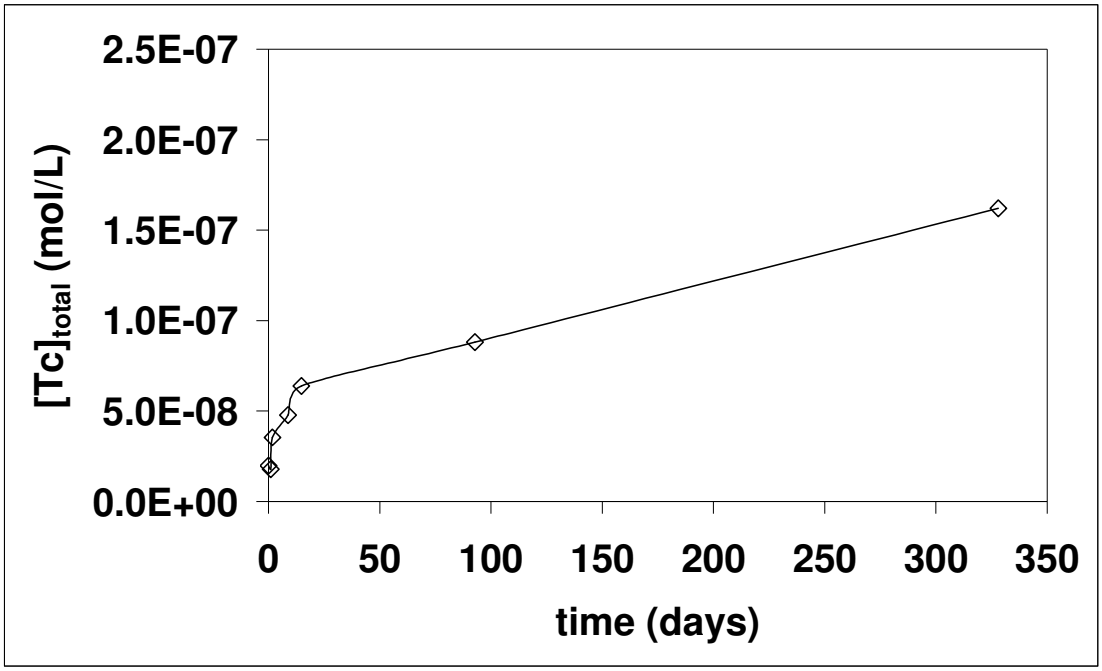

Figure 3-10. Total Tc concentration in solution (mol/L) versus time (days) upon contacting natural Gorleben Groundwater with a previously prepared Tc-precipitate. pH = 8.5.

Figure 3-10 shows a slowly increasing solubility of Tc with time. Gel permeation chromatography on the supernatant demonstrated the formation of Tc-HS species. However, the Tc solubilities observed in the previous systems (starting from pertechnetate) was 10^{-6} mol/L whereas the solubility observed in the last point of the present systems (starting from the precipitate) was only 1.5×10^{-7} mol/L. It seems therefore that resolubilisation is a very slow process and equilibrium was not reached in this experiment.

3.4 Conclusions

In this chapter, suitable environments for pertechnetate reduction both in the absence and presence of humic substances were determined. The presence of a reducing solid phase was absolutely necessary for pertechnetate reduction in both cases (absence and presence of humic substances). Pyrite and magnetite are suitable electron donors for this purpose and are recommended for further use for pertechnetate reduction both in the presence and absence of humic substances in synthetic reducing systems. In addition, sufficiently pre-equilibrated lab scale natural systems will provide also a suitable reducing environment for pertechnetate reduction. In these lab scale natural systems, the presence of charcoal particles within the sand were identified as necessary for pertechnetate reduction.

The measured Tc solubility in the absence of humic substances was in agreement with the range of solubilities found in literature for $TcO_2.nH_2O$. In the presence of humic substances, enhanced solubilitiy levels are observed. This enhanced solubility is interpreted as a formation of Tc-humic substance species, which were verified by gel permeation chromatography. The valence state and speciation of Tc within these humic substances is unknown and is studied hereafter.

CHAPTER 4

EVIDENCE FOR THE EXISTENCE OF Tc(IV) - HUMIC SUBSTANCE SPECIES BY X-RAY ABSORPTION NEAR - EDGE SPECTROSCOPY

4.1 Introduction

In the previous chapter, suitable reducing environments were determined for a full and quick reduction of pertechnetate in the presence and absence of humic substances. Systems containing different reducing solid phases (pyrite, magnetite, ironsulphide and Gorleben sand) on the one hand and natural Gorleben groundwater, which contains a high amount of humic substances, on the other hand, were found able to ensure a sufficient reducing environment for the reduction of pertechnetate. In the presence of humic substances, Tc concentrations were observed which exceeded the solubility in the absence of humic substances a 100 fold. This enhanced solubility was interpreted as an association between reduced Tc species and dissolved humic substances. Neither the valence state or the chemical environment of Tc within the humic substances was determined.

As also stated in Chapter 1, only few research groups investigated directly the interaction between reduced Tc species and humic substances. However, in most cases strong reducing agents such as Zn and thiourea were used to reduce the pertechnetate in the presence of humic substances and additionally the experiments were performed in a low pH range (Stalmans, 1986, Sekine *et al.*, 1993 and 1997, Röβler *et al.* 2000, Tkac *et al.*, 2000). Hence, it will be very difficult or impossible to extrapolate these results to *in situ* situations.

Stalmans (1986) proved the existence of Tc-humic substance species by gel permeation chromatography after reduction of pertechnetate in a Boom clay environment. The valence state of technetium within this species was unknown but was assumed to be +IV. On the other hand Sekine *et al.* (1993) concluded from an indirect measurement that in presence of humic acids, Tc(III) species are formed and associate with the humic acids. However these experiments were done at low pH (pH = 4). Speciation calculations with the CHESS speciation programme (using the EQ3/6 database), shows the Tc^{3+} species as the dominant species at pH=4, sufficiently low redox potential and in absence of humic substances (see chapter 1). At higher pH (higher than 4), Tc(IV) species are becoming more dominant. Hence, in neutral and alkaline environments, associations between Tc(IV) species and humic substances are more likely to occur, but experimental evidence is lacking.

The aim of the present chapter is to elucidate the valence state of reduced Tc in neutral to alkaline reducing environments, in the presence of humic substances. X-ray Absorption Near-Edge Spectroscopy (XANES) measurements were made to determine the valence state of Tc in solution and were combined with gel permeation chromatographic results and a so-called La-precipitation method[8] to determine chemically the reduced Tc species in solution. All measurements are made on very dilute supernatants relevant for natural conditions.

4.1 X-ray absorption spectroscopy: theoretical background

X-ray absorption spectroscopy is based on the fact that atoms in molecules can absorb X-rays. Generally, the proportion of X-rays absorbed (the absorption coefficient) will decrease as their energy increases, but at certain values of energy (specific to each element), a sudden increase in the amount of energy absorbed is observed (the absorption edge). These energies correspond to the ejection of an electron from the atom in question (i.e. when the energy of the incident X-rays is equal to the threshold ionisation energy). The ejected electron can be considered as a wave, travelling outwards from the central absorbing atom. For atoms either in a molecule or in a condensed phase, the presence of other atoms around the absorber causes oscillations in the absorption coefficient near the edge. These oscillations in the post edge region arise from the back-scattering of the emitted wave of neighbouring atoms and so the structure of the post edge region of the X-ray absorption spectrum is related to the radial distribution of atoms in the sample. Hence, by analysing this structure (the frequency and amplitude of the oscillations), information about the local environment of the absorbing element can be derived.

XAS does not require long-range order (*i.e.* crystalline samples) and can be performed on elements in amorphous solids, surface complexes, and aqueous species. Therefore XAS is extremely useful for our studies.

X-ray absorption spectroscopy is commonly divided into two spectral regions, the first is the X-ray absorption near edge structure (XANES) spectral region. The more distant region of the X-ray absorption spectrum is termed the extended X-ray absorption fine structure (EXAFS) region. This latter technique will be used in the next chapter.

XANES spectroscopy can be used as a method to determine the oxidation state and coordination environment of a certain element. XANES spectra are commonly compared to standards to determine which species or which valence state is present in an unknown sample. Once the different valence states are identified, their relative abundance is quantified using linear-combination fitting (or other curve-fitting algorithms) using XANES standards to reconstruct the experimental data. It is important to note that XANES is sensitive to bonding environment as well as oxidation state. Consequently, XANES is capable of discriminating species of similar formal oxidation state but different coordination. For example, Arsenic(III) oxide is easily differentiated from Arsenic(III) sulfide (Bostick and Fendorf, 2003a), and

[8] This newly developed so-called "La-precipitation method" will be studied *in extenso* in Chapter 7

octahedral Mo(VI) can be differentiated from tetrahedral Mo(VI) (Bostick and Fendorf, 2003b).

The oscillations in the post edge absorption coefficient are small compared to the absorption resulting form the electron ejection (ionisation), hence, a strong X-ray source is required, to produce features sufficiently intense to be analysed. Synchrotron X-ray sources meets this requirement: they produce X-ray radiation by accelerating in a circular path, pulses of electrons to a speed approaching that of light.

The XAS experiment involves placing a sample of the compound under investigation in the path of the X-ray beam, selecting an absorbing element and changing the X-rays incident on the sample so that it varies above and below the absorption edge of interest. This variation is done in a series of small steps; at each stage, the amount of X-rays before and after the sample is measured, so that the amount absorbed by the sample can be determined as a function of energy.

4.2 Experimental set-up

The geochemical behaviour of Tc in reducing conditions and its possible interaction with humic substances from the Gorleben sandy aquifer system (Germany) is studied. On the one hand, the natural situation was simplified by using different iron(II) containing solid phases (magnetite, pyrite and synthetic iron(II)sulphide) - necessary for the reduction of technetium-99 - dispersed in synthetic and natural Gorleben groundwater. On the other hand, a more relevant mimic of the natural condition was studied by using natural Gorleben sand pre-equilibrated in natural Gorleben groundwater.

Sample preparation

The reduction of pertechnetate was followed versus time by preparing sufficient duplicate samples as batch experiments. 100 mg of the selected minerals (magnetite, pyrite and ironsulphide) or 10 g of Gorleben Sand were weighted in polypropylene vials and 19 ml Synthetic Gorleben Water or original Gorleben groundwater (GoHy-2227) was added. After a pre-equilibration period (three days for the magnetite, pyrite, ironsulphide and 3 weeks for the Gorleben sand) 1 ml of a 99-TcO_4^- solution was added and the vials were shaken end-over-end for different time periods. The initial pertechnetate concentrations were 1.0×10^{-4} mol/L (Fe_3O_4 and FeS), 1.2×10^{-4} mol/L Tc (FeS_2) and 2.9×10^{-4} mol/L (FeS_2, Gorleben sand). The batch experiments were carried out at ambient temperature (22°C) in a controlled atmosphere glovebox flushed with a mixture of N_2 (95%) and H_2 (5%).

Speciation determination

To assess the speciation of Tc in solution, the samples were centrifuged (30 min, 39191×g) and the supernatant was analysed by various methods:

1) Total Tc in solution was measured by Liquid Scintillation Counting.
2) Gel permeation chromatography was used to qualitatively identify Tc species associated with humic substances in solution and free Tc species.
3) A method based on induced flocculation of organic matter and colloids with La^{3+} was used to separate and concentrate Tc species in solution. This method is called

the "La^{3+}-precipitation method" and is based on the observation that trivalent ions such as La^{3+}, Eu^{3+} and Al^{3+} are able to precipitate organic matter and colloids in solution. The method works according to the following procedure: 0.01 Equiv./L $La(NO_3)_3$ is added to an aliquot of the supernatant solution. The humic substances (and the associated Tc) precipitate during centrifugation (15 min, 39191×g) and a clear solution is obtained (absorbance equal to zero). The Tc concentration in the supernatant after La precipitation corresponds to the sum of the TcO_4^- (which was tested not to be flocculated with La^{3+}) and (part of the) dissolved free Tc species. The concentration of Tc which is found in the centrifugate after La^{3+} precipitation can correspond to Tc associated with humic substances or with inorganic colloids, or to finely dispersed Tc colloids or Tc precipitate, all of which co-precipitate with the flocculated material.

4) XANES measurements were performed on selected supernatants of the batch experiments (see table 4-2). A sample containing, 10^{-2} mol/L TcO_4^- was used as a reference (sample 1). From each of the selected batch systems, one supernatant was taken in the course of the reduction process and used for the XANES measurements. Small plastic vials (content: 0.7 ml) were filled with an aliquot of the selected supernatants and were sealed off and further placed in heat-sealed nitrogen-containing polyethylene bags to ensure containment during XANES data acquisition. All samples were transported in a nitrogen containing box. The technetium K-edge X-ray absorption spectra were collected at the Rossendorf beamline (ROBL) located at the bending-magnet port BM 20 at the European Synchrotron Radiation Facility (Grenoble, France). The monochromatic X-ray beam delivered to the sample positions is conditioned by two X-ray mirrors and a double-crystal monochromator (Si(111)) in between. Due to the very low Tc concentration, data were collected in fluorescence mode, using a quad-pixel Ge fluorescence detector. A minimum of 8 scans per sample was collected to improve data quality. All data were collected at ambient temperature. Molybdenum was used for energy calibration and was measured simultaneously with the samples.

4.3 Results and discussion

4.3.1 Pertechnetate reduction in absence of humic substances

For the three different surfaces (magnetite, pyrite and ironsulphide), the solubility of Tc in synthetic Gorleben groundwater is followed as a function of time. A gradual decrease in the total Tc solution concentration with time is observed in all systems. All systems reached constant Tc concentration levels after 10 weeks of equilibration. Table 4-1 gives an overview of the initial and final total Tc concentration in solution, measured after 31 weeks equilibration time.

Similarly as in the previous chapter, via gel permeation chromatography, it was possible to qualitatively separate the reduced Tc species from pertechnetate species. This is demonstrated in figure 4-1 (absence of humic substances): the first and second peak respectively corresponds to pertechnetate and reduced Tc species. But, it was not possible to quantitatively determine the relative amounts of the two species due to partial sorption of both Tc species on top of the column, resulting in a too low recovery (<15%). No Tc(VII) was detected by GPC in the final equilibrium solutions. The equilibrium Tc concentration ranged between 4.8×10^{-7} and 1.32×10^{-6} mol/L

(given in table 4-1). This decrease in Tc concentration in the supernatant solution after centrifugation is interpreted as a reduction of pertechnetate species to the much less soluble Tc(IV) species, most probably $TcO_2.nH_2O$. The found Tc solubility at equilibrium exceeds considerably the solubility concentration found in the previous chapter (~10^{-6} versus ~10^{-8} mol/L).

	pH	$[Tc]_{initial}$ (mol/L)	$[Tc]_{final}$ (mol/L)	$[Tc]_{afterLaprecipitation}$ (mol/L)
pyrite	9.2	2.9×10^{-4}	1.32×10^{-6}	4.1×10^{-8}
pyrite	9.2	1.2×10^{-4}	4.80×10^{-7}	9.3×10^{-9}
magnetite	9	1.0×10^{-4}	1.11×10^{-6}	2.4×10^{-8}
iron(II)sulphide	8.7	1.0×10^{-4}	8.36×10^{-7}	1.6×10^{-8}

Table 4-1. Tc concentrations in the initial solution, the final supernatant solution and the supernatant solution after La precipitation in systems containing synthetic Gorleben groundwater in presence of three different surfaces (pyrite, magnetite and iron(II)sulphide) after 31 weeks of equilibrium time.

Upon applying the La^{3+}-precipitation method to the above systems, it was observed that Tc could be precipitated for more than 97% as is shown by comparing the data given in the 4th ($[Tc]_{final}$) and 5th ($[Tc]_{afterLaprecipitation}$) column in table 4-1. It was verified that pertechnetate could not be precipitated with La^{3+}, therefore, the Tc species in solution must be in a lower oxidation state than +7. The final Tc concentration (4th column) observed in the supernatant solution after centrifugation (30 min, 39191×g) are ascribed to the formation (from supersaturation) of Tc(IV) colloidal species or polynuclear Tc(IV) species. And these colloidal Tc species (co-)precipitate with La^{3+}-hydroxide formation. It is important to notice that the final amount of these colloidal Tc(IV) species was always less than 1 % of the total initial Tc concentration in the studied systems.

It is apparent that after reduction of pertechnetate, the colloidal Tc species in solution are related to the initial pertechnetate concentration, and increase with increasing initial pertechnetate concentration. This phenomenon will be further explored in Chapter 6.

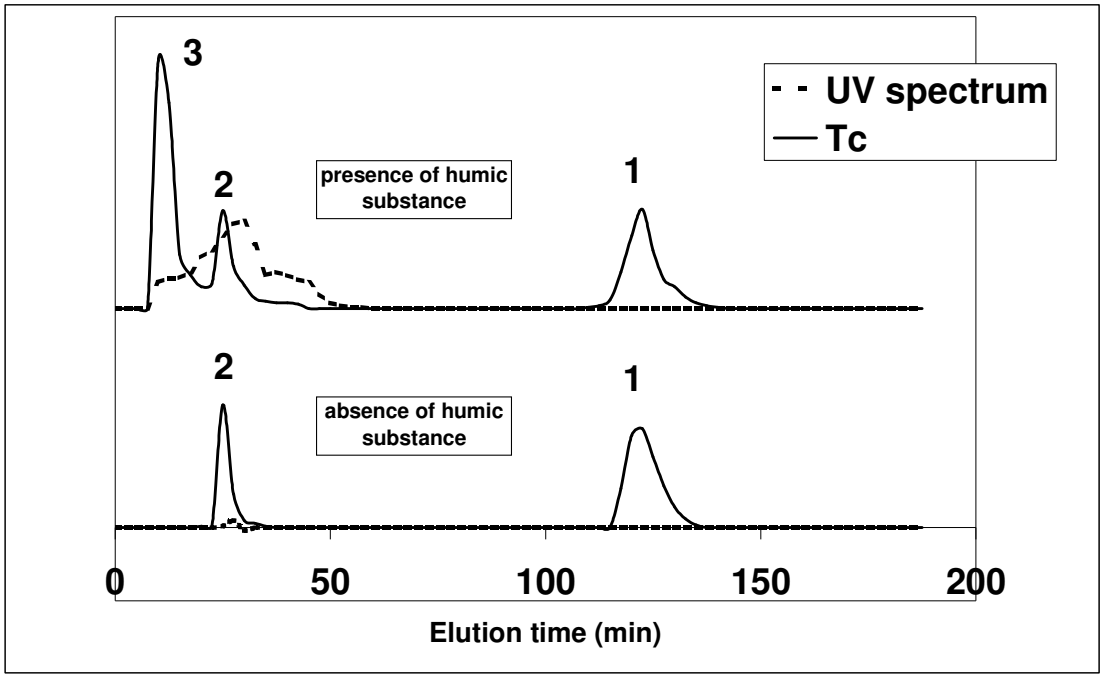

Figure 4-1. Gel permeation chromatograms of solutions containing different Tc species: pertechnetate (peak 1), reduced Tc species (peak 2) and reduced Tc species in presence of humic substances (peak 3). Supernatant solutions originating from systems where Tc was reduced in presence of pyrite in synthetic (absence of humic substances) and natural Gorleben groundwater (presence of humic substances).

4.3.2 Pertechnetate reduction in presence of humic substances

Figure 4-2 shows the results of the interaction of pertechnetate added to the four different reducing solid phases but now in presence of humic substances. Equilibrium is reached in all cases. Concentrations in solution in the range of 4×10^{-5} - 10^{-4} mol/L are measured after 31 weeks equilibration time. Thus, the observed solubility is much higher (factor 100) compared with the previous results (when no humic substances were present). The differences between the two systems are only the absence versus presence of humic substances and since TcO_4^- is known not to interact with humic substances, this increased solubility is (again) interpreted as an association between reduced Tc species and the dissolved humic substances.

The formation of Tc species associated with humic substances compared to the reference systems without organic matter was also qualitatively verified by gel permeation chromatography. The chromatogram (figure 4-1, presence of humic substances) shows now a third Tc peak at the exact same place where high molecular humic substances elute. It was again not possible to quantitatively determine the relative amounts of the different species due to technetium and humic substance retention on the column. But also in these systems, after 31 weeks, no Tc(VII) could be detected in the supernatant solution.

Figure 4-2 also shows that the amount of Tc, which could be precipitated with La^{3+}, gradually increases with time up to a given equilibrium Tc solution concentration. At

equilibrium, La^{3+} could precipitate more than 99% of all Tc in solution. This means that Tc is present as Tc(IV) inorganic colloids and/or Tc(IV) organic colloids, both of which are precipitated out. Thus less than 1% of the total Tc in solution was present as either TcO_4^- (not detectable by GPC) or Tc(IV) species not associated with inorganic and organic colloids or not co-precipitated with inorganic and organic colloids in solution.

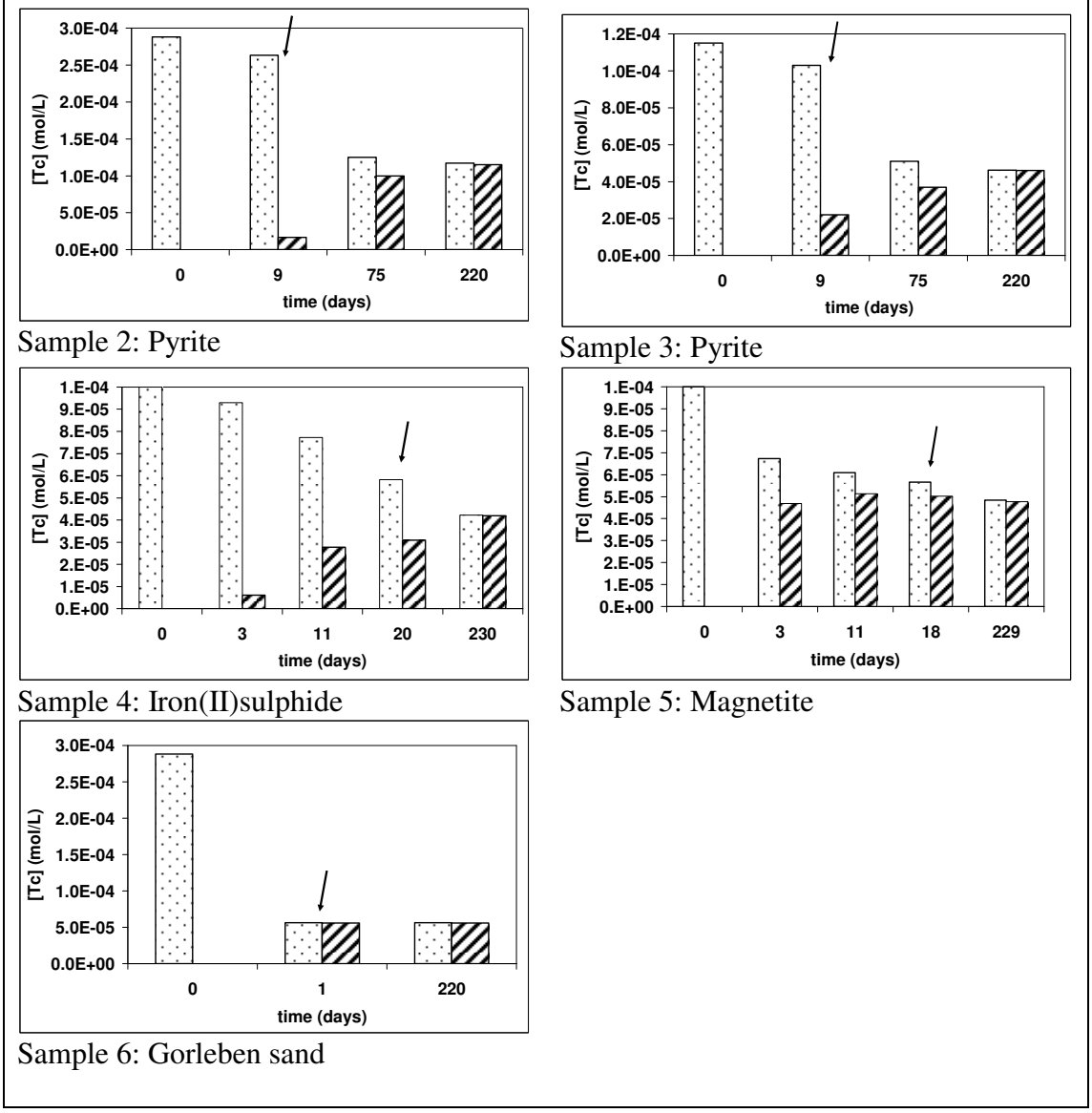

Figure 4-2. Tc speciation as a function of time in Gorleben groundwater in presence of different (reducing) solid phases. The total concentration of Tc in solution (left dotted block) and the amount of Tc associated with humic substances (right shaded block) is given in mol/L. The arrows indicate systems used in the XANES measurements.

The previous observations clearly demonstrate again that in the presence of humic substances, a dramatic increase in Tc solubility is found in reducing conditions (neutral to alkaline pH) compared to the absence of humic substances, and that nearly

all (99% from La precipitation) Tc species in solution are present in a reduced state, either as Tc(IV) colloids or as Tc associated with the dissolved humic substances (from GPC). However the valence state of the Tc in the Tc-humic substance associates is still unknown and is further determined by XANES.

4.3.3 XANES measurements

Samples used for the XANES measurements were taken in the course of the reduction process and are indicated in figure 4-2. The composition of the samples used for the XANES measurements is given in table 4-2. The individual reaction conditions (pH, total initial pertechnetate concentration and reaction time) as well as the final total Tc concentration and Tc concentration after La^{3+} precipitation of the supernatant solution are given. A series of samples with varying pertechnetate and reduced Tc concentrations was thus analysed by XANES. A reference sample containing 10^{-2} mol/L pertechnetate (sample 1) was also measured.

sample N°	solid	time (days) [a]	TcO_4^- start conc. (mol/L)	[Tc] (mol/L) [b]	[$Tc_{afterLa\ precipitation}$] (mol/L) [c]	pH
1	-	-	-	10^{-2}	-	7
2	pyrite	9	$2.9x10^{-4}$	$2.63x10^{-4}$	$2.46x10^{-4}$	8.5
3	pyrite	9	$1.2x10^{-4}$	$1.03x10^{-4}$	$8.09x10^{-5}$	8.5
4	ironsulphide	20	$1.0x10^{-4}$	$5.83x10^{-5}$	$2.73x10^{-5}$	8.7
5	magnetite	18	$1.0x10^{-4}$	$5.66x10^{-5}$	$6.40x10^{-6}$	8.6
6	Gorleben sand	1	$2.9x10^{-4}$	$5.65x10^{-5}$	$4.08x10^{-7}$	8.1

Table 4-2. Overview of the different samples used for XANES measurements.
[a] Reaction time between Tc, solid phase and humic substances before analysis
[b] Concentration of Tc in supernatant solution
[c] Concentration of Tc in supernatant solution after La precipitation

The raw data were pre-edge subtracted and further smoothed with spline estimation using Savitzky-Golay splines (with nurbs) and normalised at an energy level of 21111 eV (see figure 4-3). At this level, the absorption values are not longer supposed to be influenced by the existence of other atoms around the central Tc atom. Figure 4-3 shows the normalised XANES spectra for the six samples indicated in table 4-2.

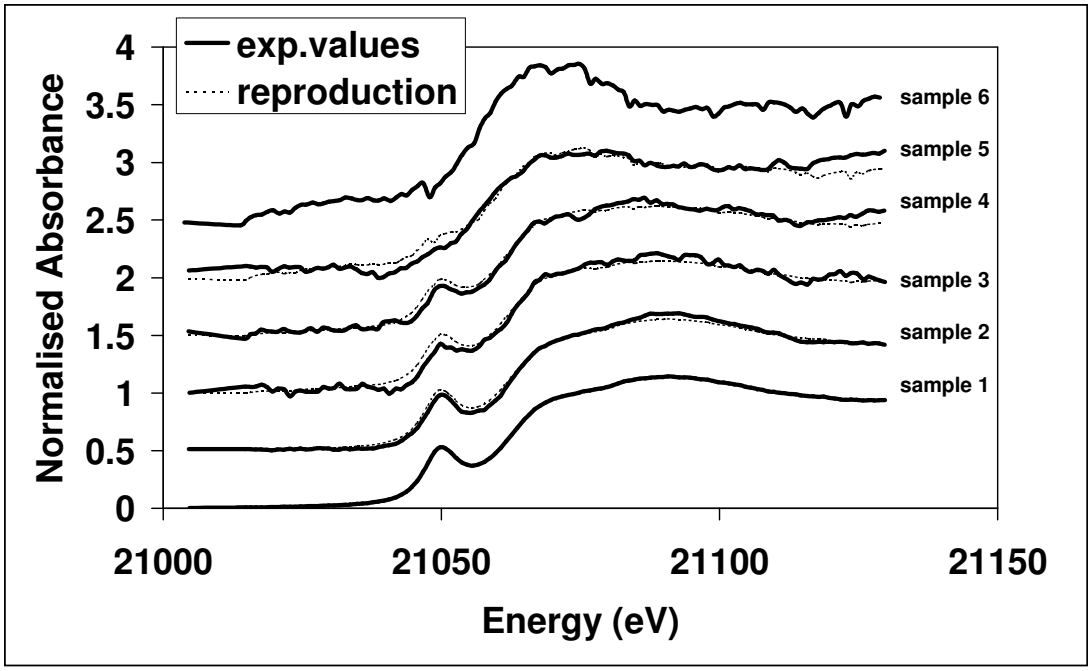

Figure 4-3. XANES spectra (exp. values) of Tc in solution for the six samples described in table 4-2. Calculated spectra (reproduction) for sample 2 to 5 were obtained from linear combinations of sample 1 and 6.

The observed XANES spectrum of pertechnetate is shown in figure 4-3 (sample 1) and agrees with published spectra (Almahamid *et al.*, 1995, Allen *et al.*, 1997). Typically, XANES spectra for pertechnetate always show 2 peaks. The first and small peak (so-called pre-edge absorption peak (Allen *et al.*, 1997) is due to a "forbidden" 1s → 4d transition, but is frequently observed due to p orbital mixing with the final d state. The first inflection point of the pre-edge absorption peak for this reference sample 1 was found at 21047 eV.

Due to the non-centrosymmetric, tetrahedral pertechnetate anions, the aforementioned forbidden transition becomes more allowed. However, when pertechnetate is reduced to lower valence states, the formed species are no more in a tetrahedral geometry and hence, the pre-adsorption edge disappears (Allen *et al.*, 1997). Therefore the presence of the first peak at 21047 eV in a spectrum from a sample containing technetium-99 is typical for the presence of pertechnetate in this sample.

The Tc concentrations in samples 2 to 6 (see table 4-1) were extremely low for X-ray absorption spectroscopy. Nevertheless, the obtained spectra could all be well analysed. Edge positions were determined using the first-derivative method. In sample 6 the pertechnetate signature has completely vanished and an edge shift of 7.02 eV occurs. Almahamid *et al.* (1995) found also an edge shift of around 7 eV corresponding to a reduction of Tc(VII) to Tc(IV). The Tc-species in sample 6 can therefore be interpreted as Tc(IV) species. According to the La^{3+}-precipitation method result for sample 6, more than 99% of the technetium present in solution is precipitated with the humic substances (see table 4-1). Hence, it can be concluded from the XANES measurement and the previously mentioned results on pertechnetate reduction in absence and in presence of humic substances, that the overwhelming amount of Tc species in the humic rich supernatant solution are Tc(IV)-humic

substance species. The exact nature of these Tc(IV) species is unknown. It may be monomeric TcO^{2+}, $TcO(OH)_2$ or even polynuclear or colloidal Tc(IV) species, but experimental evidence is lacking. Maes *et al.* (2003), proposed a hydrophobic sorption mechanism between monomeric and dimeric Tc(IV) ($(TcO(OH)_2)_n$, n = 1, 2) species and humic substances. The nature of Tc(IV)-humic substance species will be studied in the next chapter by EXAFS spectroscopy.

The other 4 samples show the main features present in both samples 1 and 6. Indeed: 1) the main absorption edge lies in between sample 1 and 6, and 2) the pre-edge absorption peak is decreasing compared with sample 1. Assuming that only Tc(IV) species interact with humic substances and that unbound Tc left in solution is mainly unreduced pertechnetate, the spectra of samples 2 to 5 were analysed as a binary mixture of sample 1 and 6. The position of the main absorption edge has been taken as most important feature. Spectra from sample 2 to 5 were fitted to obtain the correct main absorption edge, by combining spectra 1 and 6 in given amounts, independent of each other. The error on the fitted spectrum is calculated as the difference of the sum of the two relative amounts from 100. The results are shown in table 4-3 and can be compared with the percentage $Tc(IV)_{Laprecipitation}$ calculated from the Tc speciation measured by the La^{3+}-precipitation method (given in table 4-2). The percentage Tc(IV) determined by XANES in sample 2 till 5 is smaller than the percentage $Tc(IV)_{Laprecipitation}$ determined by chemical methods. The reason is at present unknown. At first sight slow oxidation during transport or measurement could explain the smaller values measured by XANES. However precautions were taken to avoid oxidation during transport (nitrogen container) and during measuring time (sealed nitrogen containing polyethylene bags surrounded the sealed sample vials).

sample	Tc(VII) % [a]	Tc(IV) % [a]	Error	$Tc_{La\ precipitation}$ % [b]
1	100	0	0	0
2	99.85	0.01	0.14	6.38
3	89.20	13.00	-2.20	21.46
4	81.15	19.50	-0.65	53.17
5	41.02	52.44	6.54	88.69
6	0	100	0	99.29

Table 4-3. Comparison of the XANES - and chemical speciation results.
[a] relative amount as determined by XANES
[b] amount of precipitated Tc species as determined by La-precipitation method

4.4 Conclusions

In the absence of humic substances, pertechnetate was reduced in synthetic reducing conditions. At equilibrium enhanced Tc solubilities, compared to the results of the previous chapter, were observed. These enhanced Tc concentrations were ascribed to the formation of colloidal or polynuclear Tc species. These colloidal or polynuclear Tc species could be excluded from solution by (co-)precipitation with La^{3+}-hydroxides. It is apparent that the amount of colloidal Tc species formed after reduction of pertechnetate is related to the initially added pertechnetate concentration in the system.

Secondly, it was demonstrated for the first time by XANES spectroscopy of the humic substance containing supernatant solutions, that after pertechnetate reduction, Tc(IV) species were formed in such systems. Gel permation chromatography indicated an association between these Tc(IV) species and the humic substances. Therefore, the existence of Tc(IV)-humic substance species was proven. The exact nature of these Tc(IV) species within the humic substances is unknown.

In different supernatant solutions containing a mixture of Tc(VII) and Tc(IV) species, their relative abundance was determined, by comparing the experimental XANES spectra with theoretical spectra of known mixtures of the Tc(VII) and Tc(IV) species. The Tc-humic substance species could also be precipitated using the La-precipitation method. Because, La^{3+} does not interact with pertechnetate, the relative distribution of Tc(VII) and Tc(IV) in the supernatant solution could also chemically be determined and compared with the results obtained by XANES spectroscopy. The percentage Tc(IV) determined by XANES is smaller than the percentage Tc(IV) determined by La-precipitation. The reason for this behaviour is unknown, but slow oxidation during transport and XANES measurements could have occurred.

CHAPTER 5

EVIDENCE FOR THE FORMATION OF TECHNETIUM COLLOIDS IN HUMIC SUBSTANCES BY X-RAY ABSORPTION SPECTROSCOPY

5.1 Introduction

In the previous chapter, it was demonstrated for the first time by XANES spectroscopy of the humic substance containing supernatant solutions, that after pertechnetate reduction, Tc(IV) species were formed in such systems. Gel permeation chromatography indicated an association between these Tc(IV) species and the humic substances. Therefore, the existence of Tc(IV)-humic substance species was proven. The exact nature of these Tc(IV) species within the humic substances is, however, unknown.

Therefore, the overall objective of this chapter is, to obtain straightforward spectroscopic evidence on the redox state and chemical environment of technetium-99 in a selected series of samples, via X-ray absorption spectroscopy (XAS). In this chapter, XANES spectroscopy (see also chapter 4) will be used to verify the existence of Tc(IV) species in all samples and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy will be used to determine the chemical environment of technetium.

5.2 EXAFS methodology

An introduction to X-ray absorption spectroscopy is already given in chapter 4, therefore in this section, only some general aspects of EXAFS are described. The extended X-ray absorption fine structure (EXAFS) region spans the range ~20 - 1200 eV past the edge and can be used to determine the identity of near-neighbour atoms (Z±2-6), their coordination numbers (N±20%), and bond lengths (R±0.01 Å). The Fourier transform (FT) of the EXAFS structure results in a radial distribution function of the neighbouring atoms around the absorber atom.

EXAFS spectra can be described as a series of periodic sine waves that decay in intensity as the incident energy increases from the absorption edge. These sine waves result from the interaction of the elected photoelectron with the surrounding atomic environment and their amplitude and phase depend on the local structure of excited atom. The local structure of the excited atom can be determined by matching a theoretical spectrum with the experimental spectrum. This fitting yields many types of

information, including the identity of neighboring atoms, their distance from the excited atom, the number of atoms in the shell, and the degree of disorder in the particular atomic shell (as expressed by the Debye-Waller factor). These distances and coordination numbers are diagnostic of a specific mineral or adsorbate-mineral interaction; consequently, the data are useful to identify and quantify major mineral phases, adsorption complexes, and crystallinity.

A major drawback of the method, however, is the extremely high concentrations needed of the atom studied. Therefore, the relevancy of the studied for trace level concentrations can be questioned. But as will be demonstrated in chapter 6, the behaviour of technetium at high concentrations are found being similar as for low conditions (*i.e.* indicating that (most probably) the same Tc species are involved), overcomes this grief.

5.3 Experimental set-up

All experiments prior to the XAS measurements, were carried out at ambient temperature (22°C) in two controlled atmosphere glove boxes flushed with either a mixture of N_2 (95%) and H_2 (5%) (glove box 1 – for batch systems with Gorleben groundwater) or with a mixture of N_2 (99.6%) and CO_2 (0.4%) (glove box 2 – for batch systems with Boom clay). The box atmospheres were circulated over a catalytic converter (Pt) in order to remove excessive oxygen. The mean concentration of O_2 in the glove boxes throughout the experiments was below 2 ppm.

Preparation of batch systems

a. Synthetic reducing systems

In a first series of batch experiments 95 ml synthetic Gorleben groundwater or 95 ml natural Gorleben groundwater was mixed in glove box 1 with 1 g FeS_2 or 1 g Fe_3O_4 in polypropylene cups (resulting in systems "pyrite + SGW", "pyrite + GW", "magnetite + SGW" and "magnetite + GW"). The synthetic reducing systems were pre-equilibrated during 3 days, and subsequently, 5 ml of a pertechnetate solution (in SGW) was added, to obtain a pertechnetate starting concentration in all systems equal to 2.2×10^{-3} mol/L. The vials were turned slowly head over head to ensure good mixing. Since pertechnetate reduction is known to be kinetically controlled (see previous chapters), all systems were studied as a function of time in order to estimate when equilibrium was established. Phase separation was performed by centrifugation (Beckman Centrifuge J2-21, rotor JA-14, 2h, 15.344×g).

b. Lab scale natural reducing systems

In a second series of batch experiments two types of "lab scale natural reducing systems" were prepared:

1) 2 samples of 10 g Gorleben sand were mixed with 19 ml natural Gorleben groundwater (system "GS + GW") . All systems were prepared in glove box 1. To ensure suitable reducing conditions for pertechnetate reduction, the lab scale natural systems were pre-equilibrated during 3 weeks. Subsequently, 1 ml pertechnetate solved in SGW was added, to obtain a pertechnetate starting concentration of 2.2×10^{-3} mol/L. The vials were turned slowly head over head to

ensure good mixing. The phase separation was performed by centrifugation (rotor JA-20, 30 min, 39191×g). Upon centrifugation, the aforementioned three layers could be distinguished: 1) a bottom sandy phase, 2) a black pasta of humic substances and 3) the liquid phase containing dissolved humic substances.

2) A polypropylene vial containing 50 g of Boom clay (BC) and 200 ml of Synthetic Boom Clay Water (SBCW) (system "BC") was prepared in glove box 2 and was left standing for 5 days with regular gentle mixing to allow wetting of Boom clay. Then 2 ml of a pertechnetate solution in SBCW was added, to obtain a starting concentration of 4.4×10^{-4} mol/L. This system was shaken 20 days end-over-end. The samples were centrifuged (Beckman Centrifuge J2-21, rotor JA-20, 2h, 27000×g) for phase separation. Upon centrifugation of the Boom clay systems, different layers could be obtained: 1) a bottom clayey phase, 2) a black pasta of humic substances and 3) the liquid phase containing dissolved humic substances.

Analysis of batch systems

The supernatant of all systems was analysed for ^{99}Tc, pH, Eh and humic substance concentration (by both methods). Gel permeation chromatography was performed on the supernatant solutions of nearly all experiments to verify the presence of Tc-HS, reduced free Tc species and/or pertechnetate species.

XANES/EXAFS measurements were made on samples taken from the previous batch systems (table 5-1):

- Samples 1 to 4 were taken from the homogenized pellets obtained after centrifugation of the 4 types of synthetic reducing systems.
- The black pasta of humic substances obtained after centrifugation from GS + GW systems was collected after 9 days (sample 5) and 24 days (sample 6). For both samples, the pertechnetate reduction was complete as judged from the absence of pertechnetate in the gel permeation chromatograms of the supernatant solution. The supernatant of system 6 was treated with La^{3+} in order to precipitate the humic substances and served as sample 8. The sample was prepared by mixing 50 ml of the supernatant with an equal volume of solution containing 0.01 Equiv./L $La(NO_3)_3.6H_2O$. Sample 7 was collected from the humic substance rich second layer of the Boom clay system.

All samples were taken when equilibrium was reached in the studied batch systems, with the exception of sample 3, which was taken in the course of the reduction process. (System 3 was however further studied to determine the equilibrium composition). The samples were transferred into small plastic vials (content 0.7 ml), which were sealed off (paraffin) and further placed in heat-sealed nitrogen-containing polyethylene bags to ensure containment during XANES/EXAFS data acquisition. All samples were transported to the European Synchrotron Radiation Facility (Grenoble, France) in a sealed nitrogen flushed metal container.

The technetium K-edge X-ray absorption spectra were collected at the Rossendorf beamline (ROBL) located at the bending-magnet port BM 20 of the ESRF. The monochromator of ROBL, equipped with a water-cooled Si(111) double-crystal system, was used in channel-cut measuring mode. Higher harmonics were rejected by two Pt coated mirrors. Energy steps in the EXAFS spectra were calculated giving

corresponding *k*-space steps of 0.05 $Å^{-1}$. Data were collected in fluorescence mode, using a four-pixel Ge fluorescence detector. A minimum of 5 scans per sample were collected to improve data quality. All data were collected at ambient temperature. The first inflection point of the Mo K edge at 20000 eV was used for energy calibration and was measured simultaneously with the samples.

The obtained raw data were analysed by using EXAFSPAK, developed by G.N. George and I.J. Pickering (1995). The program FEFF7 (Ankudinov *et al.*, 1998) was used to calculate the backscattering phase and amplitude of neighbouring atoms. FEFF7 calculations were done using parameters from the previously determined structure for crystalline TcO_2 (Almahamid *et al.*, 1995). The scaling factor, S_0^2, was set to 0.9.

5.4 Results

5.4.1 Batch experiment systems

The equilibrium concentration of Tc in the batch experiments (synthetic and lab scale natural systems) are given in table 5-1. In all systems the pH varied between 7.9 and 8.6. The redox potentials varied between -304 and -247 mV and were sufficient to reduce pertechnetate to Tc(IV). In all systems pertechnetate was completely reduced as verified by its absence in the gel permeation chromatograms taken from samples of the supernatant solutions after centrifugation.

Judged from i) the removal rate of Tc(VII) species in the GPC results, and ii) the change in the observed equilibrium solubility in the supernatant solutions, it is noticed that in the case of Gorleben sand/Gorleben groundwater systems, complete reduction and equilibrium was reached after 1 day of reaction, whereas in the synthetic systems with magnetite and pyrite, it took more than 200 days, similar to the observations made in the previous chapters. Pertechnetate reduction in Boom clay was complete in less than 6 days. In the absence of humic substances (systems 1 and 3), the pertechnetate reduction took about 50 days for the pyrite containing sample and more than 300 days for the magnetite containing sample.

The results in table 5-1 demonstrate again that in the absence of humic substances, Tc was precipitated or adsorbed onto pyrite and magnetite since the initial Tc concentration (2.2×10^{-3} mol/L) in solution has decreased to 10^{-6} mol/L after phase separation. In all systems where humic substances were present (synthetic systems with magnetite and pyrite, lab scale natural systems with Gorleben sand and Boom clay) Tc was found to be associated with the humic substances, based on the enhanced Tc concentration in the supernatant solution compared to the Tc concentration in the absence of humic substances, and on results from gel permeation chromatography.

system	[Tc] (mol/L)	(HS) g/L	Mol Tc/g HS	Occ. %(1)	pH	Eh (mV)
1 : pyrite + SGW	9.40×10^{-7}	-	-	-	8.3	- 250
2 : pyrite + GW	5.30×10^{-5}	0.059	8.98×10^{-4}	17.0	8.6	- 247
3 : magnetite + SGW	1.10×10^{-6}	-	-	-	8.4	- 267
4 : magnetite + GW	1.26×10^{-4}	0.148	8.51×10^{-4}	15.6	8.5	- 250
5 : GS + GW	1.86×10^{-4}	0.179	1.04×10^{-3}	19.1	7.9	- 298
6 : GS + GW	2.85×10^{-4}	0.289	9.86×10^{-4}	18.8	7.9	- 304
7 : BC	3.71×10^{-6}	0.175	2.15×10^{-5}	1.1	8.3	- 253

Table 5-1. Equilibrium composition of the supernatant solutions of the different batch systems (GS – Gorleben sand, SGW – Synthetic Gorleben groundwater, GW – Gorleben groundwater, BC – Boom clay, HS – Humic substances)

(1) Occ. (%) is the number of mol Tc/ mol charge humic substance functional groups. Mol charge/g humic substances were taken from literature and are 5.23×10^{-3} and 2×10^{-3} for Gorleben (Kim *et al.*, 1990) and Boom clay (Dierckx *et al.*, 2000) humic substances, respectively.

For all systems containing humic substances the Tc content of the dissolved humic substances is given both in mol Tc/g HS and as %occupancy of the HS functional group content. Mol charge/g humic substances were taken from literature and are 5.23×10^{-3} and 2×10^{-3} for Gorleben (Kim *et al.*, 1990) and Boom clay (Dierckx *et al.*, 2000) humic substances, respectively.

5.4.2 Description and justification of XAS samples

Table 5-2 gives an overview of the origin and the composition of the 8 samples, which were investigated by XAS. All samples (except sample 3) were taken at equilibrium from the previously discussed 7 batch systems. In fact, the Tc species in the samples can be classified into 4 types:

1) Tc species formed on the solid phases magnetite and pyrite after reduction of pertechnetate in synthetic groundwater (absence of humic substances) (samples 1 and 3).
2) Tc species formed on the solid phases magnetite and pyrite after reduction of pertechnetate in natural Gorleben groundwater (presence of humic substances) (samples 2 and 4).
3) Tc species associated with the precipitated humic substances after reduction of pertechnetate in lab scale natural systems (Gorleben sand /Gorleben groundwater and Boom clay suspensions) (samples 5, 6 and 7).
4) Tc species associated with dissolved humic substances after reduction of pertechnetate in the lab scale natural system of Gorleben sand and Gorleben groundwater and after precipitation of dissolved humic substances using La^{3+} (sample 8).

The total Tc and HS content in the samples were estimated as the difference between the initial and final Tc- and humic substance concentration in solution and are given in table 5-2. Samples 1 and 3 contain no humic substances. In samples 2 and 4, a

small amount of humic substances is associated and/or centrifuged off with the solid phases. However, the amount of Tc associated with these humic substances correspond only to 4.39 and 0.66% of the total Tc in the pellet, and is based on the assumption that dissolved and centrifuged humic substances have identical Tc occupancies. Samples 2 and 4 are therefore considered as relevant samples to investigate the influence of the presence of humic substances on the Tc species formed on the solid phases pyrite and magnetite upon pertechnetate reduction.

System	Sample	Tc content (mol / g)	HS content (mg / g)
1: pyrite + SGW	1: Tc – pyrite pellet	2.2×10^{-4}	-
2: pyrite + GW	2: Tc – pyrite pellet	2.15×10^{-4}	10.5
3: magnetite + SGW	3: Tc – magnetite pellet	5×10^{-5}	-
4: magnetite + GW	4: Tc – magnetite pellet	2.07×10^{-4}	1.6
5: GS + GW	5: Tc – Gorleben HS pellet	4.03×10^{-5}	38.76
6: GS + GW	6: Tc – Gorleben HS pellet	3.83×10^{-5}	38.83
7: BC	7: Tc – Boom clay HS pellet	8.72×10^{-5}	n.d.
6: GS + GW	8: Tc – Gorleben HS pellet	1.43×10^{-5}	14.45

Table 5-2. Overview of the composition of the 8 samples for XAS measurements (GS – Gorleben sand, SGW – Synthetic Gorleben groundwater, GW – Gorleben groundwater, BC – Boom clay, HS – Humic substances, n.d.- not determined).

Sample 5, 6 (GS/GW) and 7 (BC) were taken from the "black pasta of humic substances" present in the upper layer of the pellet after centrifugation at respectively 39191×g (GS/GW) and 27000×g (BC). The amount of black pasta and associated Tc can be controlled by using different centrifugation speeds for phase separation. By increasing the centrifugation speed, the amount of suspended humic substances containing Tc decreased and the amount of humic substances containing Tc present in the black pasta increased.

5.4.3 X-ray absorption spectroscopic measurements

- XANES measurements

Figure 5-1 shows the normalised XANES fluorescence spectra for the humic substance samples 5 to 8 from table 5-3. The spectra were recorded by simultaneously measuring a Mo sample together with the Tc samples. The Mo edge position was used as calibration edge. After calibration, the raw data were pre-edge subtracted and normalised at an energy level of 21111 eV. At this level, the absorption values are no longer supposed to be influenced by the existence of other atoms around the central Tc atom.

Typically, XANES spectra for pertechnetate always show 2 peaks (figure 5-2). The first absorption feature, the so-called pre-edge absorption peak (Allen *et al.*, 1997), occurs in the frame of a "forbidden" 1s → 4d transition, observed due to p orbital mixing with the final d state in the non-centrosymmetric, tetrahedral pertechnetate

anions. The first inflection point of the pre-edge absorption peak for pertechnetate and the main pertechnetate edge position have previously been measured during the previous measurements (see also chapter 4) and were respectively found at 21047.6 eV and 21061.7 eV. When pertechnetate is reduced to lower valence states, 1) the species formed are no more in a tetrahedral coordination and hence the pre-absorption edge disappears, and 2) the lower valence state of the absorbing atom causes an edge shift to lower energy values (Allen *et al.*, 1997). This behaviour reflects the decreased energy required to ionise the Tc by excitation of the 1s electron. Almahamid *et al.* (1995) established the chemical shifts of the technetium K edge by XANES in the formal oxidation states 0, I, II, IV, VI and VII, and defined them relative to the main edge position of pertechnetate. A significant correlation between chemical shift and formal oxidation state was observed.

The samples 5 to 8 do not show a pre-edge feature and by analysing the first derivative, it was observed that all samples have an identical edge position located at -6.8 eV from the edge position of pertechnetate. Applying the correlation found by Almahamid *et al.* (1995), it can be concluded that Tc(IV) species are formed in the humic substance samples. The present observations are in agreement with the previous XANES results on Tc-Gorleben humic substance containing solutions given in chapter 4.

Due to the high iron content of samples 1 to 4 the transmission signal vanished completely. However, by inserting a chromium filter, the Fe-induced background scattering could be reduced and good Tc fluorescence spectra were recorded. It was not possible to calibrate these samples using the known edge position of the simultaneously measured Mo sample. Due to the high stepper motor reproducibility of the monochomator, edge positions of the Mo reference measured in advance and afterwards did not show energy deviations. The following calibration procedure was therefore used for the samples 1 to 4. It was expected that Tc(IV) species are present on the solid phase. This assumption is reasonable and based on similar experiments in literature, where pertechnetate has been reduced in the presence of magnetite (Cui and Eriksen, 1996) or mackinawite (Wharton *et al.*, 2000) and Tc(IV) phases (respectively $TcO_2.nH_2O$ and TcS_2) were proven to be formed. XANES spectra of samples containing Tc(IV) species described in literature (Almahamid *et al.*, 1995, Allen *et al.*, 1997, Wharton *et al.*, 2000, Lloyd *et al.*, 2000, Lukens *et al.*, 2002, Vichot *et al.*, 2002) were found to have varying edge shifts between -6.40 and -7.1 eV energy shift compared to the main edge position observed for pertechnetate. The raw data of samples 1-4 showed (average) edge positions of 21055 (± 2) eV. Therefore, the samples 1 to 4 also have an edge shift of about -7 eV compared to the edge position of pertechnetate, which proves the existence of Tc(IV) phases. Samples 1 to 4 were therefore calibrated at 21055 eV.

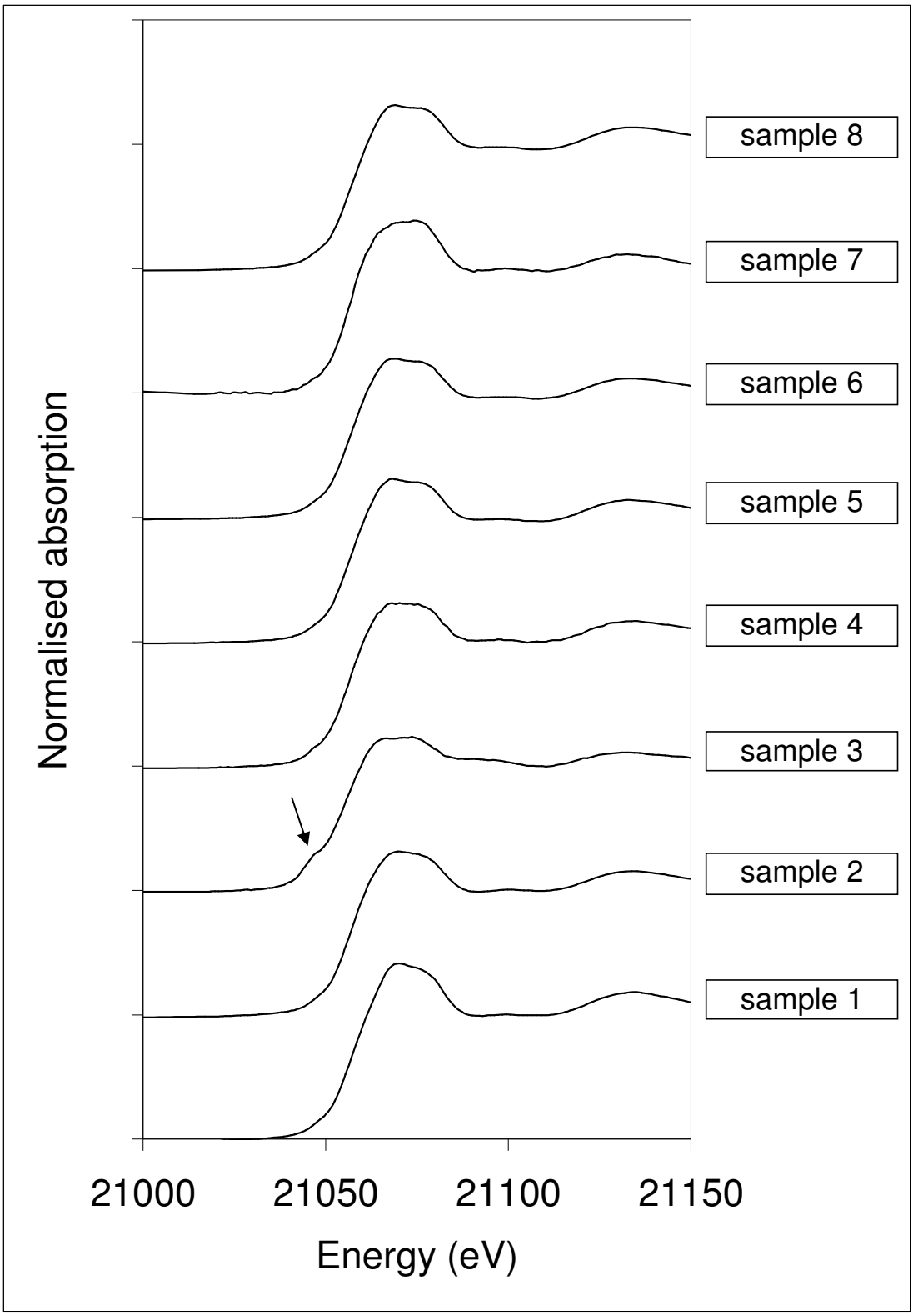

Figure 5-1. Normalised XANES spectra of all 8 samples

The calibrated XANES spectra of all 8 samples show the same edge position with a maximum in the first derivative at 21055 eV (figure 5-1). This observation indicates that in all samples Tc species with the same valence state (+IV) are present. When

looking in more detail at the post-edge pattern of all the studied samples, some small differences are noticed. The observed small differences in size and shape of the edge jump of the spectra of samples 1 and 7 can be due to a difference in the local environment of the absorbing atom. The spectrum of sample 3 comprises a pre-edge peak of pertechnetate (see arrow in figure 5-1). This observation is attributed to the presence of a small amount of pertechnetate within the sample and is in line with the observation that this sample was taken in the course of the reduction process. The supernatant solution indeed contained a relative high concentration of pertechnetate as found by gel permeation chromatography. Upon preparing sample 3 for the XAS measurements, also a small amount of the pertechnetate containing solution was sampled in the vial, which ends up in about 5% of the total Tc concentration.

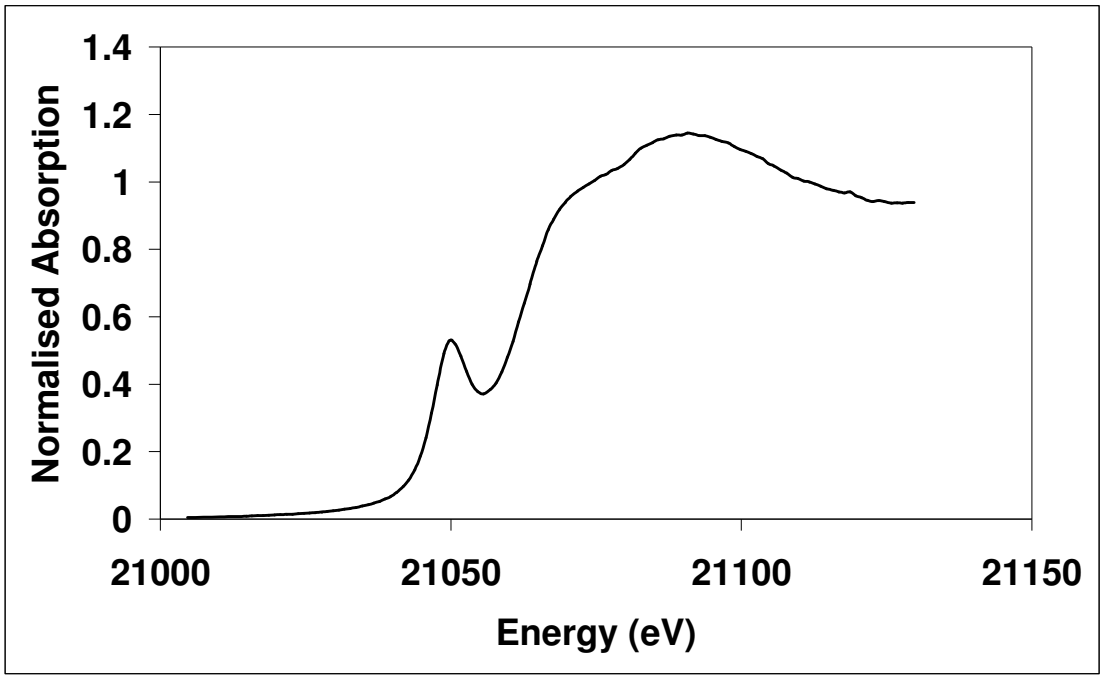

Figure 5-2. Normalised Absorption spectrum of pertechnetate

- EXAFS results

Figure 5-3 show the background subtracted, normalised and k^3-weighted EXAFS spectra and their Fourier transforms of the 8 different samples (dark grey line). All Fourier transform spectra were calculated using the same k-window of 2.25-13.0 $Å^{-1}$. Visual inspection of all the EXAFS and FT spectra reveals that all samples are very similar. The Fourier transforms show two pronounced peaks indicated as A and B in the figures. At higher distance only peaks with low intensities are present.

The Fourier transform (FT) function represents a radial distribution function of the near-neighbours present around the absorbing Tc atom. Hence, each obtained peak in the FT can be considered as a Tc-X bond, where X has to be further determined and is considered to be O or S for the first shell, and Tc, O or, when humic substances are present, C for the following shells.

Sample	Tc - O C.N.	Tc - O R (Å)	Tc - O σ^2 (Å^2)	Tc - Tc C.N.	Tc - Tc R (Å)	Tc - Tc σ^2 (Å^2)
1	7.0	2.03	0.0051	1.8	2.56	0.0040
2	6.8	2.03	0.0061	1.9	2.56	0.0053
3	6.4	2.02	0.0059	1.9	2.56	0.0054
4	6.1	2.01	0.0061	1.5	2.56	0.0043
5	7.2	2.01	0.0049	1.6	2.56	0.0035
6	6.3	2.02	0.0056	1.4	2.56	0.0041
7	7.0	2.02	0.0066	2.0	2.53	0.0083
8	6.4	2.01	0.0052	1.4	2.57	0.0043
$TcO_2.nH_2O$ [a]	3.9	2.04	0.0028	1.2	2.59	0.0032
	5.3	2.08	0.0058	1.0	2.63	0.0030
				0.8	2.91	0.0040
$TcO_2.nH_2O$ [b]	5.9	2.01	0.0048	2.4	2.57	0.0059
	3.9	2.02	0.0022	1.7	2.57	0.0029
	1.4	2.47	0.0050			
$TcO_2.nH_2O$ [c]	0.7	1.81	10^{-5}	1	2.53	0.0049
	5.3	2.02	0.0071			
polymeric Tc(IV) [c]	0.7	1.87	0.0001	1	2.48	0.0063
	5.3	2.04	0.0051			
polymeric Tc(IV) [c]	1.6	1.85	0.0017	1	2.51	0.0041
	4.4	2.04	0.0057			
crystalline TcO_2 [d]	6	1.98	0.0038	1	2.61	0.0038
				1	3.10	0.0035
				4	3.64	0.0040
				4	3.67	0.0040
				3	4.59	0.0065
				3	4.77	0.0054
				6	5.26	0.0056
				10	5.47	0.0084

Table 5-3. Results of EXAFS data fitting for the 8 samples. Uncertainties in coordination numbers are ± 20% and in distances are ± 0.02 Å. The second part of the table give values taken from literature for hydrated $TcO_2.nH_2O$, polymeric Tc(IV) and crystalline TcO_2 species. Literature data taken from (a) Allen *et al.*, 1997, (b) Lukens *et al.*, 2002, (c) Vichot *et al.*, 2002 and (d) Almahamid *et al.*, 1995.

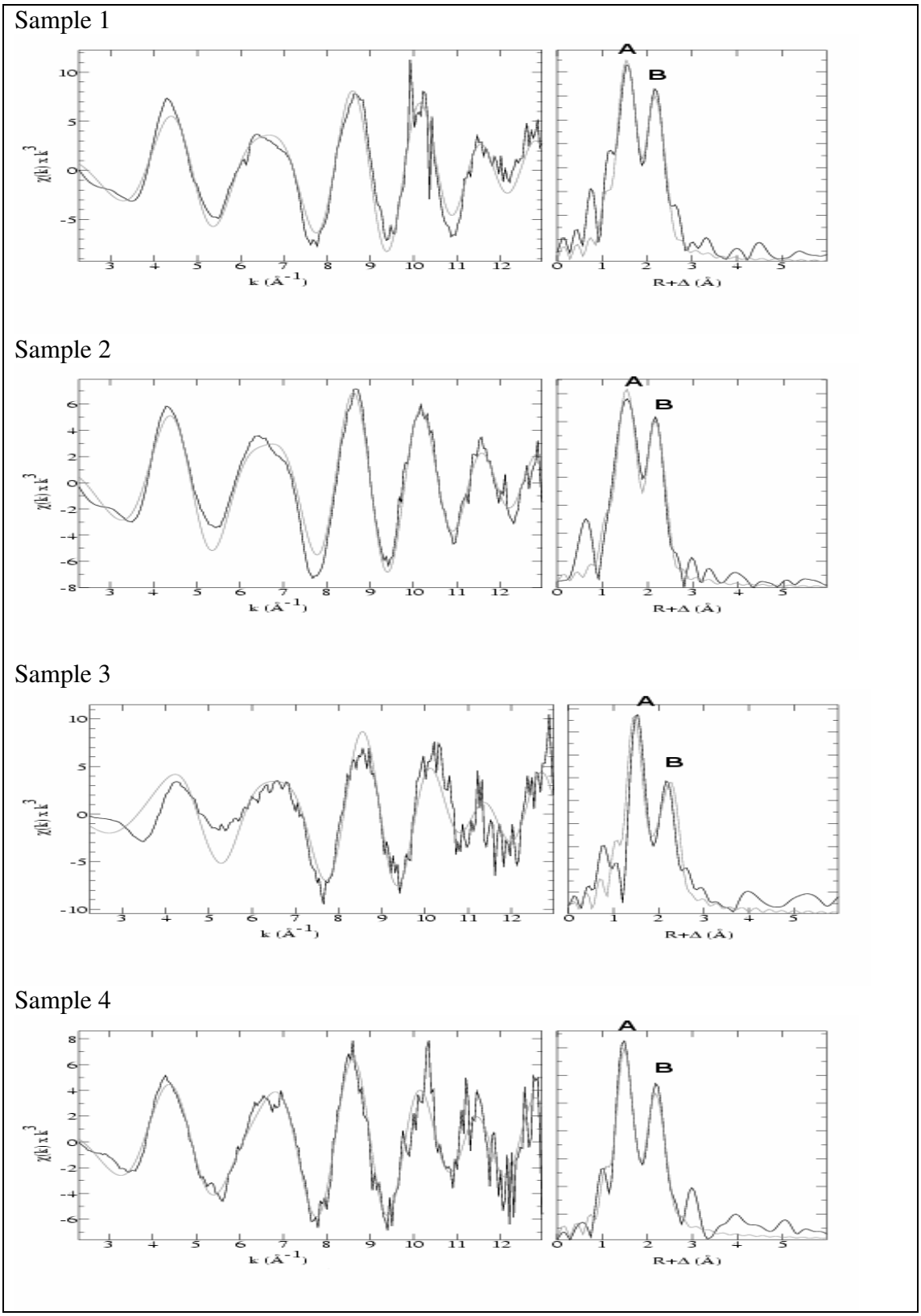

Figure 5-3. EXAFS $\chi(k).k^3$ spectra and FT transform spectra of samples 1 to 4

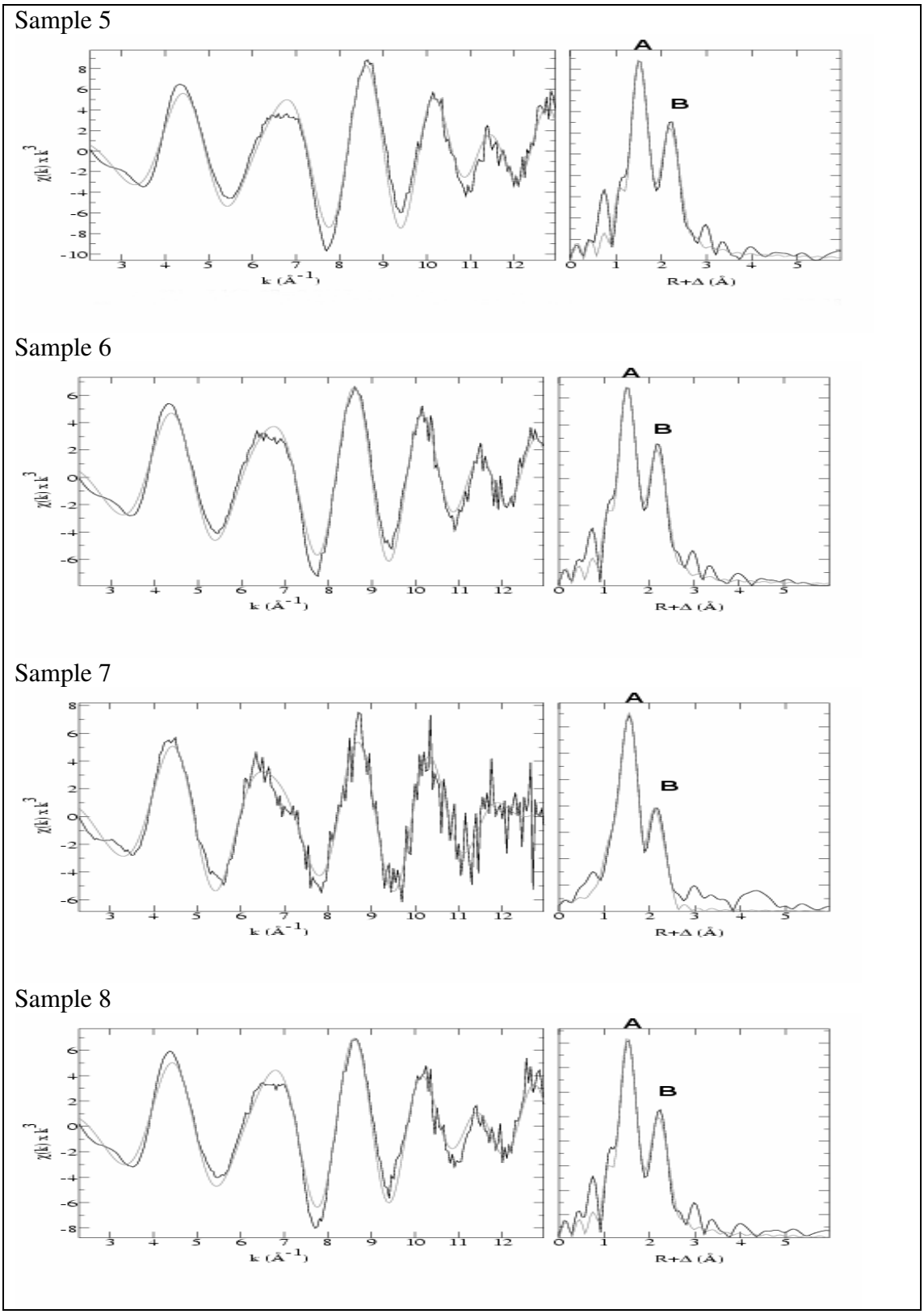

Figure 5-3 (continued). EXAFS $\chi(k).k^3$ spectra and FT transform spectra of samples 5 to 8

The curve fitting results are given in table 5-3 and are represented by the light grey line in figure 5-3. For all 8 samples an almost identical coordination number between 6.1 and 7.2 oxygen atoms in the first shell (peak A) at a distance of 2.01 - 2.03 Å is found. The Debye-Waller factors are in the range of 0.0049 and 0.0066 $Å^2$. The second shell (peak B) for the samples 1 to 6 and 8 is fitted with 1.37 - 2 Tc atoms at a distance of 2.56 - 2.57 Å, with Debye-Waller factors varying between 0.0035 and 0.0054 $Å^2$. Only for sample 8 a significant smaller Tc-Tc bond length (2.53 Å) and a larger Debye-Waller factor of 0.0083 $Å^2$ are obtained. Typically for EXAFS spectroscopy, the errors on the co-ordination numbers and bond lengths are 20% and 0.02 Å, respectively.

None of the samples containing FeS_2 could be fitted by using sulphur in the first shell. The main difference between Tc-S and Tc-O bonds in the first shell is the difference in bond length for Tc-S (2.24-2.55 Å) compared to Tc-O (1.94 - 2.08 Å) (Allen *et al.*, 1997). This result indicates that only in the case of minerals with a higher S/Fe ratio (e.g. mackinawite, FeS), the formation of TcS_2 is favoured as was found by Wharton *et al.* (2000), and Allen *et al.* (1997).

5.5 Discussion

The XANES spectra of crystalline TcO_2, $TcO_2.nH_2O$ or polymeric Tc(IV) species, given in literature (Almahamid *et al.*, 1995, Allen *et al.*, 1997, Wharton *et al.*, 2000, Lloyd *et al.*, 2000, Lukens *et al.*, 2002, Vichot *et al.*, 2002), are very similar to our spectra. Crystalline TcO_2 has two small but pronounced peaks in the post-edge region. In most XANES spectra of our samples, these two peaks are also observed but are less pronounced. The flattening of the peaks in our spectra is interpreted as being caused by the presence of a less ordered structure compared to crystalline TcO_2. A similar observation was also found for ReS_2 (Allen *et al.*, 1997) and can be seen on XANES spectra of Ru-oxides with a different hydration degree (RuO_2, $RuO_2.0.29H_2O$ and $RuO_2.2.32H_2O$) (McKnown *et al.*, 1999).

Our EXAFS fit results can be compared with results obtained for crystalline TcO_2 (Almahamid *et al.*, 1995), hydrated $TcO_2.nH_2O$ (Vichot *et al.*, 2002, Lukens *et al.*, 2002) or polymeric Tc(IV) species (Vichot *et al.*, 2002), which are also shown in table 5-3. The fitted bond lengths and local environments in the first and second shell of all our samples are in close agreement with those parameters observed for the three different Tc(IV) species described in literature. Independent of the crystallinity, these Tc(IV) species possess a distorted octahedral structure, with 6 oxygen atoms in the first shell and 1 or 2 Tc-Tc bonds in the second shell.

In EXAFS results of crystalline TcO_2, a very pronounced peak, consisting of 4 oxygen atoms at 3.64 Å and 4 oxygen atoms at 3.67 Å, in the fourth shell, is present due to a well-defined structure of TcO_6 octahedrons connected to each other in a 3 dimensional structure (Almahamid *et al.*, 1995). When this 3D structure becomes less well connected and exhibit no chain-to-chain linking or three-dimensional order, the resulting EXAFS spectra show only peaks beyond the second shell with significantly decreased amplitudes. In all our spectra, only peaks with very low intensity are observed at ~3.65 Å. It was not possible to find reasonable fits for any of the peaks beyond the second shell.

The present FT spectra and fitted EXAFS parameters (C.N, R and σ^2) deviate from the parameters of crystalline TcO_2 and correspond to the hydrated $TcO_2.nH_2O$ or polymeric Tc(IV) species, studied by Lukens *et al.* (2002) and Vichot *et al.* (2002). Vichot *et al.* (2002) proposed a general formula as "$Tc_nO_p^{(4n-2p)+}(H_2O)_q$", which leads to the precipitation of $TcO_2.nH_2O$ as n increases. The polymeric Tc(IV) species are a precursor for the $TcO_2.nH_2O$ precipitates and have the same EXAFS signal. Lukens *et al.* (2002) proposed a general structure for a $TcO_2.nH_2O$ species, which is shown in figure 5-4. The local structure of $TcO_2.nH_2O$ is a 1-dimensional chain structure consisting of edge-sharing TcO_6 octahedra with water molecules in trans arrangement. In crystalline TcO_2 the trans-water ligands are replaced by the bridging oxo ligands of the neighbouring chains.

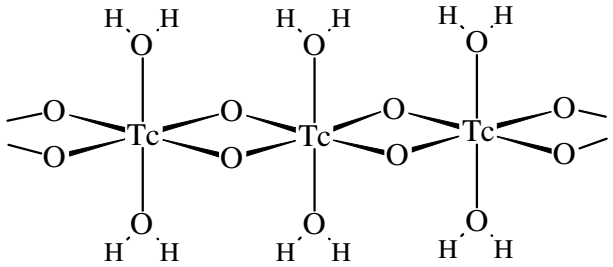

Figure 5-4. Proposed structure for hydrated $TcO_2.nH_2O$ species
(from Lukens *et al.*, 2002)

$TcO_2.nH_2O$ species exhibiting a structure of interconnected, distorted $Tc(OH)_4(OH_2)_2$ octahedra as proposed in figure 5-4, should theoretically be characterized by 4 shorter and 2 longer Tc-O bonds. These structural considerations have been confirmed by experimental results from XRD and EXAFS smeasurements on TcO_2 (Almahamid *et al.*, 1995, Allen *et al.*, 1997, Lukens *et al.*, 2002). In other cases however 6 identical Tc-O distances were observed by EXAFS measurements on $TcO_2.nH_2O$ precipitates prepared using different methods (Almahamid *et al.*, 1995, Lukens *et al.*, 2002). Lukens *et al.* observed both a 4+2 and a 6 Tc-O coordination on a study on $TcO_2.nH_2O$ precipitates prepared by different methods. It can therefore be concluded from literature that the observation of a 4+2 or a 6 coordination is dependent on the specific characteristics of the $TcO_2.nH_2O$ precipitate being examined. Smaller Tc clusters would possibly display a spectrum with 6 identical Tc-O bonds, whereas crystalline TcO2 precipitated would show 4 longer and 2 shorter Tc-O bonds. This could be explained as follows: as the technetium clusters become smaller the effect of differently coordinated edge octahedral, containing one or more terminal hydroxyl ligands, could significantly influence EXAFS results. As EXAFS is a bulk characterization technique, in case of small clusters, the effect of the edge octahedra could effectively mask small features in the EXAFS signal resulting form the 4+2 coordination. In our study, fitting attempts with 4 shorter and 2 longer Tc-O bonds did not result in better fits. We ascribe this observation to the presence of small $TcO_2.nH_2O$ species.

In the study by Mcknown *et al.* (1999) where Ru-oxides with a different degree of hydration are investigated, it was concluded that the Debye-Waller factors of samples with a different degree of hydration grows as function of increasing hydration. In view of the limited variations in Debye-Waller factors for the different samples (except sample 7: BC), it is concluded that in all samples $TcO_2.nH_2O$ species of

similar degree of hydration are present. Only, a small difference in Tc-Tc bond length and a slightly higher Debye-Waller factor in the second shell is noticed for the Boom clay sample compared to the other samples. This could be explained by the fact that only 1% Tc occupation was present in Boom clay compared to the other samples. The Tc(IV) species are probably low molecular weigth polymeric $TcO_2.nH_2O$ species with a higher degree of hydration. In the other samples with a much higher Tc content the hydrated Tc(IV) species have aggregated into larger colloidal units of polymeric $TcO_2.nH_2O$ species..

Both the XANES as the EXAFS results reveal that in all studied samples but one, $TcO_2.nH_2O$ species with the same hydration degree, are present. Only in sample 7, a more hydrated structure was observed. Focussing on the different types of samples studied, the foregoing results indicate that:

1) in the absence of humic substances, pertechnetate is reduced to Tc(IV) and hydrated $TcO_2.nH_2O$ species are formed in presence of pyrite or magnetite. The batch experimental results, however, showed in the supernatant solution an enhanced solubility (~10^{-6} mol/L) for the $TcO_2.nH_2O$ species compared to the literature value of 10^{-8} - 10^{-9} mol/L (Lieser and Bauscher, 1988, Meyer *et al.*, 1991, Cui and Eriksen, 1996 and Nguyen-Trung *et al.*, 1999). The enhanced solubility is ascribed to formation of $TcO_2.nH_2O$ polymers or colloids (see also chapter 1).

2) in the presence of humic substances, pertechnetate is reduced to Tc(IV) and hydrated $TcO_2.nH_2O$ species are formed in presence of pyrite and magnetite. The batch experimental results showed an enhanced solubility for the found $TcO_2.nH_2O$ species (~10^{-4} mol/L) in the supernatant solutions of these synthetic systems compared to absence of humic substances. The enhanced solubility is explained by a formation of Tc(IV)-humic substance species in solution as was verified by a combination of gel permeation chromatography, La-precipitation of the humic substances and XANES measurements. In the presence of humic substances, however, the kinetics of $TcO_2.nH_2O$ formation on the solid pyrite or magnetite phases, have slowed down judged from the slow removal rate of Tc(VII) species in the GPC results. A similar decreased formation rate for precipitation of dicalcium phosphate dihydrate, rhodocrosite, …in the presence of humic substances has frequently been noticed in literature (Inskeep and Silvertooth, 1998, Grossl and Inskeep, 1991, Lebron and Suarez, 1999).

3) In the labscale natural systems, pertechnetate is reduced to Tc(IV) and hydrated $TcO_2.nH_2O$ species are formed. The same species are found in sample 8 (La precipitate of the supernatant solution) compared to the samples 5, 6 and 7, which indicates that after reduction of pertechnetate, the reduced Tc species are distributed between solid and the liquid phase. An association between $TcO_2.nH_2O$ and humic substances was observed in the solid phase and in solution. However, from the present EXAFS results, a direct connection between $TcO_2.nH_2O$ and the humic substances, by way of e.g. a Tc-C bond in any of the further shells could not be detected. Tc(IV) can form binuclear complex compounds with carboxyl ligands (Schwochau, 2000, Shuh *et al.*, 2000). However, these complexes show shorter Tc-O (1.9 Å) and Tc-Tc (2.36 Å) bond lengths than the distances observed in humic substance containing samples. Therefore, the association between Tc(IV) species and humic substances can not

be described in terms of a complexation between a molecular species and humic substance functional groups, as is normally done for metal-humate interaction (Hummel, 1997). It was also concluded that the behaviour of technetium in Boom clay suspensions could not be described by an ordinary complexation mechanism. It is therefore proposed that ordered polynuclear species are involved in the Tc(IV)-humic substance interaction. There is a tendency that with increasing amount of Tc(IV) associated with the humic substances also larger hydrated $TcO_2.nH_2O$ polymers (larger colloidal size) are involved. This new mechanism is proposed to be called colloidal inclusion into humic substances and opens new views on the possible pathways of metals and radionuclides in humic rich environments. Further investigations are, however, necessary to elucidate on the real interaction mechanism of inorganic colloids with humic substances (see chapter 6).

4) The results indicate that La-precipitation of humic substances does not interfere with Tc(IV) present in the samples. This results support the method of precipitation of humic substances and the associated Tc-species using La^{3+} being useful in the quantification of the Tc(IV) association with humic substances (see Chapters 7 and 8).

The comparison of the present XAS data with literature data on Tc(IV) species proved that the same Tc(IV) species are formed using different preparation techniques. Preparation via hydrolysis (Vichot *et al.*, 2002), via radiolysis (Vichot *et al.*, 2002), via reduction potential of pyrite or magnetite, or in a lab scale natural system (such a Gorleben sand/Gorleben groundwater of a Boom clay suspension), lead to the reduction of Tc(VII) and to the formation of hydrated $TcO_2.nH_2O$ species having similar EXAFS features. The results presented in this chapter, however, are the first real mimic of a natural reducing environment containing humic substances.

5.6 Conclusions

Straightforward EXAFS spectroscopic evidence was obtained on the chemical environment of ^{99}Tc(IV) atoms formed upon introduction of TcO_4^- into 4 types of systems which gradually mimic *in situ* natural reducing conditions in humic rich geochemical environments: a) magnetite/pyrite in synthetic groundwater in the absence of humic substances, b) magnetite/pyrite in natural Gorleben groundwater in the presence of humic substances, c) Boom clay sediment mixed with synthetic groundwater, and d) Gorleben sand mixed with natural Gorleben groundwater.

All the investigated systems refer to pH 8-9 conditions and all measured samples show similar EXAFS spectra for Tc which could be fitted by a hydrated $TcO_2.nH_2O$ phase. The results are interpreted as follows: upon introduction of TcO_4^- to chemically reducing environments, small Tc(IV) oxidic polymers are formed which either may aggregate into larger units (colloids) and finally precipitate, or may interact in their polymeric form with (dissolved and immobile) humic substances. This latter type of interaction seriously differs from the generally accepted metal-humate complexation and therefore offers new views on the possible pathways of metals and radionuclides in humic rich environments.

CHAPTER 6

DETERMINATION OF THE CONDITIONAL INTERACTION CONSTANT BETWEEN COLLOIDAL TECHNETIUM(IV) AND GORLEBEN HUMIC SUBSTANCES

6.1 Introduction

The association between technetium and humic substances was extensively demonstrated before, mainly by gelpermeation chromatography (Stalmans, 1986, Sekine *et al.*, 1993 and 1997, Röβler *et al.*, 2000, Tkac *et al.*, 2000, Maes *et al.*, 2003). In chapter 4, it was proven for the first time by XANES that under neutral and alkaline conditions, the valence state of Tc species interacting with humic substances was Tc(IV).

In Maes *et al.* (2003), the interaction of Tc(IV) with dissolved Boom Clay HS was quantified using a modified Schubert approach. Experimental Tc(IV) distributions between Boom clay solid and synthetic clay water solution (containing dissolved HS) were obtained at various Tc concentrations (3.5×10^{-6}, 1.8×10^{-5} and 7.1×10^{-5} mol/L) and 4 Boom clay/synthetic clay water ratios (0.02, 0.06, 0.15 and 0.25 kg/L) at the in situ pH of the Boom Clay (pH 8.3). From these distributions an interaction constant with dissolved HS was calculated. Maes *et al.* (2003) concluded that the interaction of Tc with dissolved HS should not be described by a conventional complexation mechanism but by the interaction between non-ionic Tc(IV) species (monomeric and dimeric $TcO(OH)_2$ - $(TcO(OH)_2)_2$) and dissolved HS:

$$\Sigma[TcO(OH)]_{n=1,2} + HS = [TcO(OH)]_{n=1,2}\text{-}HS \qquad (6\text{-}1)$$

The value of the concentration quotient (or otherwise named the conditional interaction constant) K^{HS} for the above reaction remained constant over a wide range of Tc loadings and Log $K^{HS} = 2.6 \pm 0.3$ when expressing the HS concentration on a g HS/L basis, or Log $K^{HS} = 5.3 \pm 0.3$ on an Equiv. HS/L basis (using 2×10^{-3} Equiv. HS/g). The obtained constant is a conditional interaction constant since activity coefficient corrections were only made for inorganic $[TcO(OH)]_{n=1,2}$ species.

In chapter 5, EXAFS spectroscopy was used to study the speciation of Tc(IV) species in systems where rather high concentrations (up to 10^{-4} mol/L) of pertechnetate were reduced in the presence and absence of HS (*eg.* by Magnetite or Pyrite) or in lab-scale natural systems (such as Gorleben sand mixed with Gorleben water, or in Boom Clay mixed with synthetic Boom clay water). Similar EXAFS spectra were observed in the

pellets of all systems under consideration, which could be fitted to hydrated polynuclear TcO_2 species. The same EXAFS spectrum however was also obtained for the Tc species in the HS-rich supernatant, indicating that the previously established mechanism (equation (6-1)) can therefore be rewritten to incorporate the interaction of polynuclear or colloidal Tc(IV) species with humic substances:

$$\Sigma[TcO(OH)_2]_n + HS = [TcO(OH)_2]_n\text{-}HS \qquad (6\text{-}2)$$

This mechanism is proposed to be called "colloidal inclusion into humic substances" and is further investigated in the present study. For this purpose, well-defined synthetic systems were studied in which pertechnetate was reduced in the absence and presence of Gorleben humic substances with the aid of Magnetite, a reducing iron(II) containing surface. The behaviour of Tc(IV) was, for the first time, extensively examined under various geochemical conditions, *i.e.* variation in amount of reducing surface, variation in pH, variation in amount of Gorleben humic substances and variation in initial Tc(VII) dose. The present study differs from the research presented in Maes *et al.* (2003) due to the fact that in the present systems under consideration, only two well defined sinks are competing for Tc(IV), *i.e.* the reducing solid phase (Fe_3O_4) and dissolved humic substances. In the aforementioned study of Maes *et al.*, a range of ill-defined components (immobile humic substances, Pyrite, Siderite, clay minerals, …) in the Boom clay sediment competed for Tc with dissolved humic substances and only the in situ pH (8.3) was considered.

6.2 Experimental set-up

All experiments were carried out at ambient temperature (22°C) in a controlled atmosphere glove box flushed with a mixture of N_2 (95%) and H_2 (5%). The box atmosphere was circulated over a catalytic converter (Pt) in order to remove excessive oxygen. The mean concentration of O_2 in the glove box throughout the experiments was below 2 ppm.

Natural Gorleben groundwater (GoHy-2227 - GW) containing 165 mg/L organic matter and Gorleben sand (GS) from the potential disposal site at Gorleben (Germany) were used as supplied by Forschungszentrum Karlsruhe (Germany). The water was stored in a closed bottle covered with Al foil to shield off light. Synthetic Gorleben groundwater (SGW) was prepared as a mixture of 3.2×10^{-2} mol/L NaCl and 8×10^{-3} mol/L $NaHCO_3$, and was taken as representative for the inorganic composition of the natural Gorleben groundwater (Artinger *et al.*, 1998a). Diluted Gorleben groundwater solutions were prepared by mixing different volumes of natural Gorleben groundwater and SGW. This resulted in solutions containing humic substance concentrations between 16.5 and 165 mg/L HS.

A second type of humic substance-containing solutions were prepared by mixing (for a period of three weeks) different amounts of Gorleben sand (between 5 and 20 g) and natural Gorleben groundwater solutions (20 ml), and taking the supernatant solutions of these systems after centrifugation (30 min, 39191×g). These solutions contained dissolved humic substance concentrations between 165 and 520 mg/L. Artinger *et al.* (2000) observed previously that in similar systems increased dissolved humic substance concentrations are obtained due to the dissolution of charcoal-like particles present in the Gorleben sand. No differences between the humic substances present in

natural Gorleben groundwater and 'new' supernatant solutions prepared by mixing Gorleben sand with natural Gorleben groundwater were detected by Artinger.

Magnetite (Fe_3O_4) was purchased from a local mineral shop. Small-sized fractions (<125 μm) of the minerals were obtained by sieving after crushing the solids in the glove box using an Agate mortar and pestle. The phase purity was verified by powder X-ray diffraction measurements.

All chemicals were of analytical grade. The water used was de-ionised, treated by a Water Purification System (Milli-Q) and finally boiled out to obtain oxygen-free water. ^{99}Tc was purchased from Amersham in 0.1 mol/L NH_4OH aqueous solution. The Tc concentration was verified from absolute activity measurements. TcO_4^- solutions were prepared by diluting aliquots of a stock solution (5×10^{-2} mol/L TcO_4^-) in a SGW solution.

Four series of batch experiments were prepared by mixing appropriate amounts of solid and liquid phases in polypropylene vials in the glove box:

1) Series 1 consists of 19 ml synthetic Gorleben groundwater (absence of humic substances) mixed with 50 to 200 mg Fe_3O_4.
2) Series 2 consists of 19 ml natural Gorleben groundwater mixed with 10 to 500 mg Fe_3O_4.
3) Series 3 consists of the diluted (16.5 – 165 mg/L HS) and more concentrated (165 – 520 mg/L HS) Gorleben groundwater solutions mixed with 50 mg Fe_3O_4.
4) In series 4, the influence of pH was investigated by preparing systems similar to series 2, but by adding small volumes of 0.1 mol/L NaOH or HCl to cover a pH range between 7 and 10.5.

Before adding pertechnetate, all 4 series were pre-equilibrated during three days to ensure suitable redox conditions for pertechnetate reduction. Subsequently, 1 ml of TcO_4^- solutions (Tc concentration varying between 10^{-5} and 1.2×10^{-2} mol/L Tc in SGW) were added to obtain total pertechnetate starting concentrations in the range between 5×10^{-7} and 6.5×10^{-4} mol/L. The vials were turned slowly head over head to ensure good mixing.

After a certain equilibrium time, the samples were centrifuged (30 min, 39191×g) and the supernatant was analysed for ^{99}Tc, pH, Eh and humic substance concentration. Since pertechnetate reduction is known to be kinetically controlled (Cui and Eriksen, 1996a and b, previous chapters), duplicates of all systems were studied as a function of time in order to estimate when equilibrium was reached. Only data obtained on systems at equilibrium are further considered.

The technetium concentration was determined by liquid scintillation counting of the emitted β^- particle (E_{max} = 300 keV) using a Packard Liquid Scintillation Analyser (Tricarb 1600 CA) and Ultima Gold Liquid Scintillation Cocktail (Packard). The collected counts correspond to less than 2% error at 2σ level. The pH measurements were made by a Portatest 655 and a WTW SenTix 50 glass electrode. The redox potentials were monitored by a combined redox Toledo Mettler P14805-DXK-S8/120 electrode connected to the Portatest 655. The humic substances concentration was obtained from Absorbance measurements at 280 nm (LKB spectrophotometer).

Diluted solutions of the natural Gorleben groundwater (165 mg/L) were taken as standard solutions.

Gel permeation chromatography was performed on the supernatant solutions of nearly all experiments to verify the presence of Tc-HS, inorganic Tc(IV) species and/or pertechnetate species. The analysis was carried out by eluting a 1 ml sample aliquot over a glass column (30x1 cm), filled with Superdex 30 Prep Grade gel (Pharmacia Biotech). The eluent was a 0.15 mol/L NaCl solution containing 0.002% NaN_3 to prevent microbial growth. The U.V.-absorbance (280 nm) was measured continuously and the collected fractions (1.5 ml) were analysed for Tc by Liquid Scintillation Counting. This method allowed only to determine Tc qualitatively because a part of the humic substances and reduced Tc species are retained at the top of the column.

6.3 Results and Discussion

Table 6-1 gives an overview of the detailed experimental conditions and of the observed Tc concentrations at equilibrium after phase separation by centrifugation (39191×g, cut-off 50 nm) both in absence (series1) and presence of HS (series 2,3,4). All data correspond to equilibrium conditions. Indeed, for all series studied, sufficient duplicates were made in order to allow the follow-up of the evolution of the Tc solution concentration as a function of time. A gradual decrease in the total Tc concentration in solution with time was observed. Depending on the initially added amount of pertechnetate and the S/L ratio, a constant Tc concentration was reached after 2 to 20 weeks of equilibration. The shortest equilibration periods were observed for the lowest initially added pertechnetate concentrations.

The decrease of the Tc solution concentration was interpreted as the result of the reduction of Tc(VII) to the sparingly soluble Tc(IV). The reduction was verified to be complete by the absence of TcO_4^- in the gel permeation chromatograms (data not shown). The gel permeation chromatograms also showed the formation of soluble Tc species of a larger hydrodynamic size in solution witnessed by the fast elution of the ejected Tc from the porous column. This observation was made both in the absence and presence of humic substances.

The pertechnetate reduction process is known to be kinetically controlled (Cui and Eriksen, 1996a and b, Ben Said *et al.*, 1998) and is slower in presence of humic substances (see chapter 3). A similar decreased precipitation rate of dicalcium phosphate dihydrate, rhodocrosite, … in the presence of humic substances has frequently been noticed in literature (Inskeep and Silvertooth, 1988, Grossl and Inskeep, 1991, Lebron and Suarez, 1999). The observed reduction rates in the present study are comparable to the reduction rates for similar systems with Gorleben humic substances shown in chapters 3 and 4.

6.3.1 The reduction of pertechnetate with Magnetite (in the absence of humic substances)

Table 6-1 shows that the Tc solution concentration in equilibrium with Magnetite, in the absence of humic substances (series 1), varies between 4×10^{-9} and 2×10^{-6} mol/L. This means that some observed Tc concentrations are over-saturated with respect to known $TcO_2.nH_2O$ solubilities; depending on the source, a solubility of either 2×10^{-9}

or 2×10^{-8} mol/L has been reported in literature (Rard, 1983, Meyer *et al.*, 1991, Cui and Eriksen, 1996a and b, Rard *et al.*, 1999, Rard, 2005). The observed oversaturation (in the absence of humic substances) is ascribed to the formation of Tc(IV) colloids smaller than the cut-off by centrifugation (50 nm) and was already communicated for single systems of rather high pertechnetate concentrations (10^{-4} mol/L) which were reduced by Pyrite (FeS_2), Magnetite (Fe_3O_4) and FeS (chapter 4). In these systems as well as in the present study the aforementioned Tc species of larger hydrodynamic size were observed in the gel permeation chromatograms which also points to colloid formation. These results confirm therefore the existence of Tc(IV) colloids upon reduction of pertechnetate (even at a near-solubility concentration) made by several authors (Rard, 1983, Hanke *et al.*, 1986, Meyer *et al.*,1991, Naito *et al.*, 1998, Rard *et al.*,1999, Sekine *et al.*, 1998, 2002, 2004, Schwochau, 2000, Vichot *et al.*, 2002, Rard, 2005).

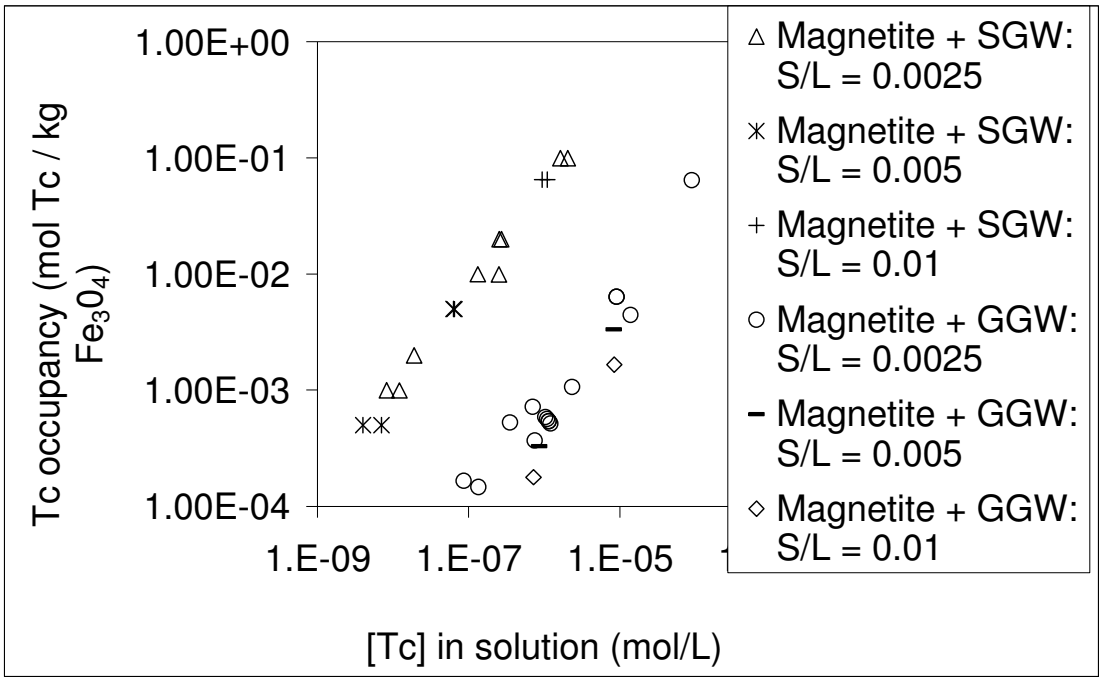

Figure 6-1. Concentration of Tc (mol/L) associated with the solid phase Magnetite versus concentration of Tc (mol Tc/kg Fe_3O_4) present in solution after reduction of pertechnetate ($[Tc]_{initial}$ varied between 5×10^{-7} and 2.5×10^{-4} mol/L) catalysed by Magnetite in a synthetic groundwater solution (SGW) or a natural groundwater solution (GW) at pH = 8.5. Experimental points are shown on a log-log scale.

The Tc(IV) distribution data between the solid and the liquid phase (in the absence of HS) for different initial pertechnetate doses combined with three Magnetite doses are given in table 6-1, and are also presented in figure 6-1 as an adsorption isotherm, *i.e.* the amount of Tc associated with the solid Magnetite (mol Tc/kg Magnetite) is plotted on a log-log scale versus the Tc(IV) solution concentration (mol/L) in the supernatant. The observed linear trend in figure 6-1 is only apparent because of the log-log plot. Indeed, if the distribution coefficient $K_D°$ (superscript "°" means absence of humic substances) is displayed as a function of the Tc occupancy (mol/kg) as in figure 6-2, the $K_D°$ values slightly decrease with the Tc occupancy from about 1.25×10^5 to 4.84×10^4 L/kg.

The fact that combinations of different total Magnetite (sorbent) doses with varying pertechnetate gifts leads to a unique relationship (see figures 6-1 and 6-2) points to a sorption equilibrium. The process at hand is thus not solely "reductive precipitation" as was proposed by Cui and Eriksen (1996b), but rather a reductive sorption process. Pepper *et al.* (2003) observed a similar linear sorption isotherm on a log-log scale upon reduction of pertechnetate in presence of Green rust. Upon reduction of pertechnetate in the presence of Magnetite, in chapter 5 the formation of hydrated $TcO_2.nH_2O$ species on the solid phase was observed. Pepper *et al.* (2003) also found "a TcO_2 – like local chemical environment" in the presence of green rust but suggested that TcO^{2+} was sorbed by surface complex formation. It is therefore plausible to propose that two processes contribute to the overall sorption: (1) a surface complexation process of cationic Tc(IV) species, and (2) a sorption of colloidal Tc(IV) species on the solid (oxidised?) Magnetite phase. The relative contribution of the proposed reactions to the total sorption process is unknown. However, the observation that $K_D°$ changes only slightly for a range of Tc occupancies (figure 6-2) is an indication that mainly the non-ionic sorption process is occurring.

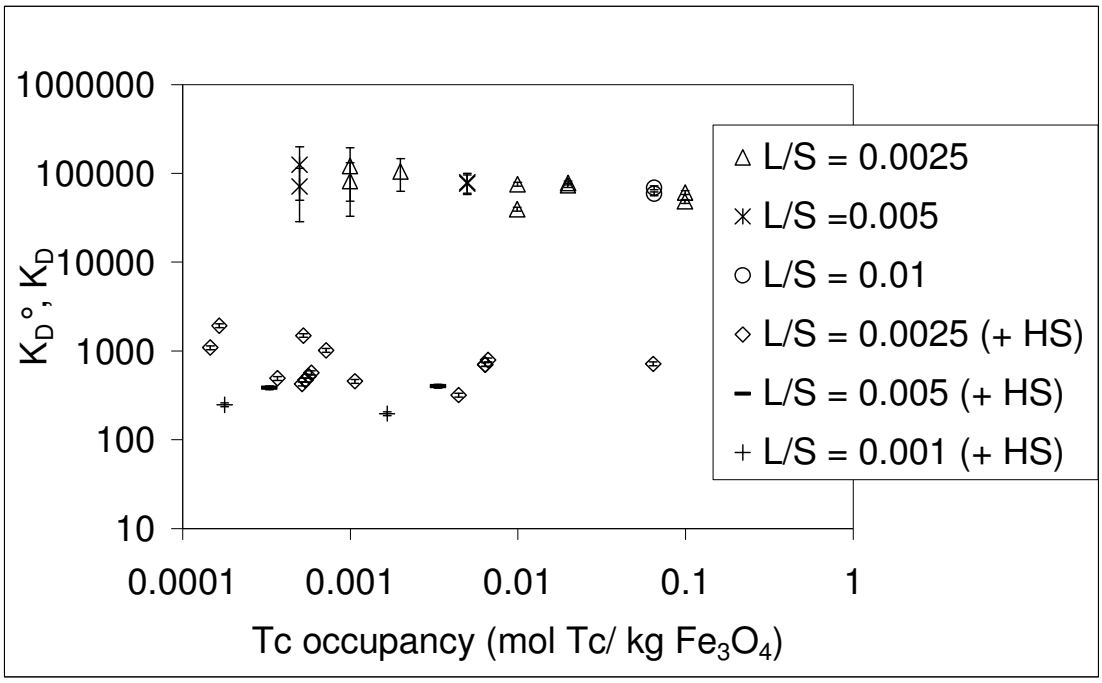

Figure 6-2. K_D^o (absence of HS) and K_D (presence of HS) versus Tc occupancy onto Magnetite. All points refer to systems where pertechnetate was reduced in a synthetic groundwater or Gorleben groundwater solution/ Magnetite mixture at different S/L ratios. pH = 8.5. Experimental points are shown on a log-log scale. Errorbars are also indicated.

The reduction of pertechnetate in presence of Magnetite involves and coincides with the oxidation of the Magnetite phase to an iron(III)-precipitate. This statement is in line with the observation, by X-ray diffraction spectroscopy, of Fe(III) precipitates (maghemite or goethite) upon reduction of Tc(VII) by freshly prepared Fe(II)-precipitates in brine solutions (Lee and Bondietti, 1983) and the observations of Liger *et al.* (1999) where U(VI) was reduced by iron(II). Probably the oxidized Fe(III) sites at the Magnetite surface play the role of active sorption sites in agreement with observations of Walton *et al.* (1985) who showed that Tc(IV) species are removed

from bicarbonate solutions by Fe(III)-oxyhydroxides. However, since our data demonstrate that Tc(IV) species (monomeric to colloidal) are involved in a sorption process it cannot be excluded that unaltered Magnetite surface sites also take part in the sorption process.

Summarising, it is proposed that after reduction of pertechnetate by Fe(II) present in the Magnetite phase, the final Tc concentration in solution is governed by the sorption of monomeric, dimeric and polymeric (or colloidal) Tc(IV); the monomeric species concentration being a minority. The surface on which sorption occurs is either a growing iron(III) precipitate and/or the unaltered Magnetite phase.

The following global reaction mechanism between $[TcO(OH)_2]_n$ species and the solid surface is proposed:

$$\Sigma[TcO(OH)_2]_n + \text{surface} = \text{Surface-}[TcO(OH)_2]_n \quad (6\text{-}3)$$

The corresponding concentration quotient reads:

$$K = \frac{\left[Surface - \left[TcO(OH)_2\right]_n\right]}{\left[\Sigma\left[TcO(OH)_2\right]_n\right] * (Surface)} \quad (6\text{-}4)$$

In this reaction $\Sigma[TcO(OH)_2]_n$ stands for the sum of monomeric, dimeric and polynuclear or polymeric (colloidal) Tc(IV) species present in the equilibrium solution (in mol/L). (Surface) stands for the concentration of surface functional groups (mol/kg). In view of the uncertainty on the nature and amount of surface functional groups on the solid Magnetite phase and their detailed interaction mechanism with the various Tc(IV) species it was not realistic to calculate the concentration quotient K.

The proposed sorption process differs from the surface complexation model put forward by Pepper *et al.* (2003) describing the interaction between Tc(IV) and green rust. These authors modelled their adsorption data at circumneutral pH using the surface complexation model of Dzomback and Morel (1990). They suggested that the reaction between Tc(IV) and green rust occurs through surface complexation of TcO^{2+} and calculated a conditional interaction constant $K = 10^{20.8}$. The authors admit that this result was only a fitting exercise since the number of surface functional groups concentrations and specific surface area of green rust were unknown and were assumed to be the same as for amorphous hydrous ferric oxides. In addition, their model by far underestimates the observed enhanced adsorption with increasing ionic strength. On the basis of our results we suggest that this enhanced adsorption can be interpreted as due to enhanced Tc colloid aggregation and their subsequent adsorption onto the green rust.

Further experimental work is necessary to unravel the detailed interaction process between the various Tc(IV) species and the iron-containing mineral phases(s) in the samples. However, for the purpose of this chapter it is sufficient to dispose of a description of the sorption process as given by the variation of $K_D°$ with Tc(IV) loading.

6.3.2 The reduction of pertechnetate in the presence of Gorleben humic substances

The equilibrium Tc solution concentration in the presence of humic substances varies between 10^{-7} and 10^{-4} mol/L as shown in table 6-1 (series 2, 3 and 4) and largely exceed the Tc solution concentration for comparable systems in series 1 (absence of HS). The enhanced Tc solution concentration in the presence of humic substances is generally accepted as due to the formation of soluble Tc(IV)-humate species. Two main parameters, the HS concentration and the Tc loading on the mineral surface, contribute to the observed variations and will be illustrated hereafter.

In the adsorption isotherm plot, experimental data are shown for samples containing a constant HS concentration (0.165 g/L) but varying Tc concentrations and S/L ratios at pH 8.5 (series 2). For all samples, no HS sorption onto Magnetite was detected. Again the linear trend which exhibits a similar slope as the data set in the absence of HS, indicates that the Tc(IV) solution concentration is ruled by the aforementioned sorption reaction (6-2) but combined with the constant HS concentration. However, the spreading on the data is large despite the good counting statistics. The proportional decrease in Tc(IV) sorption in the presence of HS compared to the absence of HS is due to the formation of dissolved Tc(IV)-HS species. This decrease is also shown in figure 6-2, and it is observed that K_D runs parallel to $K_D°$.

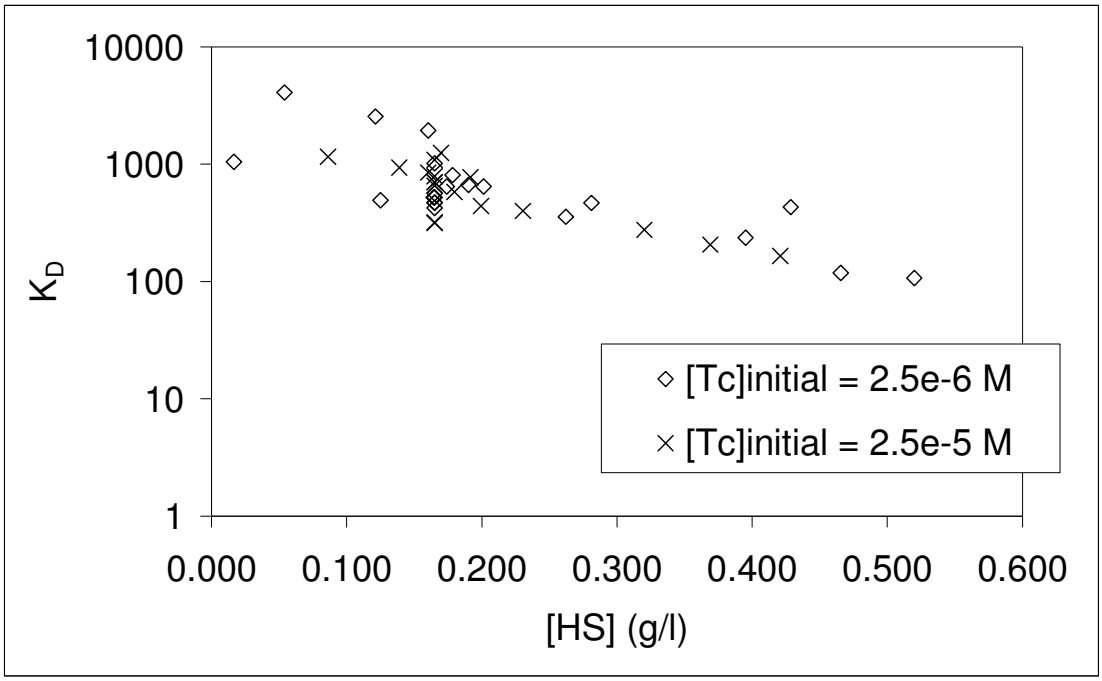

Figure 6-3. Tc distribution coeffient K_D between the solid and the liquid phase after reduction of pertechnetate by Magnetite in the presence of Gorleben humic substances, versus concentration of humic substances [HS] (g/L). $[Tc]_{initial} = 2.5\times10^{-6}$ mol/L (◊) or 2.5×10^{-5} mol/L (x), S/L = 2.5 and pH = 8.5.

An additional variation in Tc distribution is induced when changing the HS concentration in the above systems. This is shown in figure 6-3 for one S/L ratio and two different initial pertechnetate doses all at pH 8.5. The distribution coefficient K_D

is smaller than in absence of HS and decreases with increasing humic substance concentrations, which can be attributed to the increasing competition of Tc(IV)-humate formation with Tc(IV) sorption onto Magnetite. A similar trend was noticed by Maes *et al.* (2003) for the distribution of Tc(IV) in humic substances rich Boom clay suspensions.

6.3.3 Quantitative description of Tc interaction with Gorleben humic substances

The foregoing data are used to determine the conditional interaction constant of Tc(IV) with HS by adapting Schuberts ion exchange approach (Schubert, 1948) to the present system set-up. For this purpose, we consider the solid Magnetite phase to act as an adsorption sink according to reaction (6-3):

$\Sigma[TcO(OH)_2]_n$ + surface = Surface-$[TcO(OH)_2]_n$

with concentration quotient: $K = \frac{\left[Surface - \left[TcO(OH)_2\right]_n\right]}{\left[\Sigma\left[TcO(OH)_2\right]_n\right] * (Surface)}$.

This sink competes with dissolved Gorleben humic substances for hydrated neutral Tc(IV) species. In chapter 5, it was already demonstrated by EXAFS that hydrated $TcO_2.nH_2O$ colloids interact both with dissolved humic substances and with solid phases such as Magnetite and Pyrite.

The distribution coefficient $K_D°$ in the absence of humic substances is defined as

$$K_D^\circ = \frac{\left(molTc(IV)sorbed\right)}{\left[\Sigma\left[TcO(OH)_2\right]_n\right] * A} \qquad (6\text{-}5)$$

A is the side reaction coefficient which equals $10^{0.00}$ since the overwhelming fraction of Tc species in solution consists of neutral Tc(IV) species, following the EQ3/6 database (Wolery, 1992) and equals $10^{0.076}$ following the NEA database (Wanner, 1988) (See chapter 1).

The variation of $K_D°$ as a function of Tc occupancy is described by the regression line on figure 6-2: $K_D^o = -8808.9 * \ln (Tc_{occupation}) + 34699$ (6-6)

The interaction of HS with all neutral Tc species (monomeric, dimeric and polymeric or colloidal) is described by equation (6-2) already presented in the introduction part:

$\Sigma[TcO(OH)_2]_n$ +HS = $[TcO(OH)_2]_n$-HS

The corresponding conditional interaction constant K^{HS} reads:

$$K^{HS} = \frac{\left[\left[TcO(OH)_2\right]_n - HS\right]}{\left[\Sigma\left[TcO(OH)_2\right]_n\right] * (HS)}$$

The distribution coefficient of Tc(IV) in presence of Magnetite and HS can then be written as:

$$K_D = \frac{\left(molTc(IV)sorbed\right)}{\left[\Sigma\left[TcO(OH)_2\right]_n\right] * (A + K^{HS}(HS))} \qquad (6\text{-}7)$$

The value of K^{HS} can be obtained by combining equations (6-6) and (6-7) into the familiar Schubert equation (6-8):

$$\text{Log}(K_D°/K_D\text{-}1) = \log K^{HS} + \log [HS] - \log A \quad (6\text{-}8)$$

For the purpose of calculating K^{HS}, the HS concentration is expressed in g/ l.

Two important conditions need to be fulfilled in order for equation (6-8) to be valid: first, the formed Tc-humic substance species do not sorb onto the competing surface, and second, the values of $K_D°$ and K_D should refer to the same metal occupancy on the competing surface. The first condition is fulfilled since the amount of HS present in the supernatant solution after centrifugation equals the initial dissolved HS concentration, see table 6-1. The second condition can also be fulfilled when calculating $K_D°$ from the regression line through the data in figure 6-2 at any particular Tc occupancy.

The classic Schubert plot obtained by combining the experimental K_D values and the K_D^0 values given in table 6-1 is shown in figure 6-4. The $\log(K_D^0/K_D\text{-}1)$ versus log(HS) plot has a slope close to unity indicating that the rather simple reaction mechanism (equation (6-8)) can be written. The HS concentration was calculated using 5.23×10^{-3} Equiv. HS/g following Kim *et al.* (1990). Due to the fact that in the present approach the HS concentration is expressed in g/L instead of Equiv. HS/L, it was chosen to further illustrate the used Schubert approach by figure 6-5 where the calculated K^{HS} as a function of Tc occupancy on HS for all experimental data at pH 8.5 (series 2 and 3) is plotted. One unique value of 2.9 (± 0.3) is obtained following the EQ3/6 database and 3.0 (± 0.3) following the NEA database. The constancy of K^{HS} with Tc-loading on HS is in accordance with similar observations made in Boom clay suspensions (Maes *et al.*, 2003) and is in line with the proposed reaction mechanism of humic colloid interacting with neutral Tc(IV) species including $TcO_2.nH_2O$ colloids (Chapter 5).

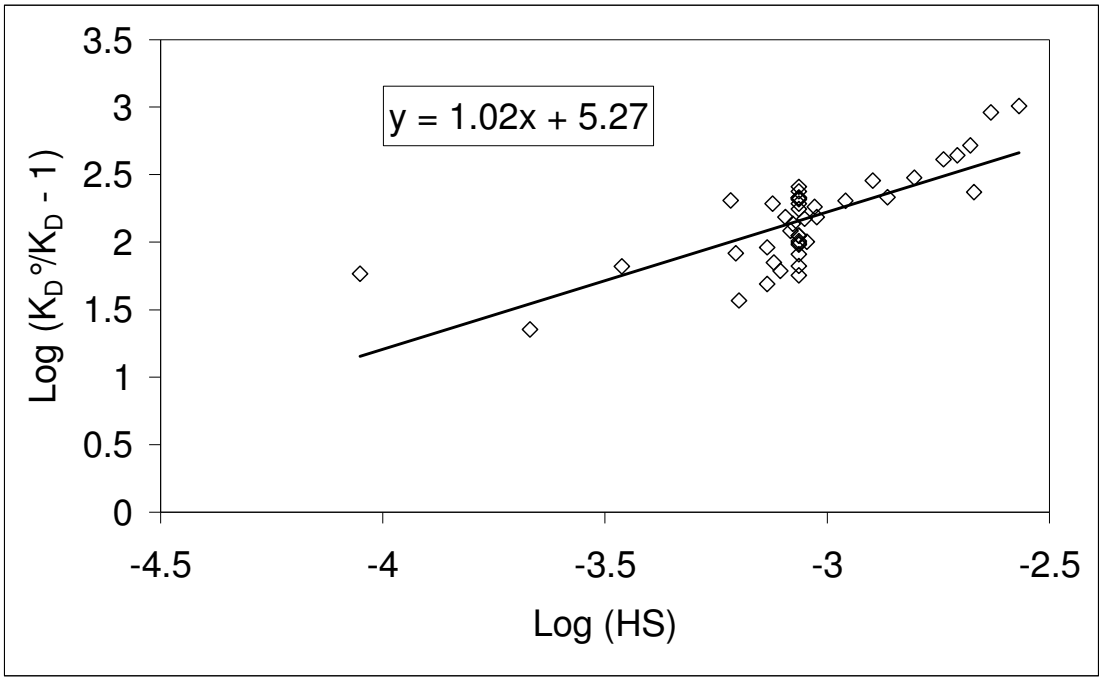

Figure 6-4. $\text{Log}(K_D^0/K_D\text{-}1)$ versus Log(HS) for all systems where pertechnetate (varying initial doses) was reduced by Magnetite in a natural Gorleben groundwater at a pH of 8.5.

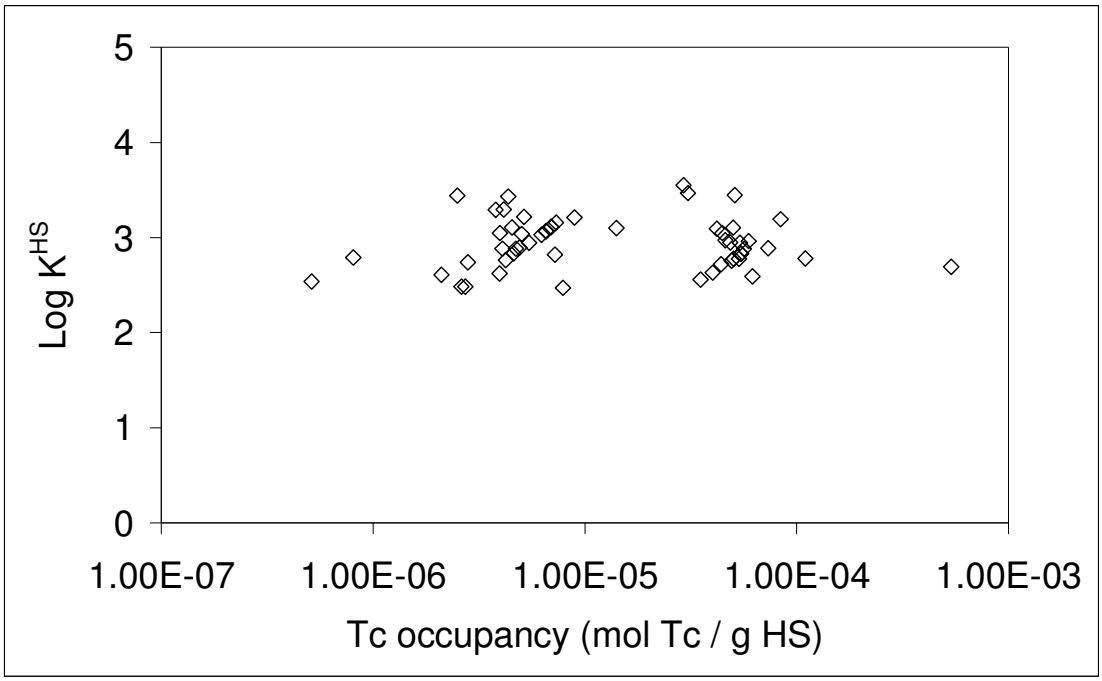

Figure 6-5. Calculated log K^{HS} versus Tc occupancy onto HS (mol Tc / g HS).

In addition, figure 6-6 shows the calculated K^{HS} values as a function of Tc loading of the solid phase Magnetite. No significant influence of the Tc occupancy is observed, indicating that the monomer, dimer or polynuclear Tc(IV) species all have equal interaction affinities towards the humic substances. Only at the highest Tc occupancies, a slight decrease of the K^{HS} values is observed. A possible explanation could be the fact that with increasing Tc concentrations, the polymerisation of Tc(IV) species is enhanced, resulting in larger polynuclear or colloidal Tc(IV) species with interior sites who do not have a direct contact with the phramework of the humic substances. As a consequence, the interaction constant is not independent on the degree of polynuclearity. Therefore, further experimental work is necessary to determine the relative abundance of the different monomer, dimer or polynuclear Tc(IV) species in solution and associated with humic substances or surfaces. This would lead to a refinement in the calculated interaction constant K^{HS}.

The proposed reaction mechanism was further verified by varying the pH in the studied systems. Additional experiments were conducted in a pH range from 7.0 till 10.5 for systems containing Magnetite and natural Gorleben groundwater (L/S = 0.4) and three initial TcO_4^- concentrations: 2.5×10^{-6}, 2.5×10^{-5} and 2.5×10^{-4} mol/L. Using the experimental results from series 4 given in table 6-1, $\log K^{HS}$ values are calculated and plotted versus pH in figure 6-7. The average $\log K^{HS}$ remains equal to 2.9 (± 0.3), which is represented by the dotted line in figure 6-7. Figure 6-7 gives only data calculated using the side reaction coefficient following the EQ3/6 database. For the NEA database (data not shown), the results are of course similar but an average value of 3.0 (± 0.3) is now obtained. For our experiments, the $K_D°$ value is assumed to remain independent of pH in agreement with literature results (Lieser and Bauscher, 1988, Liu and Fan, 2005). The $K_D°$ versus Tc occupancy relationship measured at pH

8.5 (figure 6-1) was therefore used to calculate K^{HS} values at different pH values (equation (6-6)).

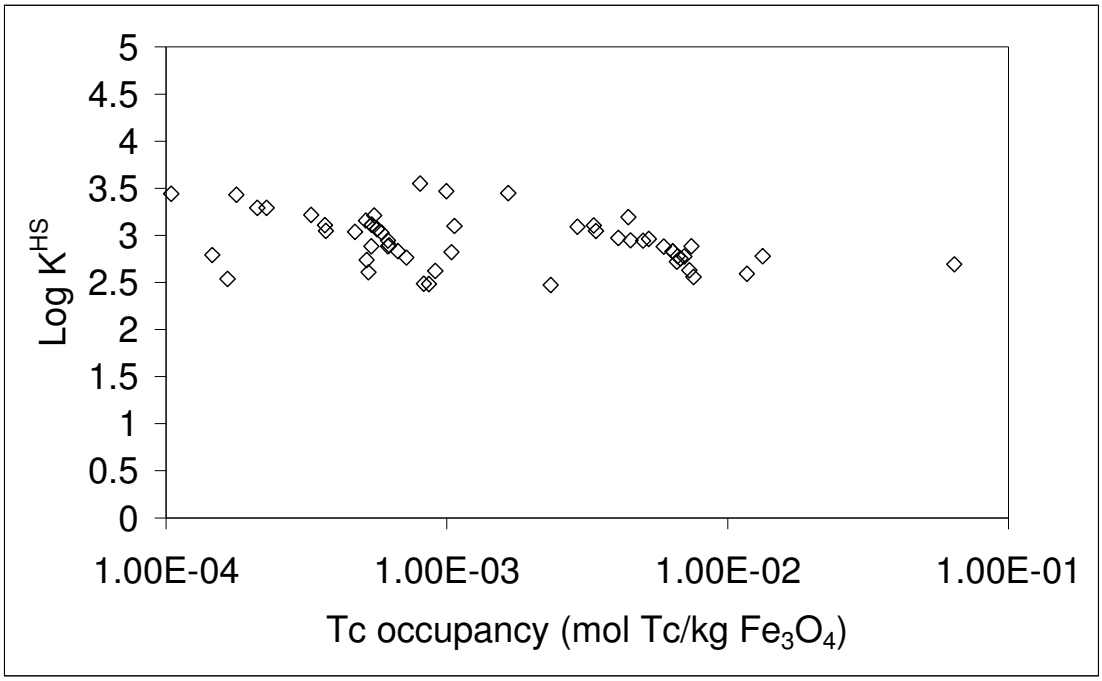

Figure 6-6. Calculated log K^{HS} versus Tc occupancy onto Magnetite (mol Tc / kg Magnetite).

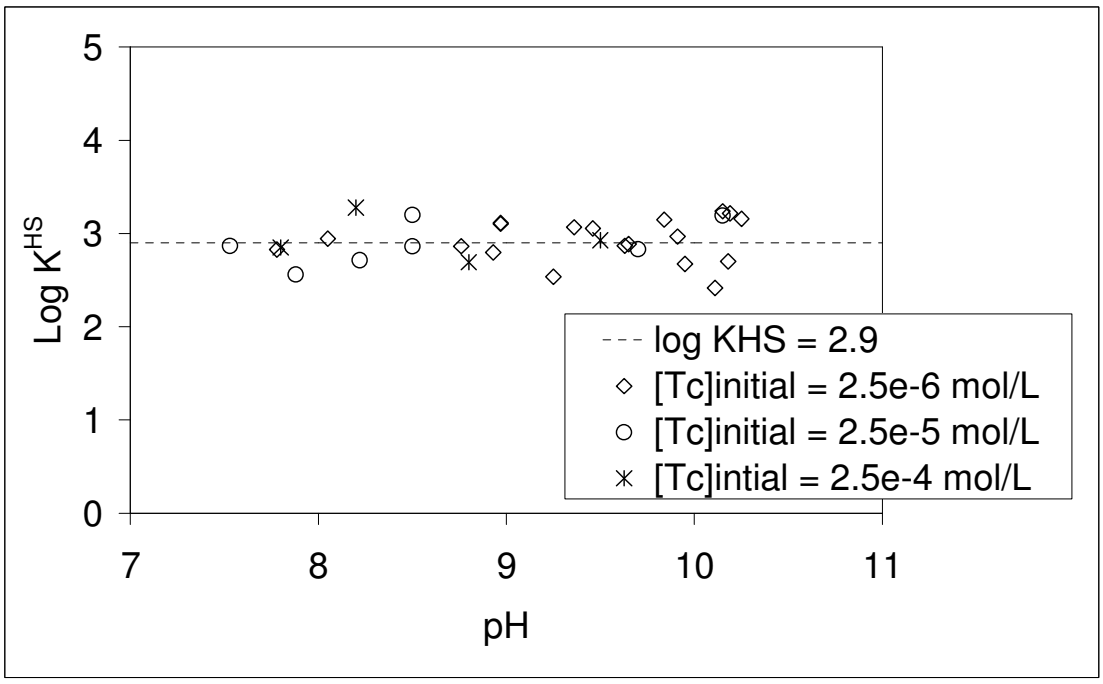

Figure 6-7. Calculated logK^{HS} values versus pH for systems where pertechnetate (three different initial doses) was reduced by Magnetite (S/L = 2.5) in a natural Gorleben groundwater.

The results given in figure 6-7 are a further proof of the proposed interaction mechanism between Tc(IV) colloids and humic substances, because no differences with pH are expected for the non-ionic colloid-colloid interaction mechanism. In chapter 8, a conditional interaction constant K^{HS} for the interaction between Tc(IV) and Gorleben HS is quantified using the La^{3+} precipitation method (La^{3+} is added as a flocculant to the supernatant in order to precipitate HS and Tc-HS; hence inducing a separation of the bound and unbound Tc species, see chapter 7) and it is also demonstrated that the obtained K^{HS} is independent of pH.

Wolfrum and Bunzl (1986) investigated the sorption and desorption of technetium by peat under anoxic conditions and reported their results as distribution constants K_D. The presence of pertechnetate was not verified, nor was the nature of the interaction mechanism discussed. Their study was performed for comparable Tc doses as was done in the present study and their main observations correspond to our observations: 1) a linear sorption isotherm was found even at (very) high Tc loading on the peat, 2) no pH effect (pH ranged between 1.6 and 5.4) was observed on the interaction between Tc and peat and 3) a reversible sorption-desorption behaviour was observed for the interaction between Tc and peat.

The reversibility of the interaction mechanism between Tc(IV) colloids and HS colloids in the present study was not explicitly verified in the sense that no desorption studies were undertaken. However, the reduction of various systems was followed as a function of time, until pertechnetate was absent and the Tc solution concentration remained constant. The presented data all correspond to equilibrium concentrations. Since all Tc(IV) distributions lead to the same unique description of data it is assumed that a reversible equilibrium was attained.

The value of $\log K^{HS}$ = 2.9 (± 0.3) obtained on Gorleben HS is (slightly) higher than the $\log K^{HS}$ = 2.6 (± 0.3) for dissolved Boom clay HS (both calculated for the EQ3/6 database). The difference between both values cannot be explained since both HS are not sufficiently characterised in terms of differences in molecular weight, nature and composition (hydrophobicity, functional group amounts) of the humic colloids. Therefore, the detailed processes governing the interaction between neutral Tc colloids and HS colloids remain up to date unknown and studies with synthetic HS or selected HS precursors are needed to elucidate the contribution of HS fragments in the observed reaction behaviour.

6.4 Conclusions

Foregoing results differ from most literature data on the geochemical behaviour of technetium. Indeed it was always assumed that the solution concentration of Tc under natural reducing conditions is determined by the amorphous precipitate $TcO_2.nH_2O$ having a low solubility equal to 10^{-9} – 10^{-8} mol/L and not controlled by a sorption mechanism. The difference between the present study and the literature results is the fact that for the first time the interaction between Tc and Magnetite over a wide range of Tc concentrations was studied.

One single interaction constant $\text{Log}K^{HS}$ = 2.9 (± 0.3) (EQ3/6) or 3.0 (± 0.3) (NEA) was calculated for the interaction of a range of monomeric to colloidal Tc(IV) species

with dissolved humic substances from Gorleben groundwaters. This interaction constant was found to describe the distribution of dissolved Tc(IV) species between humic substance – containing solutions and the solid Magnetite for varying conditions of humic substance concentration, Magnetite solid concentration, pH and total Tc concentration. The experimental conditions corresponded to oversaturation with respect to the solubility of $TcO_2.nH_2O$ and infers the presence of varying amounts of Tc(IV) polynuclear complexes or colloids which interact with both dissolved humic substances and Magnetite, thereby allowing interpretation of our systems through a Schubert-like approach. The derived K-value is a global value since no detailed information can be given on the relative abundance of the different (monomeric, dimeric and polymeric) Tc(IV) species in the system nor on the detailed interaction mechanism of each component with the humic substance colloids.

Table 6-1. Experimental conditions and results for experimental series 1 to 4.

Series	S/L (kg/L)	$[Tc]_{initial}$ (mol/L)	[HS] (g/L)	pH	$[Tc]_{equilibrium}$ (mol/L)	Tc occ. (mol Tc/ kg Fe_3O_4)	K_D (L/kg)	K_D° (L/kg)	log K^{HS} (EQ3/6)	log K^{HS} (NEA)
1	0.0025	2.50E-06	-	8.5	8.23E-09	9.97E-04	-	1.21E+05	-	-
1	0.0025	2.50E-06	-	8.5	1.21E-08	9.95E-04	-	8.22E+04	-	-
1	0.0025	5.00E-06	-	8.5	1.90E-08	1.99E-03	-	1.05E+05	-	-
1	0.0025	2.50E-05	-	8.5	1.32E-07	9.95E-03	-	7.54E+04	-	-
1	0.0025	2.50E-05	-	8.5	2.51E-07	9.90E-03	-	3.95E+04	-	-
1	0.0025	5.00E-05	-	8.5	2.55E-07	1.99E-02	-	7.79E+04	-	-
1	0.0025	5.00E-05	-	8.5	2.71E-07	1.99E-02	-	7.34E+04	-	-
1	0.0025	2.50E-04	-	8.5	1.64E-06	9.93E-02	-	6.06E+04	-	-
1	0.0025	2.50E-04	-	8.5	2.05E-06	9.92E-02	-	4.84E+04	-	-
1	0.005	2.50E-06	-	8.5	4.00E-09	4.99E-04	-	1.25E+05	-	-
1	0.005	2.50E-06	-	8.5	7.00E-09	4.99E-04	-	7.12E+04	-	-
1	0.005	2.50E-05	-	8.5	6.27E-08	4.99E-03	-	7.95E+04	-	-
1	0.005	2.50E-05	-	8.5	6.50E-08	4.99E-03	-	7.67E+04	-	-
1	0.01	6.50E-04	-	8.5	9.40E-07	6.49E-02	-	6.90E+04	-	-
1	0.01	6.50E-04	-	8.5	1.10E-06	6.49E-02	-	5.90E+04	-	-
2	0.0005	2.50E-06	0.165	8.5	1.33E-06	2.35E-03	1.77E+03	8.80E+04	2.47	2.55
2	0.00125	2.50E-06	0.165	8.5	1.20E-06	1.04E-03	8.63E+02	9.52E+04	2.82	2.90
2	0.0025	5.00E-07	0.165	8.5	1.34E-07	1.46E-04	1.09E+03	1.12E+05	2.79	2.87

Table 6-1 (continued). Experimental conditions and results for experimental series 1 to 4.

Series	S/L (kg/L)	$[Tc]_{initial}$ (mol/L)	[HS] (g/L)	pH	$[Tc]_{equilibrium}$ (mol/L)	Tc occ. (mol Tc/ kg Fe_3O_4)	K_D (L/kg)	K_D° (L/kg)	log K^{HS} (EQ3/6)	log K^{HS} (NEA)
2	0.0025	5.00E-07	0.165	8.5	8.59E-08	1.66E-04	1.93E+03	1.11E+05	2.54	2.61
2	0.0025	1.67E-06	0.165	8.5	7.49E-07	3.68E-04	4.92E+02	1.04E+05	3.11	3.18
2	0.0025	1.67E-06	0.165	8.5	3.52E-07	5.26E-04	1.49E+03	1.01E+05	2.61	2.68
2	0.0025	2.50E-06	0.165	8.5	1.09E-06	5.65E-04	5.20E+02	1.01E+05	3.07	3.14
2	0.0025	2.50E-06	0.165	8.5	1.03E-06	5.86E-04	2.97E+02	1.00E+05	3.03	3.10
2	0.0025	2.50E-06	0.165	8.5	1.21E-06	5.15E-04	4.25E+02	1.01E+05	3.16	3.23
2	0.0025	2.50E-06	0.165	8.5	7.05E-07	7.18E-04	1.02E+03	9.85E+04	2.76	2.84
2	0.0025	2.50E-06	0.165	8.5	1.15E-06	5.41E-04	4.72E+02	1.01E+05	3.11	3.19
2	0.0025	2.50E-06	0.165	8.5	1.15E-06	5.40E-04	4.70E+02	1.01E+05	3.11	3.19
2	0.0025	5.00E-06	0.165	8.5	2.34E-06	1.07E-03	4.56E+02	9.50E+04	3.10	3.18
2	0.0025	2.50E-05	0.165	8.5	9.07E-06	6.37E-03	7.03E+02	7.92E+04	2.83	2.91
2	0.0025	2.50E-05	0.165	8.5	9.07E-06	6.37E-03	7.02E+02	7.92E+04	2.83	2.91
2	0.0025	2.50E-05	0.165	8.5	1.39E-05	4.44E-03	3.19E+02	8.24E+04	3.19	3.27
2	0.0025	2.50E-04	0.165	8.5	8.96E-05	6.42E-02	7.16E+02	5.89E+04	2.69	2.77
2	0.0050	2.50E-06	0.165	8.5	8.55E-07	3.29E-04	3.85E+02	1.05E+05	3.22	3.29
2	0.01	2.50E-06	0.165	8.5	7.19E-07	1.78E-04	2.48E+02	1.11E+05	3.43	3.51
2	0.02	2.50E-06	0.165	8.5	4.13E-07	1.04E-04	2.52E+02	1.15E+05	3.44	3.52
2	0.0005	2.50E-05	0.165	8.5	1.83E-05	1.33E-02	2.39E+02	7.27E+04	2.78	2.85

Table 6-1 (continued). Experimental conditions and results for experimental series 1 to 4.

Series	S/L (kg/L)	$[Tc]_{initial}$ (mol/L)	[HS] (g/L)	pH	$[Tc]_{equilibrium}$ (mol/L)	Tc occ. (mol Tc/ kg Fe_3O_4)	K_D (L/kg)	K_D° (L/kg)	log K^{HS} (EQ3/6)	log K^{HS} (NEA)
2	0.00125	2.50E-05	0.165	8.5	1.04E-05	1.17E-02	1.82E+02	7.39E+04	2.59	2.67
2	0.0025	2.50E-05	0.165	8.5	8.40E-06	6.64E-03	1.75E+02	7.89E+04	2.78	2.85
2	0.00375	2.50E-05	0.165	8.5	8.07E-06	4.51E-03	1.48E+02	8.23E+04	2.95	3.02
2	0.005	2.50E-05	0.165	8.5	8.30E-06	3.34E-03	1.50E+02	8.49E+04	3.11	3.18
2	0.01	2.50E-05	0.165	8.5	8.43E-06	1.66E-03	1.31E+02	9.11E+04	3.45	3.52
2	0.02	2.50E-05	0.165	8.5	5.07E-06	9.97E-04	9.59E+01	9.56E+04	3.47	3.54
3	0.0025	2.50E-06	0.017	8.5	4.90E-07	8.04E-04	1.05E+03	9.75E+04	3.55	3.63
3	0.0025	2.50E-06	0.041	8.5	2.23E-07	9.11E-04	4.08E+03	9.64E+04	2.62	2.70
3	0.0025	2.50E-06	0.116	8.5	1.12E-06	5.52E-04	4.93E+02	1.01E+05	3.21	3.29
3	0.0025	2.50E-06	0.121	8.5	3.39E-07	8.64E-04	2.55E+03	9.68E+04	2.48	2.56
3	0.0025	2.50E-06	0.140	8.5	4.27E-07	8.29E-04	1.94E+03	9.72E+04	2.49	2.56
3	0.0025	2.50E-06	0.144	8.5	1.09E-06	5.65E-04	5.20E+02	1.01E+05	3.07	3.14
3	0.0025	2.50E-06	0.154	8.5	9.55E-07	6.18E-04	6.47E+02	9.98E+04	2.94	3.02
3	0.0025	2.50E-06	0.158	8.5	8.27E-07	6.69E-04	8.09E+02	9.91E+04	2.83	2.91
3	0.0025	2.50E-06	0.170	8.5	9.39E-07	6.24E-04	6.65E+02	9.97E+04	2.89	2.97
3	0.0025	2.50E-06	0.181	8.5	9.56E-07	6.18E-04	6.46E+02	9.98E+04	2.88	2.96
3	0.0025	2.50E-06	0.242	8.5	1.32E-06	4.71E-04	3.56E+02	1.02E+05	3.04	3.11
3	0.0025	2.50E-06	0.261	8.5	1.15E-06	5.39E-04	4.68E+02	1.01E+05	2.88	2.96

Table 6-1 (continued). Experimental conditions and results for experimental series 1 to 4.

Series	S/L (kg/L)	$[Tc]_{initial}$ (mol/L)	[HS] (g/L)	pH	$[Tc]_{equilibrium}$ (mol/L)	Tc occ. (mol Tc/ kg Fe_3O_4)	K_D (L/kg)	K_D° (L/kg)	log K^{HS} (EQ3/6)	log K^{HS} (NEA)
3	0.0025	2.50E-06	0.375	8.5	1.57E-06	3.71E-04	2.36E+02	1.04E+05	3.05	3.12
3	0.0025	2.50E-06	0.409	8.5	1.20E-06	5.18E-04	4.30E+02	1.01E+05	2.74	2.81
3	0.0025	2.50E-06	0.446	8.5	1.93E-06	2.29E-04	1.18E+02	1.09E+05	3.29	3.37
3	0.0025	2.50E-06	0.516	8.5	1.97E-06	2.11E-04	1.07E+02	1.09E+05	3.29	3.37
3	0.0025	2.50E-05	0.066	8.5	6.42E-06	7.43E-03	1.16E+03	7.79E+04	2.89	2.96
3	0.0025	2.50E-05	0.119	8.5	7.49E-06	7.00E-03	9.35E+02	7.84E+04	2.78	2.85
3	0.0025	2.50E-05	0.140	8.5	8.00E-06	6.80E-03	8.50E+02	7.87E+04	2.76	2.83
3	0.0025	2.50E-05	0.145	8.5	6.71E-06	7.32E-03	1.09E+03	7.80E+04	2.63	2.71
3	0.0025	2.50E-05	0.150	8.5	6.07E-06	7.57E-03	1.25E+03	7.77E+04	2.56	2.63
3	0.0025	2.50E-05	0.160	8.5	1.02E-05	5.92E-03	5.80E+02	7.99E+04	2.88	2.96
3	0.0025	2.50E-05	0.172	8.5	8.50E-06	6.60E-03	7.76E+02	7.89E+04	2.72	2.80
3	0.0025	2.50E-05	0.179	8.5	1.19E-05	5.24E-03	4.40E+02	8.10E+04	2.96	3.04
3	0.0025	2.50E-05	0.210	8.5	1.25E-05	5.00E-03	4.00E+02	8.14E+04	2.94	3.02
3	0.0025	2.50E-05	0.300	8.5	1.48E-05	4.08E-03	2.76E+02	8.32E+04	2.97	3.05
3	0.0025	2.50E-05	0.349	8.5	1.65E-05	3.40E-03	2.06E+02	8.48E+04	3.05	3.12
3	0.0025	2.50E-05	0.401	8.5	1.77E-05	2.92E-03	1.65E+02	8.61E+04	3.09	3.17
4	0.0025	2.50E-06	0.165	7.8	7.81E-07	6.88E-04	8.81E+02	9.88E+04	2.83	2.90
4	0.0025	2.50E-06	0.165	8.1	9.24E-07	6.30E-04	6.82E+02	9.96E+04	2.94	3.02

Table 6-1 (continued). Experimental conditions and results for experimental series 1 to 4.

Series	S/L (kg/L)	$[Tc]_{initial}$ (mol/L)	[HS] (g/L)	pH	$[Tc]_{equilibrium}$ (mol/L)	Tc occ. (mol Tc/ kg Fe_3O_4)	K_D (L/kg)	K_D° (L/kg)	log K^{HS} (EQ3/6)	log K^{HS} (NEA)
4	0.0025	2.50E-06	0.165	8.8	8.24E-07	6.71E-04	8.14E+02	9.91E+04	2.86	2.94
4	0.0025	2.50E-06	0.165	8.9	7.45E-07	7.02E-04	9.42E+02	9.87E+04	2.80	2.87
4	0.0025	2.50E-06	0.165	9.0	1.15E-06	5.41E-04	4.72E+02	1.01E+05	3.11	3.19
4	0.0025	2.50E-06	0.165	9.0	1.14E-06	5.45E-04	4.80E+02	1.01E+05	3.10	3.18
4	0.0025	2.50E-06	0.165	9.3	4.79E-07	8.08E-04	1.69E+03	9.74E+04	2.54	2.61
4	0.0025	2.50E-06	0.165	9.4	1.09E-06	5.65E-04	5.20E+02	1.01E+05	3.07	3.14
4	0.0025	2.50E-06	0.165	9.5	1.07E-06	5.72E-04	5.35E+02	1.00E+05	3.05	3.13
4	0.0025	2.50E-06	0.165	9.6	8.27E-07	6.69E-04	8.09E+02	9.91E+04	2.87	2.94
4	0.0025	2.50E-06	0.165	9.7	8.52E-07	6.59E-04	7.74E+02	9.92E+04	2.89	2.96
4	0.0025	2.50E-06	0.165	9.8	1.20E-06	5.20E-04	4.33E+02	1.01E+05	3.15	3.23
4	0.0025	2.50E-06	0.165	9.9	9.55E-07	6.18E-04	6.47E+02	9.98E+04	2.97	3.04
4	0.0025	2.50E-06	0.165	10.0	6.08E-07	7.57E-04	1.24E+03	9.80E+04	2.67	2.75
4	0.0025	2.50E-06	0.165	10.1	3.85E-07	8.46E-04	2.20E+03	9.70E+04	2.42	2.49
4	0.0025	2.50E-06	0.165	10.2	1.32E-06	4.72E-04	3.57E+02	1.02E+05	3.24	3.31
4	0.0025	2.50E-06	0.165	10.2	6.36E-07	7.46E-04	1.17E+03	9.81E+04	2.70	2.78
4	0.0025	2.50E-06	0.165	10.2	1.29E-06	4.83E-04	3.73E+02	1.02E+05	3.22	3.29
4	0.0025	2.50E-06	0.165	10.3	1.21E-06	5.15E-04	4.25E+02	1.01E+05	3.16	3.23
4	0.0025	2.50E-05	0.165	7.53	9.54E-06	6.18E-03	6.48E+02	7.95E+04	2.87	2.94

Table 6-1 (continued). Experimental conditions and results for experimental series 1 to 4.

Series	S/L (kg/L)	$[Tc]_{initial}$ (mol/L)	[HS] (g/L)	pH	$[Tc]_{equilibrium}$ (mol/L)	Tc occ. (mol Tc/ kg Fe_3O_4)	K_D (L/kg)	K_D° (L/kg)	log K^{HS} (EQ3/6)	log K^{HS} (NEA)
4	0.0025	2.50E-05	0.165	7.88	5.96E-06	7.62E-03	1.28E+03	7.77E+04	2.56	2.63
4	0.0025	2.50E-05	0.165	8.22	7.65E-06	6.94E-03	9.07E+02	7.85E+04	2.71	2.79
4	0.0025	2.50E-05	0.165	8.50	9.48E-06	6.21E-03	6.55E+02	7.95E+04	2.86	2.94
4	0.0025	2.50E-05	0.165	8.50	1.40E-05	4.40E-03	3.14E+02	8.25E+04	3.20	3.28
4	0.0025	2.50E-05	0.165	9.70	9.07E-06	6.37E-03	7.03E+02	7.92E+04	2.83	2.91
4	0.0025	2.50E-05	0.165	10.15	1.39E-05	4.44E-03	3.19E+02	8.24E+04	3.19	3.27
4	0.0025	2.50E-04	0.165	7.80	1.10E-04	5.60E-02	5.09E+02	6.01E+04	2.85	2.93
4	0.0025	2.50E-04	0.165	8.20	1.65E-04	3.40E-02	2.06E+02	6.45E+04	3.28	3.35
4	0.0025	2.50E-04	0.165	8.80	8.96E-05	6.42E-02	7.16E+02	5.89E+04	2.69	2.77
4	0.0025	2.50E-04	0.165	9.50	1.20E-04	5.20E-02	4.33E+02	6.07E+04	2.93	3.00

CHAPTER 7

A NEW METHOD FOR TECHNETIUM(IV) SPECIATION IN HUMIC RICH NATURAL GORLEBEN GROUNDWATER

7.1 Introduction

In all reported studies on technetium-humic substance species (Stalmans, 1986, Sekine *et al.*, 1993 and 1997, Röβler *et al.*, 2000, Tkac *et al.*, 2000, Maes *et al.*, 2003) and the previous chapters, the association between technetium and humic substances was demonstrated by gel permeation chromatography. In chapter 4, it was proven for the first time by XANES that under neutral and alkaline conditions, Tc(IV) species interact with humic substances. However, in most aforementioned literature studies, no (conditional) interaction constant for the interaction between Tc(IV) and humic substances was determined, mainly due to the fact that no adequate method was available for the determination of the concentration of Tc associated with humic substances and free Tc(IV) species in solution. Nevertheless, an interaction constant for the interaction between Tc(IV) and HS was determined via a modified Schubert approach for respectively Boom clay (Maes et al., 2003) and Gorleben HS (chapter 6).

In the aforementioned Schubert method, the Tc(IV) distribution between the solid and the liquid phase is measured. However, in order to determine the interaction of Tc(IV) with humic substances in a variety of conditions, it is necessary to have a method for the direct determination of the individual concentrations of Tc(IV) associated with HS and the "free" Tc(IV). Röβler *et al*. (2000) described several chromatographic methods (Gel Permeation Chromatography, Sequential Chromatographic Analysis and Thin Layer Chromatography) for the quantification of soluble technetium-99m - humic acid species. These humic substances were labelled with Tc via reduction of pertechnetate with stannous chloride. The authors however concluded that the experimentally derived yield of Tc-humic acid species was very much depending on the chromatographic method used. Speciation techniques based on gel permeation chromatography (GPC) only offer a qualitative determination of Tc(IV)-humic substance species due to (partial) sorption of different Tc species on the column and to the relatively low recoveries obtained. Also long time use of columns could lead to preferential flow paths. The need for a simple and quick method for direct speciation in solution is therefore obvious.

In chapter 4 and 5, La^{3+} was used to precipitate and concentrate colloidal Tc(IV) – humic substance species, as a preparation step of samples for XANES and EXAFS spectroscopic measurements. The purpose of the present chapter is to investigate the conditions to obtain a quick and quantitative separation of Tc bound to HS and the

free Tc species using La^{3+}. Various parameters such as the La^{3+} concentration, the humic substance concentration, the pH and the Tc concentration on the Tc separation are tested in solutions containing Tc and Gorleben humic substances.

7.2 Experimental set-up

All experiments were carried out at ambient temperature (22°C) in a controlled atmosphere glove box flushed with a mixture of N_2 (95%) and H_2 (5%). The box atmosphere was circulated over a catalytic converter (Pt) in order to remove excessive oxygen. The mean concentration of O_2 in the glove box throughout the experiments was below 2 ppm.

Gorleben groundwater (GoHy-2227 - GW) containing 165 mg/L organic matter (82 mg/L organic carbon) (Artinger *et al.*, 1998a) from the potential disposal site at Gorleben (Germany) was used as supplied by Forschungszentrum Karlsruhe (Germany). The water was stored in a closed bottle inside the glove box. Synthetic Gorleben groundwater (SGW) was prepared as a mixture of 3.2×10^{-2} mol/L NaCl and 8×10^{-3} mol/L $NaHCO_3$, and was taken as representative for the inorganic composition of the natural Gorleben groundwater (Artinger *et al.*, 1998a). Diluted Gorleben groundwater solutions were prepared by mixing different volumes of natural Gorleben groundwater and SGW. This resulted in solutions containing humic substance concentrations of 6, 18, 55 and 165 mg/L HS, all at pH 8.5 ± 0.1.

Magnetite (Fe_3O_4) was used for the reduction of pertechnetate to Tc(IV) and was purchased from a local mineral shop. Small sized fractions (<125 µm) of the mineral were obtained by sieving after crushing the solid in the glove box using an Agate mortar and pestle. The phase purity was verified by powder X-ray diffraction measurements.

All chemicals were of analytical grade. The water used was de-ionised, treated by a Water Purification System (Milli-Q) and finally boiled out to obtain oxygen-free water (Milli-Q water). ^{99}Tc was purchased from Amersham in 0.1 mol/L NH_4OH aqueous solution. The Tc concentration was verified from absolute activity measurements. TcO_4^- solutions were prepared by diluting aliquots of a stock solution (5×10^{-2} mol/L TcO_4^-) in a SGW solution. A stock solution of 10 Equiv./L La^{3+} was prepared in the glove box by dissolving $La(NO_3)_3$ (Merck) in Milli-Q water. Before each La-experiment (see further on), freshly prepared La^{3+} solutions with concentrations varying between 10^{-5} and 1 Equiv./L, were prepared by diluting the stock solution in Milli-Q water. The pH of these solutions increased with increasing dilution from pH 4.9 (1 Equiv./L), pH 5.2 (10^{-2} Equiv./L) to pH 7.3 (10^{-5} Equiv./L).

Preparation of Tc-humic substance test solutions

100 mg Fe_3O_4 was pre-weighted in polypropylene vials in the glove box and mixed with 39 ml Gorleben groundwater. To investigate the influence of pH, similar systems were prepared, but small volumes of 0.1 mol/L NaOH or HCl were added to cover a pH range between 6 and 9. All systems were pre-equilibrated during 3 days to ensure

suitable conditions for pertechnetate reduction. Subsequently, 1 ml of varying concentration of pertechnetate in SGW was added to obtain total pertechnetate starting concentrations varying between 10^{-6} and 10^{-3} mol/L (see $[Tc]_{initial}$ in table 7-1). The vials were turned slowly head over head in the glove box to ensure good mixing.

Since pertechnetate reduction is known to be kinetically controlled (Cui and Eriksen, 1996a and b, and as observed in the previous chapters), all systems were studied as a function of time in order to estimate when equilibrium was reached. All samples were centrifuged (Beckmann JA-20, 30 min, 39191×g, cut-off value 50 nm) and the supernatant was analysed for ^{99}Tc (see $[Tc]_{test\ solution}$ in table 7-1), pH, Eh and humic substance concentration. Only supernatants of systems at equilibrium were used hereafter as test solutions.

Supernatant analysis

The total technetium concentration in the supernatant solutions was determined by liquid scintillation counting of the emitted β^- particle (E_{max} = 300 keV) using a Packard Liquid Scintillation Analyser and Ultima Gold Liquid Scintillation Cocktail (Packard). The collected counts correspond to less than 2% error at 2σ level. The pH measurements were made by a Portatest 655 and a WTW SenTix 50 glass electrode, and the redox potentials were monitored by a combined redox Toledo Mettler P14805-DXK-S8/120 electrode connected to the Portatest 655. The humic substances concentration was obtained from Absorbance measurements at 280 nm (LKB spectrophotometer). Diluted solutions of the natural Gorleben groundwater (165 mg/L, Absorbance = 3.496) were taken as standard solutions. No sorption of humic substances on the solid Magnetite phase was observed.

Gel permeation chromatography was performed on the supernatant solutions of nearly all experiments to verify the presence of Tc-HS, reduced free Tc species and/or pertechnetate species. This was carried out by eluting a 1 ml sample over a glass column (30x1 cm), filled with Superdex 30 Prep Grade gel (Pharmacia Biotech). The eluent was a 0.15 mol/L NaCl solution containing 0.002% NaN_3 to prevent microbial growth. The U.V.-absorbance (280 nm) was measured continuously and the collected fractions (1.5 ml) were analysed for Tc by Liquid Scintillation Counting. This method allowed only determining Tc qualitatively because a part of the humic substances and reduced Tc species are retained at the top of the column. The gel permeation chromatograms of all monitored solutions showed the presence of colloidal Tc species (Tc-HS and/or reduced free Tc) and proved that pertechnetate species were absent at equilibrium.

La-precipitation experiments

The above prepared supernatant solutions were used as test solutions for the development of the La-precipitation method. The following general experimental set-up is used: aliquots of the test solutions (of systems at equilibrium) were mixed with equal volumes of freshly prepared La^{3+} solutions in polypropylene vials. The solution is gently shaken by hand and further left to stand for 15 minutes inside the glove box. The samples were subsequently centrifuged (Beckmann JA-20, 30 min, 39191×g, cut-

off value 50 nm) outside the glove box and again transferred to the box for further analysis of the supernatant for ^{99}Tc (see $[Tc]_{La}$ in table 7-1), pH and Absorbance.
The following 5 experiments were conducted during the development of the method:

1) Determination of the threshold La^{3+} concentration needed for full precipitation of all humic substances (absence of Tc).

   Six original and six times three diluted Gorleben groundwater solutions (concentrations of 55, 18 and 6 mg HS/L) were mixed on a 1/1 ratio with solutions containing increasing La^{3+} concentrations varying between 10^{-4} and 1 Equiv./L (see table 7-1, experiment 1). This lead to HS concentrations in solution equal to 82.5, 27.5, 9 and 3 mg HS/L, and to La concentrations in solution between 5×10^{-5} and 0.5 Equiv./L. Tc was not present in these experiments.

2) Determination of the threshold La^{3+} concentration needed for full precipitation of all Tc- humic substances species.

   32 identical Tc-HS test solutions (pH 8.5) were obtained by the reduction of 2.5×10^{-6} mol/L pertechnetate in magnetite/Gorleben groundwater suspensions. Sets of 4 test solutions were mixed (in a 1/1 ratio) with solutions of increasing La^{3+} concentrations varying between 10^{-4} and 1 Equiv./L (see table 7-1, experiment 2). This lead to HS concentrations in solution equal to 82.5 mg HS/L, and to La concentrations in solution between 5×10^{-5} and 0.5 Equiv./L.

3) Investigation of the influence of high La concentrations (beyond the threshold concentration) on the Tc sorption on humic substances.

   Duplicate Tc-HS containing test solutions were prepared at 5 different Tc contents and were mixed (1/1 proportion) with solutions containing increasing La^{3+} concentrations between 10^{-2} and 1 Equiv./L (see table 7-1, experiment 3). This lead to a HS concentration in solution equal to 82.5 mg HS/L, and to La concentrations in solution between 5×10^{-3} and 0.5 Equiv./L. The test Tc-HS solutions were obtained by the reduction of pertechnetate (5 initial concentrations between 10^{-6} and 10^{-3} mol/L) in magnetite/Gorleben groundwater suspensions. In all test solutions, the initial pH was 8.5 ± 0.1.

4) Investigation of kinetic and competition effects of La on the Tc sorption on humic substances.

   Two times four duplicate Tc-HS test solutions are mixed in a 1/1 ratio with 10^{-2} Equiv./L La^{3+} solutions. The test Tc-HS solutions were obtained by the reduction of pertechnetate (two initial Tc concentrations of 2.5×10^{-5} and 2.5×10^{-6} mol/L) in magnetite/Gorleben groundwater suspensions (see table 7-1, experiment 4). This lead to a HS concentration in solution equal to 82.5 mg HS/L, and to a La concentration in solution equal to 5×10^{-3} Equiv./L. In all test solutions, the initial pH was 8.5 ± 0.1. The centrifugation and analysis were performed respectively 15 minutes and 24 hours after end over end mixing.

5) Investigation of the influence of pH on the Tc – humic substance interaction.

First (see table 7-1, experiment 5a), Tc-HS test solutions were prepared by executing 5 pertechnetate reductions (2 at 2.5×10^{-5} mol/L and 3 at $2.5\text{x}10^{-6}$ mol/L Tc) in the pH range 6.2 – 7.9. Then 10^{-2} Equiv./L La^{3+}-solutions, brought to the same pH of the Tc-HS test solutions were added in a 1/1 ratio. This lead to a HS concentration in solution equal to 82.5 mg HS/L, and to a La concentration in solution equal to 5×10^{-3} Equiv./L. (Only Tc-HS solutions in a pH range between 6 and 8 are prepared because it was not possible to obtain stable La^{3+} solutions of pH higher than 8, because precipitates were formed. These La solutions of pH higher than 8 were also not able to precipitate all humic substances).

Second, as a reference, duplicate Tc-HS solutions (2.5×10^{-5} and 2.5×10^{-6} mol/L) were prepared as before but 10^{-2} Equiv./L La^{3+} solutions (pH = 5.2) were added in a 1/1 ratio (see table 7-1, experiment 5b).

Third, two times eight Tc-HS test solutions were prepared with respectively 2.5×10^{-5} mol/L Tc at pH 8.7 and 2.5×10^{-6} mol/L Tc at pH 8.3. The test solutions were mixed in a 1/1 ratio with 10^{-2} Equiv./L La solutions of different pH in the range of pH 4.5 to 8.1 (see table 7-1, experiment 5c).

Although, precipitation and settling is visually obvious upon La addition, all mixtures were further centrifuged (31919×g, 30 min) and the supernatants were analysed for ^{99}Tc (see $[Tc]_{La}$ in table 7-1) and pH. UV-Vis spectroscopy (at 280 nm) was performed on all supernatants, rendering the amount of humic substances left in solution. As a reference for zero absorbance, SGW was used.

7.3 Results and discussion

Table 7-1 gives a) an overview of the experimental conditions (initial Tc concentration and HS concentration) used to prepare the test solutions, b) the Tc concentration and pH of in the test solutions, the La concentration added to the test solutions, the pH of the added La solution and c) the equilibrium pH, the Tc concentration left in solution after La-precipitation and the calculated Tc-HS concentration. The Tc-HS concentration (= $[Tc\text{-}HS]_{La}$ in table 7-1) is calculated as $[Tc]_{test\ solution}/2 - [Tc]_{La}$.

7.3.1 The threshold La^{3+} concentration for full precipitation of humic substances

Figure 7-1 shows that adding a La concentration of 10^{-2} Equiv./L in a 1/1 ratio to the Tc-HS test solution is necessary for full removal of all Gorleben humic substances irrespective of the humic substance concentration of the test solutions. It was visually observed that the brown colour of the HS solution disappeared gradually. Beyond a concentration of 10^{-2} Equiv./L La^{3+} added to the test solutions, all supernatant solutions were colourless. However, figure 7-1 shows enhanced Absorbances beyond a concentration of 10^{-2} Equiv./L La added. Therefore, a control experiment was made

in which the absorbance of pure carbonate free La solutions was measured. The data are also depicted in figure 7-1 and also show that increasing absorption values beyond 10^{-2} Equiv./L La added coincide with the absorption values of the previous colourless supernatant solutions. Therefore, the increased absorption values are assigned to the high La^{3+} concentrations left in solution. Most probably La colloids or polynuclear complexes are formed.

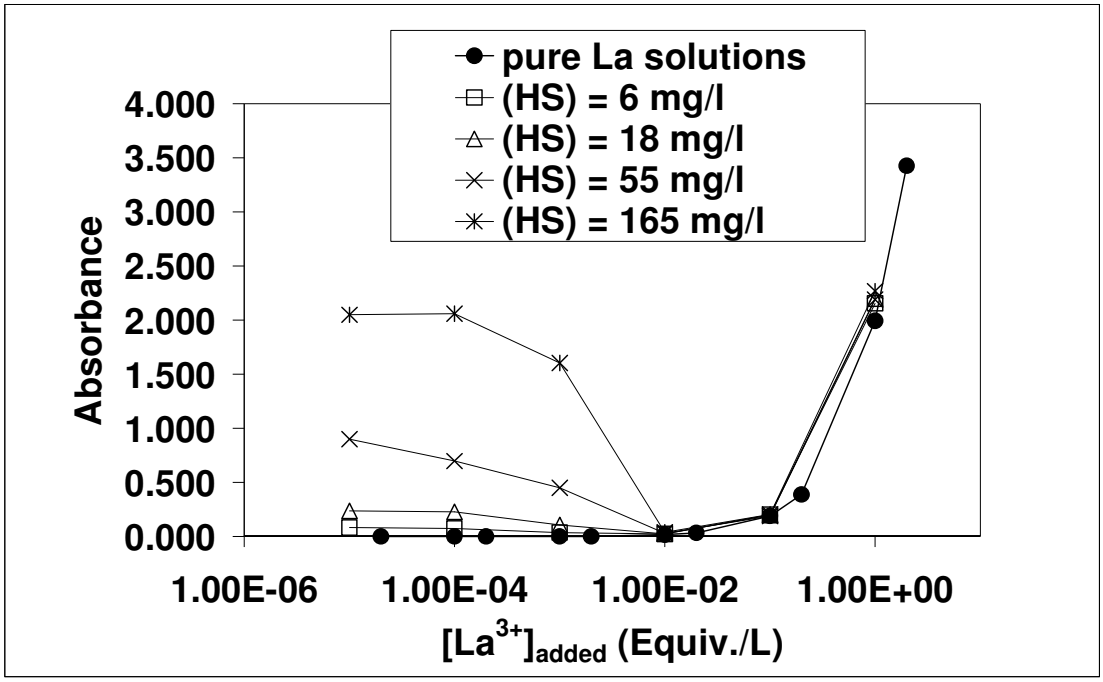

Figure 7-1. Supernatant absorbance (measured at 280 nm) as a function of the supernatant La solution concentration (Equiv./L) of Tc-HS test solutions containing originally 6 (□), 18 (Δ), 55 (×) and 165 (∗) mg/L humic substances in absence of Tc. The absorbance of pure carbonate free La solutions is also shown (●).

Bryan *et al.* (2001) proposed that the interaction of La with HS occurs by way of a charge neutralization mechanism given by equation (7-1):

$$La^{3+} + HS \rightleftharpoons La\text{-}HS \qquad (7\text{-}1)$$

$$\text{with } K = \frac{[La-HS]}{[La^{3+}]*(HS)} \qquad (7\text{-}2)$$

and where $[La^{3+}]$ is of course the free La concentration.

Maes *et al.* (1992a) have shown that precipitation of humic substances with trivalent $Co(NH_3)_6$ was only complete at nearly full charge neutralization. Assuming therefore that e.g. 99% charge neutralization is necessary for full precipitation of the HS then equation (7-2) predicts that [La-HS] / [HS] = K*$[La^{3+}]$ and thus that the same free $[La^{3+}]$ concentration is necessary irrespective of the HS concentration. This is shown as follows: assuming that 99% of the HS charge is compensated at 10^{-2} Equiv./L La added, one may calculate the La concentration left in solution after precipitation. The calculated La concentration then corresponds to 5.00×10^{-3} – $(0.99\times165/2\times10^{-3}\times5.23\times10^{-3}) = 4.57\times10^{-3}$ Equiv./L (for an initial HS concentration equal to 165

mgHS/L) to 5×10^{-3} – ($0.99\times6/2\times10^{-3}\times5.23\times10^{-3}$) = 4.98×10^{-3} Equiv./L (for an initial HS concentration equal to 6 mgHS/L). A Gorleben humic substance charge of 5.23×10^{-3} Equiv./g was taken (Kim *et al.*, 1990). Thus practically the same free La concentration is necessary to precipitate 82.5 mgHS/L or 3 mgHS/L as confirmed by the results in figure 7-1.

7.3.2 The threshold La^{3+} concentration for full precipitation of Tc- humic substance species

Figure 7-2 shows the variation of Absorbance at 280 nm (top) and the Tc content of the supernatant solutions (bottom) upon adding increasing La concentrations in 1/1 ratio to aliquots of solutions from experiment 2. The Tc content of the 32 duplicate test solutions before the addition of La^{3+} was between 8.68×10^{-7} and 1.03×10^{-6} mol/L. Such variations are commonly observed in Tc(VII) reduction.

Increasing La^{3+} concentrations again lead to the elimination of humic substances and also of Tc as respectively shown in figure 7-2a and b. As expected, the addition of a minimal total La concentration of 10^{-2} Equiv./L to the Tc-HS solutions is necessary for full removal of all Tc-humic substance species.

Since, the pH of the added La solutions decreased with increasing La concentration from pH 6.8 (10^{-4} Equiv./L La) to 4.9 (1 Equiv./L La) (see $pH_{La\ added}$ in table 7-1), the final pH of the supernatants after La-precipitation ranged from 8.3 (10^{-5} Equiv./L La) to 5.2 (1 Equiv./L La) as shown in table 7-1 (see pH_{La} in table 7-1). The influence of pH on the interaction between La and Tc-HS species and on the observed Tc-HS concentrations is discussed in experiment 5.

7.3.3 The influence of high La concentrations (beyond the threshold concentration) on the Tc interaction with humic substances

It is also noticeable in figure 7-2b, that the measured "free" Tc(IV) concentration ($[Tc]_{La}$) increased beyond the threshold concentration of 10^{-2} Equiv./L La^{3+} necessary for the complete precipitation of Tc-HS. This effect was studied in more detail in systems containing the same humic substances concentration (165 mg/L) but increasing initial pertechnetate concentrations (between 10^{-6} and 10^{-3} mol/L).

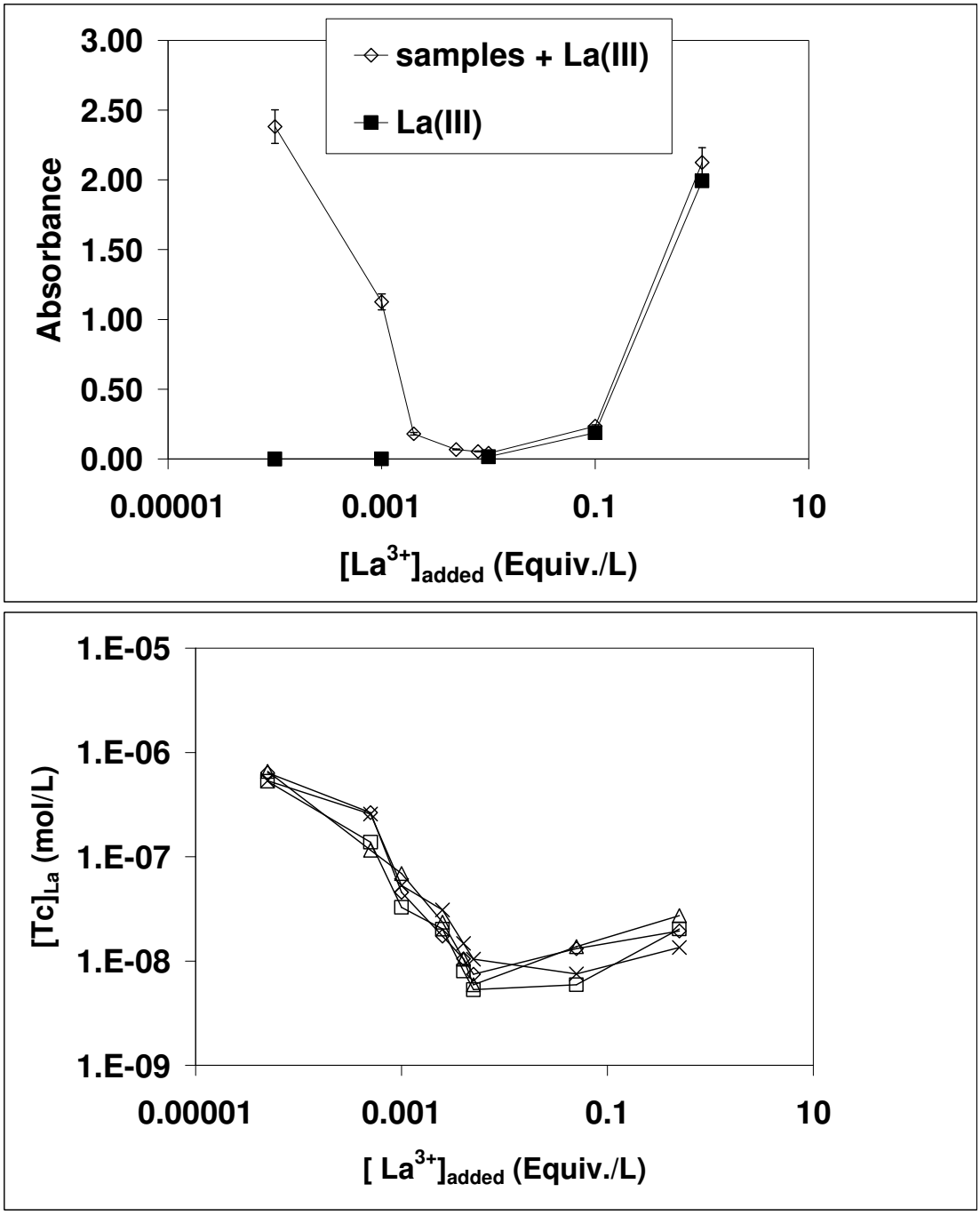

Figure 7-2. Effect of increasing La concentration (Equiv./L) added in 1/1 ratio to test solutions containing Tc-HS on a) the supernatant Absorbance (top), and b) the supernatant Tc(IV) concentration (bottom). In the top figure, the absorbance of pure La solutions are also given for comparison.

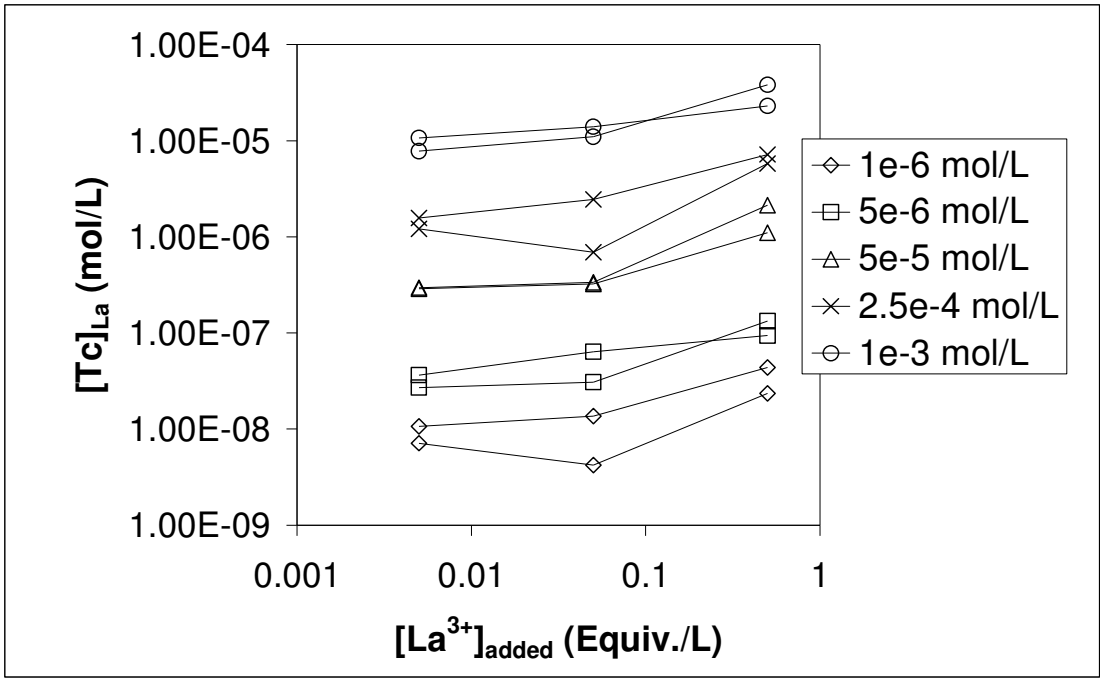

Figure 7-3. The Tc concentration (mol/L) left in the supernatant solution after La-precipitation as a function of the added La concentration (Equiv./L), for Tc-HS containing systems and increasing initial pertechnetate concentrations (between 10^{-6} and 10^{-3} mol/L).

Figure 7-3 again demonstrates that the Tc concentration left in solution passes through a minimum in the region between 10^{-2} and 0.1 Equiv./L added La^{3+}. Similar observations were made irrespective of the concentration of Tc present in solution. As before the Absorbance measurements tended to zero at 10^{-2} Equiv. /L La added (data not shown). Irrespective of the total Tc concentration in the systems, the Tc concentration after La-precipitation is enhanced by about a factor of two upon increasing the La concentration from 0.1 to 1 Equiv/L (see figure 7-3). The reason for this observation could be linked with the enhanced absorbance of the added La solutions in this La concentration range and could therefore be ascribed to the interaction of Tc with La- polynuclear complexes or La-colloids. Another and/or additional explanation could be a (small) competition between La^{3+} and certain Tc(IV) species for the available sites within the HS, inducing a (small) desorption of Tc(IV) from the HS. Such an effect is more pronounced when using higher La^{3+} concentrations. At present, the main conclusion is, however, that a concentration of 10^{-2} –10^{-1} Equiv./L La is capable to precipitate all HS and Tc-HS species without changes in the final Tc solution concentration. Adding higher concentrations of La should be avoided. In the following experiments only 0.01 Equiv/L La solutions (pH 5.2) were used as a standard procedure .

7.3.4 Kinetic effects of La^{3+} on the Tc – humic substance interaction

The contact time allowed upon mixing a La solution with a Tc-HS test solution was until now fixed at a gentle hand mixing and standing for 15 minutes (inside the glove box) followed by centrifugation (outside the glove box). Longer contact times could eventually lead to kinetic effects associated with the attainment of equilibrium in the binding of La with the HS and rearrangements of HS. The results given in table 7-1 (experiment 4) demonstrate however that no significant differences are noticeable between the Tc concentration left in solution after 15 minutes and 24 hours equilibration time with both La solutions.

7.3.5 The influence of pH on the Tc sorption on humic substances

In experiments 1, 2 and 3, it was observed that the pH of the supernatant after La application decreased with increasing La concentration, mainly due to the lower pH of the applied La solutions. Whether this pH variation influences the measured "free Tc" concentration due to potential changes in the Tc-HS interaction with pH, was therefore further investigated by 3 experiments (experiments 5a, 5b and 5c).

The results are given in table 7-1 and show that the final Tc concentration $[Tc]_{La}$ is identical independent of the initial pH of the Tc-HS test solutions (exp. 5a, pH range 6.2 – 7.9, average $[Tc]_{La}$ concentrations equal to 1.24×10^{-8} and 1.23×10^{-7} mol/L for $[Tc]_{initial}$ concentrations of respectively 2.5×10^{-6} and 2.5×10^{-5} mol/L) or the pH of the added La solution (exp. 5c, 10^{-2} Equiv./L, pH range 4.5 – 8.1, average $[Tc]_{La}$ concentrations equal to 1.21×10^{-8} and 1.35×10^{-7} mol/L for $[Tc]_{initial}$ concentrations of respectively 2.5×10^{-6} and 2.5×10^{-5} mol/L). The obtained Tc concentration $[Tc]_{La}$ in experiments 5a are also in agreement with the results after application of the standard procedure, in other words 10^{-2} Equiv./L La solution (pH 5.2) to the Tc-HS test solutions (exp. 5b, average $[Tc]_{La}$ concentrations equal to 1.26×10^{-8} and 1.22×10^{-7} mol/L for $[Tc]_{initial}$ concentrations of respectively 2.5×10^{-6} and 2.5×10^{-5} mol/L). Also the results of experiments 2 and 3 show identical $[Tc]_{La}$ concentrations irrespective of the equilibrium pH after La-precipitation as the aforementioned values when 10^{-2} Equiv./L La was added to similar test solutions as in experiment 5a, 5b and 5c.
Since the same free $[Tc]_{La}$ is obtained independent of the equilibrium pH after La addition, the pH drop due to the addition of La does not interfere with the interaction between Tc and HS. It is therefore proposed to use as a standard procedure the addition of 10^{-2} Equiv./L La (pH 5.2) in 1/1 proportion to a HS containing test solution.

Inspection of the data in table 7-1 and the results shown in figure 7-3 demonstrate that the Tc concentration after application of the proposed La-precipitation method (addition of 10^{-2} Equiv./L La excess) clearly varies, depending on the total Tc concentration in the Tc-HS test solution: for example average $[Tc]_{La}$ concentrations are obtained equal to 1.98×10^{-8}, 1.56×10^{-7} and 7.42×10^{-7} mol/L for $[Tc]_{initial}$ concentrations of respectively 5×10^{-6}, 5×10^{-5} and 2.5×10^{-4} mol/L (experiment 3).

This result shows that the La^{3+} precipitation method potentially allows to discriminate between the Tc fraction associated with HS and a fraction corresponding to the "free" (or unbound) Tc concentration. At different Tc test concentrations sufficient

duplicates were tested at different pH and showed constant $[Tc]_{La}$ concentrations and $[Tc\text{-}HS]_{La}$ concentrations independent of pH. The value of the Tc-HS interaction constant calculated for each case are therefore also constants. This value is calculated as follows:

$$K^{HS} = \frac{[Tc - HS]_{La}}{[Tc]_{La} * (HS)} \quad (7\text{-}3)$$

Attention is drawn to the fact that the used HS value is half the value as given in table 7-1, due to the experimental set-up of the La-precipitation method (two solutions are mixed in a 1/1 ratio).

For all experiments where a La concentration of 10^{-2} Equiv./L was used, the K^{HS} value was calculated and found equal to 2.7 ± 0.2. This value was being found independent of pH and total Tc concentration in the test solution. These latter observations are in line with previous results obtained in chapter 6. The value of K^{HS} however is slightly lower (in chapter 6 a value of 2.9 ± 0.3 was found).

In the next chapter, the La^{3+} precipitation method is applied to a large number of Tc-HS supernatant solutions in order to determine a conditional interaction constant for Tc(IV) and Gorleben humic substances via a quantification of the metal bound and metal free concentrations under variable experimental conditions. This allows a further verification of the La-precipitation method.

7.4 Conclusions

The precipitation of HS (and associated Tc) by La^{3+} is proposed as a quick method to determine free $[Tc]_{La}$ and $[Tc\text{-}HS]_{La}$ concentrations. All humic colloids are quantitatively precipitated from solution by adding an excess of La^{3+} sufficient to neutralise the carboxyl group capacity of the HS and to leave a free concentration of 5×10^{-3} Equiv./L La^{3+} in solution to force the neutralisation reaction to completion.

None of the investigated parameters, such as the (HS) concentration, the pH or the reaction time had an influence on the observed free $[Tc]_{La}$ concentration after La-precipitation of the humic substances. The free $[Tc]_{La}$ however depended on the Tc concentration in the test solutions. It is therefore proposed that the La-precipitation method can be used for direct speciation of Tc-HS and free Tc concentrations in solution, which are necessary to calculate the interaction constant between Tc(IV) and Gorleben humic substances. In the next chapter, the proposed La-precipitation method is used to calculate an interaction constant K^{HS} for the interaction between Tc(IV) and humic substances for a large number of Tc-HS supernatant solutions obtained under various experimental conditions.

Table 7-1. Experimental conditions and results of all experiments.
(*) Analysis after 24 h in stead of 15 min.
(**) estimated pH.

Experiment	Initial conditions		Test solution		Added La solution		Experimental results		
	$[Tc]_{initial}$ (mol/L)	[HS] (g/l)	$pH_{test\ solution}$	$[Tc]_{test\ solution}$ (mol/L)	$[La^{3+}]_{added}$ (Equiv./L)	$pH_{added\ La}$	pH_{La}	$[Tc]_{La}$ (mol/L)	$[Tc\text{-}HS]_{La}$ (mol/L)
1	-	0.165	8.5	-	10^{-5}	7.3	8.5	-	-
1	-	0.165	8.5	-	10^{-4}	6.8	8.3	-	-
1	-	0.165	8.5	-	10^{-3}	6.2	7.9	-	-
1	-	0.165	8.5	-	10^{-2}	5.5	6.1	-	-
1	-	0.165	8.5	-	0.1	5.2	5.5	-	-
1	-	0.165	8.5	-	1	4.9	5.3	-	-
1	-	0.055	8.5	-	10^{-5}	7.3	8.5	-	-
1	-	0.055	8.5	-	10^{-4}	6.8	8.2	-	-
1	-	0.055	8.5	-	10^{-3}	6.2	7.8	-	-
1	-	0.055	8.5	-	10^{-2}	5.5	6.1	-	-
1	-	0.055	8.5	-	0.1	5.2	5.6	-	-
1	-	0.055	8.5	-	1	4.9	5.2	-	-
1	-	0.018	8.5	-	10^{-5}	7.3	8.5	-	-
1	-	0.018	8.5	-	10^{-4}	6.8	8.3	-	-
1	-	0.018	8.5	-	10^{-3}	6.2	7.9	-	-
1	-	0.018	8.5	-	10^{-2}	5.5	6.1	-	-
1	-	0.018	8.5	-	0.1	5.2	5.5	-	-
1	-	0.018	8.5	-	1	4.9	5.3	-	-
1	-	0.006	8.5	-	10^{-5}	7.3	8.5	-	-
1	-	0.006	8.5	-	10^{-4}	6.8	8.4	-	-
1	-	0.006	8.5	-	10^{-3}	6.2	8.0	-	-
1	-	0.006	8.5	-	10^{-2}	5.5	6.1	-	-
1	-	0.006	8.5	-	0.1	5.2	5.5	-	-
1	-	0.006	8.5	-	1	4.9	5.4	-	-
1	-	0	-	-	2.0×10^{-4}	7.3	7.5	-	-
1	-	0	-	-	1.0×10^{-4}	7.1	7.2	-	-
1	-	0	-	-	2.0×10^{-5}	6.8	6.5	-	-
1	-	0	-	-	1.0×10^{-3}	6.5	6.2	-	-
1	-	0	-	-	2.0×10^{-4}	6.2	6	-	-
1	-	0	-	-	1.0×10^{-2}	6.0	5.5	-	-
1	-	0	-	-	0.02	5.5	5.3	-	-
1	-	0	-	-	0.1	5.2	5.2	-	-
1	-	0	-	-	0.2	5.0	5.0	-	-
1	-	0	-	-	1	4.9	4.9	-	-
1	-	0	-	-	2	4.7	4.7	-	-
2	2.5×10^{-6}	0.165	8.4	1.03×10^{-6}	10^{-4}	6.8	8.3	3.20×10^{-7}	1.96×10^{-7}
2	2.5×10^{-6}	0.165	8.5	9.20×10^{-7}	10^{-4}	6.8	8.2	2.64×10^{-7}	1.96×10^{-7}
2	2.5×10^{-6}	0.165	8.4	9.44×10^{-7}	10^{-4}	6.8	8.3	3.29×10^{-7}	1.43×10^{-7}
2	2.5×10^{-6}	0.165	8.6	8.68×10^{-7}	10^{-4}	6.8	8.2	2.67×10^{-7}	1.67×10^{-7}

Table 7-1 (continued). Experimental conditions and results of all experiments.
(*) Analysis after 24 h in stead of 15 min.
(**) estimated pH.

Experiment	Initial conditions		Test solution		Added La solution		Experimental results		
	$[Tc]_{initial}$ (mol/L)	[HS] (g/l)	$pH_{test\ solution}$	$[Tc]_{test\ solution}$ (mol/L)	$[La^{3+}]_{added}$ (Equiv./L)	$pH_{added\ La}$	pH_{La}	$[Tc]_{La}$ (mol/L)	$[Tc\text{-}HS]_{La}$ (mol/L)
2	2.5×10^{-6}	0.165	8.4	1.03×10^{-6}	10^{-3}	6.2	7.9	1.33×10^{-7}	3.82×10^{-7}
2	2.5×10^{-6}	0.165	8.5	9.20×10^{-7}	10^{-3}	6.2	7.9	6.90×10^{-8}	3.91×10^{-7}
2	2.5×10^{-6}	0.165	8.4	9.44×10^{-7}	10^{-3}	6.2	7.8	5.80×10^{-8}	4.14×10^{-7}
2	2.5×10^{-6}	0.165	8.6	8.68×10^{-7}	10^{-3}	6.2	8.0	1.28×10^{-7}	3.06×10^{-7}
2	2.5×10^{-6}	0.165	8.4	1.03×10^{-6}	2.0×10^{-3}	6.0	7.6	2.28×10^{-8}	4.92×10^{-7}
2	2.5×10^{-6}	0.165	8.5	9.20×10^{-7}	2.0×10^{-3}	6.0	7.5	1.64×10^{-8}	4.44×10^{-7}
2	2.5×10^{-6}	0.165	8.4	9.44×10^{-7}	2.0×10^{-3}	6.0	7.6	3.45×10^{-8}	4.38×10^{-7}
2	2.5×10^{-6}	0.165	8.6	8.68×10^{-7}	2.0×10^{-3}	6.0	7.6	2.65×10^{-8}	4.08×10^{-7}
2	2.5×10^{-6}	0.165	8.4	1.03×10^{-6}	5.0×10^{-3}	5.8	6.9	8.65×10^{-9}	5.05×10^{-7}
2	2.5×10^{-6}	0.165	8.5	9.20×10^{-7}	5.0×10^{-3}	5.8	6.8	1.01×10^{-8}	4.50×10^{-7}
2	2.5×10^{-6}	0.165	8.4	9.44×10^{-7}	5.0×10^{-3}	5.8	6.9	1.18×10^{-8}	4.60×10^{-7}
2	2.5×10^{-6}	0.165	8.6	8.68×10^{-7}	5.0×10^{-3}	5.8	7.0	1.55×10^{-8}	4.19×10^{-7}
2	2.5×10^{-6}	0.165	8.4	1.03×10^{-6}	8.0×10^{-3}	5.6	6.6	5.25×10^{-9}	5.10×10^{-7}
2	2.5×10^{-6}	0.165	8.5	9.20×10^{-7}	8.0×10^{-3}	5.6	6.5	4.00×10^{-9}	4.56×10^{-7}
2	2.5×10^{-6}	0.165	8.4	9.44×10^{-7}	8.0×10^{-3}	5.6	6.7	5.20×10^{-9}	4.67×10^{-7}
2	2.5×10^{-6}	0.165	8.6	8.68×10^{-7}	8.0×10^{-3}	5.6	6.5	7.40×10^{-9}	4.27×10^{-7}
2	2.5×10^{-6}	0.165	8.4	1.03×10^{-6}	10^{-2}	5.5	6.1	3.75×10^{-9}	5.10×10^{-7}
2	2.5×10^{-6}	0.165	8.5	9.20×10^{-7}	10^{-2}	5.5	6.2	2.66×10^{-9}	4.58×10^{-7}
2	2.5×10^{-6}	0.165	8.4	9.44×10^{-7}	10^{-2}	5.5	6.0	2.97×10^{-9}	4.69×10^{-7}
2	2.5×10^{-6}	0.165	8.6	8.68×10^{-7}	10^{-2}	5.5	6.1	5.20×10^{-9}	4.29×10^{-7}
2	2.5×10^{-6}	0.165	8.4	1.03×10^{-6}	0.1	5.2	5.5	6.55×10^{-9}	5.10×10^{-7}
2	2.5×10^{-6}	0.165	8.5	9.20×10^{-7}	0.1	5.2	5.6	2.97×10^{-9}	4.57×10^{-7}
2	2.5×10^{-6}	0.165	8.4	9.44×10^{-7}	0.1	5.2	5.5	6.85×10^{-9}	4.65×10^{-7}
2	2.5×10^{-6}	0.165	8.6	8.68×10^{-7}	0.1	5.2	5.5	3.75×10^{-9}	4.31×10^{-7}
2	2.5×10^{-6}	0.165	8.4	1.03×10^{-6}	1	4.9	5.3	9.70×10^{-9}	5.05×10^{-7}
2	2.5×10^{-6}	0.165	8.5	9.20×10^{-7}	1	4.9	5.2	1.02×10^{-8}	4.50×10^{-7}
2	2.5×10^{-6}	0.165	8.4	9.44×10^{-7}	1	4.9	5.3	1.36×10^{-8}	4.59×10^{-7}
2	2.5×10^{-6}	0.165	8.6	8.68×10^{-7}	1	4.9	5.3	6.70×10^{-9}	4.28×10^{-7}
3	10^{-6}	0.165	8.5	4.31×10^{-7}	10^{-2}	5.5	6.1(**)	3.56×10^{-9}	2.12×10^{-7}
3	10^{-6}	0.165	8.6	5.48×10^{-7}	10^{-2}	5.5	6.1(**)	5.35×10^{-9}	2.69×10^{-7}
3	10^{-6}	0.165	8.5	4.31×10^{-7}	0.1	5.2	5.5(**)	2.12×10^{-9}	2.14×10^{-7}
3	10^{-6}	0.165	8.6	5.48×10^{-7}	0.1	5.2	5.5(**)	1.80×10^{-9}	2.74×10^{-7}
3	10^{-6}	0.165	8.5	4.31×10^{-7}	1	4.9	5.3(**)	1.18×10^{-8}	2.04×10^{-7}
3	10^{-6}	0.165	8.6	5.48×10^{-7}	1	4.9	5.3(**)	2.18×10^{-8}	2.52×10^{-7}
3	5×10^{-6}	0.165	8.4	2.34×10^{-6}	10^{-2}	5.5	6.1(**)	1.35×10^{-8}	1.16×10^{-6}
3	5×10^{-6}	0.165	8.6	1.75×10^{-6}	10^{-2}	5.5	6.1(**)	1.82×10^{-8}	8.55×10^{-7}
3	5×10^{-6}	0.165	8.4	2.34×10^{-6}	0.1	5.2	5.5(**)	1.54×10^{-8}	1.17×10^{-6}

Table 7-1 (continued). Experimental conditions and results of all experiments.
(*) Analysis after 24 h in stead of 15 min.
(**) estimated pH.

Experiment	Initial conditions		Test solution		Added La solution		Experimental results		
	$[Tc]_{initial}$ (mol/L)	[HS] (g/l)	$pH_{test\ solution}$	$[Tc]_{test\ solution}$ (mol/L)	$[La^{3+}]_{added}$ (Equiv./L)	$pH_{added\ La}$	pH_{La}	$[Tc]_{La}$ (mol/L)	$[Tc\text{-}HS]_{La}$ (mol/L)
3	5×10^{-6}	0.165	8.6	1.75×10^{-6}	0.1	5.2	$5.5^{(**)}$	3.19×10^{-8}	8.45×10^{-7}
3	5×10^{-6}	0.165	8.4	2.34×10^{-6}	1	4.9	$5.3^{(**)}$	6.65×10^{-8}	1.11×10^{-6}
3	5×10^{-6}	0.165	8.6	1.75×10^{-6}	10^{-2}	5.5	$5.3^{(**)}$	4.70×10^{-8}	8.30×10^{-7}
3	5×10^{-5}	0.165	8.6	2.07×10^{-5}	10^{-2}	5.5	$6.1^{(**)}$	1.48×10^{-7}	1.02×10^{-5}
3	5×10^{-5}	0.165	8.4	1.12×10^{-5}	10^{-2}	5.5	$6.1^{(**)}$	1.45×10^{-7}	5.45×10^{-6}
3	5×10^{-5}	0.165	8.6	2.07×10^{-5}	0.1	5.2	$5.5^{(**)}$	1.69×10^{-7}	1.02×10^{-5}
3	5×10^{-5}	0.165	8.4	1.12×10^{-5}	0.1	5.2	$5.5^{(**)}$	1.62×10^{-7}	5.45×10^{-6}
3	5×10^{-5}	0.165	8.6	2.07×10^{-5}	1	4.9	$5.3^{(**)}$	1.07×10^{-6}	9.30×10^{-6}
3	5×10^{-5}	0.165	8.4	1.12×10^{-5}	1	4.9	$5.3^{(**)}$	5.50×10^{-7}	5.05×10^{-6}
3	2.5×10^{-4}	0.165	8.5	8.08×10^{-5}	10^{-2}	5.5	$6.1^{(**)}$	6.05×10^{-7}	3.98×10^{-5}
3	2.5×10^{-4}	0.165	8.5	1.11×10^{-4}	10^{-2}	5.5	$6.1^{(**)}$	7.85×10^{-7}	5.45×10^{-5}
3	2.5×10^{-4}	0.165	8.5	8.08×10^{-5}	0.1	5.2	$5.5^{(**)}$	3.46×10^{-7}	4.01×10^{-5}
3	2.5×10^{-4}	0.165	8.5	1.11×10^{-4}	0.1	5.2	$5.5^{(**)}$	1.23×10^{-6}	5.45×10^{-5}
3	2.5×10^{-4}	0.165	8.5	8.08×10^{-5}	1	4.9	$5.3^{(**)}$	2.90×10^{-6}	3.75×10^{-5}
3	2.5×10^{-4}	0.165	8.5	1.11×10^{-4}	1	4.9	$5.3^{(**)}$	3.60×10^{-6}	5.20×10^{-5}
3	10^{-3}	0.165	8.5	5.43×10^{-4}	10^{-2}	5.5	$6.1^{(**)}$	3.90×10^{-6}	2.68×10^{-4}
3	10^{-3}	0.165	8.4	6.21×10^{-4}	10^{-2}	5.5	$6.1^{(**)}$	5.35×10^{-6}	3.05×10^{-4}
3	10^{-3}	0.165	8.5	5.43×10^{-4}	0.1	5.2	$5.5^{(**)}$	5.50×10^{-6}	2.66×10^{-4}
3	10^{-3}	0.165	8.4	6.21×10^{-4}	0.1	5.2	$5.5^{(**)}$	7.00×10^{-6}	3.04×10^{-4}
3	10^{-3}	0.165	8.5	5.43×10^{-4}	1	4.9	$5.3^{(**)}$	1.91×10-5	2.53×10^{-4}
3	10^{-3}	0.165	8.4	6.21×10^{-4}	1	4.9	$5.3^{(**)}$	1.15×10-5	2.99×10^{-4}
4	5×10^{-5}	0.165	8.5	2.06×10^{-5}	10^{-2}	5.5	$6.1^{(**)}$	1.35×10^{-7}	1.02×10^{-5}
4	5×10^{-5}	0.165	8.5	2.06×10^{-5}	10^{-2}	5.5	$6.1^{(**)}$	1.55×10^{-7}	1.02×10^{-5}
4	5×10^{-5}	0.165	8.6	1.95×10^{-5}	10^{-2}	5.5	$6.1^{(**)}$	1.75×10^{-7}	9.60×10^{-6}
4	5×10^{-5}	0.165	8.6	1.95×10^{-5}	10^{-2}	5.5	$6.1^{(**)}$	1.00×10^{-7}	9.65×10^{-6}
4 (*)	5×10^{-5}	0.165	8.5	2.06×10^{-5}	10^{-2}	5.5	$6.1^{(**)}$	1.65×10^{-7}	1.02×10^{-5}
4 (*)	5×10^{-5}	0.165	8.5	2.06×10^{-5}	10^{-2}	5.5	$6.1^{(**)}$	2.15×10^{-7}	1.01×10^{-5}
4 (*)	5×10^{-5}	0.165	8.6	1.95×10^{-5}	10^{-2}	5.5	$6.1^{(**)}$	1.30×10^{-7}	9.60×10^{-6}
4 (*)	5×10^{-5}	0.165	8.6	1.95×10^{-5}	10^{-2}	5.5	$6.1^{(**)}$	1.25×10^{-7}	9.65×10^{-6}
5a	$2.5x10^{-6}$	0.165	6.2	5.76×10^{-7}	10^{-2}	6.2	6.2	1.29×10^{-8}	2.75×10^{-7}
5a	$2.5x10^{-6}$	0.165	7	7.99×10^{-7}	10^{-2}	7	7	1.09×10^{-8}	3.89×10^{-7}
5a	$2.5x10^{-6}$	0.165	7.9	8.85×10^{-7}	10^{-2}	7.9	7.9	1.34×10^{-8}	4.29×10^{-7}
5a	$2.5x10^{-5}$	0.165	6.9	8.15×10^{-6}	10^{-2}	6.9	6.9	1.47×10^{-7}	3.93×10^{-6}
5a	$2.5x10^{-5}$	0.165	7.9	9.13×10^{-6}	10^{-2}	7.9	7.9	9.80×10^{-8}	4.47×10^{-6}
5b	$2.5x10^{-6}$	0.165	6.2	5.76×10^{-7}	10^{-2}	5.5	5.8	1.08×10^{-8}	2.78×10^{-7}
5b	$2.5x10^{-6}$	0.165	7.0	7.99×10^{-7}	10^{-2}	5.5	6.1	1.41×10^{-8}	3.86×10^{-7}
5b	$2.5x10^{-6}$	0.165	7.9	8.85×10^{-7}	10^{-2}	5.5	6.2	1.29×10^{-8}	4.30×10^{-7}

Table 7-1 (continued). Experimental conditions and results of all experiments.
(*) Analysis after 24 h in stead of 15 min.
(**) estimated pH.

Experiment	Initial conditions		Test solution		Added La solution		Experimental results		
	$[Tc]_{initial}$ (mol/L)	[HS] (g/l)	$pH_{test\ solution}$	$[Tc]_{test\ solution}$ (mol/L)	$[La^{3+}]_{added}$ (Equiv./L)	$pH_{added\ La}$	pH_{La}	$[Tc]_{La}$ (mol/L)	$[Tc\text{-}HS]_{La}$ (mol/L)
5b	$2.5x10^{-5}$	0.165	6.5	8.15×10^{-6}	10^{-2}	5.5	6.0	1.26×10^{-7}	3.95×10^{-6}
5b	$2.5x10^{-5}$	0.165	7.9	9.13×10^{-6}	10^{-2}	5.5	6.1	1.18×10^{-7}	4.55×10^{-6}
5c	2.5×10^{-6}	0.165	8.3	1.12×10^{-6}	10^{-2}	8.1	8.0	1.03×10^{-8}	5.50×10^{-7}
5c	2.5×10^{-6}	0.165	8.3	9.85×10^{-7}	10^{-2}	8.1	8.1	1.58×10^{-8}	4.77×10^{-7}
5c	2.5×10^{-6}	0.165	8.3	1.12×10^{-6}	10^{-2}	6.5	7.2	1.25×10^{-8}	5.48×10^{-7}
5c	2.5×10^{-6}	0.165	8.3	9.85×10^{-7}	10^{-2}	6.5	7.2	1.44×10^{-8}	4.78×10^{-7}
5c	2.5×10^{-6}	0.165	8.3	1.12×10^{-6}	10^{-2}	5.3	6.2	1.25×10^{-8}	5.48×10^{-7}
5c	2.5×10^{-6}	0.165	8.3	9.85×10^{-7}	10^{-2}	5.3	6.2	1.04×10^{-8}	4.82×10^{-7}
5c	2.5×10^{-6}	0.165	8.3	1.12×10^{-6}	10^{-2}	4.5	5.6	9.60×10^{-9}	5.50×10^{-7}
5c	2.5×10^{-6}	0.165	8.3	9.85×10^{-7}	10^{-2}	4.5	5.6	1.13×10^{-8}	4.81×10^{-7}
5c	2.5×10^{-5}	0.165	8.7	1.09×10^{-5}	10^{-2}	8.1	8.3	1.53×10^{-7}	5.30×10^{-6}
5c	2.5×10^{-5}	0.165	8.7	1.21×10^{-5}	10^{-2}	8.1	8.3	1.61×10^{-7}	5.90×10^{-6}
5c	2.5×10^{-5}	0.165	8.7	1.09×10^{-5}	10^{-2}	6.5	7.5	1.70×10^{-7}	5.30×10^{-6}
5c	2.5×10^{-5}	0.165	8.7	1.21×10^{-5}	10^{-2}	6.5	7.4	1.62×10^{-7}	5.90×10^{-6}
5c	2.5×10^{-5}	0.165	8.7	1.09×10^{-5}	10^{-2}	5.3	7.0	1.34×10^{-7}	5.30×10^{-6}
5c	2.5×10^{-5}	0.165	8.7	1.21×10^{-5}	10^{-2}	5.3	7.0	1.30×10^{-7}	5.90×10^{-6}
5c	2.5×10^{-5}	0.165	8.7	1.09×10^{-5}	10^{-2}	4.5	6.1	4.47×10^{-8}	5.40×10^{-6}
5c	2.5×10^{-5}	0.165	8.7	1.21×10^{-5}	10^{-2}	4.5	6.1	1.28×10^{-7}	5.90×10^{-6}

CHAPTER 8

QUANTIFICATION OF THE CONDITIONAL INTERACTION BETWEEN TECHNETIUM(IV) AND GORLEBEN HUMIC SUBSTANCES USING THE LA-PRECIPITATION METHOD

8.1 Introduction

In the previous chapter, La^{3+} was used to separate Tc(IV) – humic substance species from the free inorganic Tc(IV) species. The conditions to obtain a quick and quantitative experimental method for the separation were investigated. None of the investigated parameters (the (HS) concentration, the pH or the time of application of the method) had an influence on the observed [Tc] concentration after La-precipitation of the humic substances. The free $[Tc]_{La}$ concentration however depended on the Tc concentration in the test solutions. It was therefore proposed that the La-precipitation method can be used for direct speciation of Tc-HS and free Tc concentrations in solution to quantify the interaction between Tc(IV) and Gorleben humic substances. The purpose of this chapter is therefore to quantify and investigate the interaction between colloidal Tc(IV) species and Gorleben humic substances using the proposed La-precipitation method and to compare the obtained $LogK^{HS}$ value with the value derived through the modified Schubert approach (see chapter 6).

8.2 Experimental set-up

All experiments were carried out at ambient temperature (22°C) in a controlled atmosphere glove box flushed with a mixture of N_2 (95%) and H_2 (5%). The box atmosphere was circulated over a catalytic converter (Pt) in order to remove excessive oxygen. The mean concentration of O_2 in the glove box throughout the experiments was below 2 ppm.

Gorleben groundwater (GoHy-2227 - GW) containing 165 mg/L organic matter (82 mg/L organic carbon) and Gorleben sand (GS) from the potential disposal site at Gorleben (Germany) were used as supplied by Forschungszentrum Karlsruhe (Germany). The water was stored in a closed bottle inside the glove box. Synthetic Gorleben groundwater (SGW) was prepared as a mixture of 3.2×10^{-2} mol/L NaCl and 8×10^{-3} mol/L $NaHCO_3$, and was taken as representative for the inorganic composition of the natural Gorleben groundwater (Artinger *et al.*, 1998a). Diluted Gorleben

groundwater solutions were prepared by mixing different volumes of natural Gorleben groundwater and SGW. This resulted in solutions containing humic substance concentrations between 6 and 165 mg/L HS. Solutions with increased humic substance concentrations were prepared by mixing (for a period of three weeks) different amounts of Gorleben sand (between 5 and 20 mg) and natural Gorleben groundwater solutions (20 ml), and taking the supernatant solutions of these systems after centrifugation (30 min, 39191×g). These solutions contained dissolved humic substance concentrations between 165 and 520 mg/L. Artinger *et al.* (2000) observed previously that in similar systems increased dissolved humic substance concentrations are obtained due to the dissolution of charcoal-like particles present in the Gorleben sand. No differences between the humic substances present in either the original Gorleben groundwater solutions or the 'newly' formed solutions were detected.

Magnetite (Fe_3O_4) and pyrite (FeS_2) were purchased from a local mineral shop. Small sized fractions (<125 μm) of the minerals were obtained by sieving after crushing the solids in the glove box using an Agate mortar and pestle. The phase purity was verified by powder X-ray diffraction measurements.

All chemicals were of analytical grade. The water used was de-ionised, treated by a Water Purification System (Milli-Q) and finally boiled out to obtain oxygen-free water (Milli-Q water). ^{99}Tc was purchased from Amersham in 0.1 mol/L NH_4OH aqueous solution. The Tc concentration was verified from absolute activity measurements. TcO_4^- solutions were prepared by diluting aliquots of a stock solution (5×10^{-2} mol/L TcO_4^-) in a SGW solution. A stock solution of 10 Equiv./L La^{3+} was prepared in the glove box by dissolving $La(NO_3)_3$ (Merck) in Milli-Q water. Before application of the La-precipitation method, freshly prepared 0.01 Equiv./L La^{3+} solutions were prepared by diluting the stock solution in Milli-Q water.

Six series of batch experiments were prepared in polypropylene vials in the glove box. The first four series were exactly the same as those studied in chapter 6. We repeat their preparation for completeness:

1) Series 1 consisted of 19 ml synthetic Gorleben groundwater (absence of humic substances) mixed with 50 to 200 mg Fe_3O_4.
2) Series 2 consisted of 19 ml natural Gorleben groundwater mixed with 10 to 500 mg Fe_3O_4.
3) Series 3 consisted of the diluted (16.5 – 165 mg/L HS) and more concentrated (165 – 520 mg/L HS) natural Gorleben groundwater solutions mixed with 50 mg Fe_3O_4.
4) In series 4, the influence of pH was investigated by preparing systems containing 19 ml natural Gorleben groundwater mixed with 50 mg Fe_3O_4, but by adding small volumes of 0.1 mol/L NaOH or HCl to cover a pH range between 7 and 10.5.

Two additional experimental series were conducted:

5) Series 5 was studied to mimic in situ Gorleben conditions and consisted in mixing 19 ml natural Gorleben groundwater with 4 to12 g Gorleben sand.
6) In series 6, Pyrite instead of Magnetite was used as the reducing solid. These systems were prepared by mixing 50 mg FeS_2 with 19 ml diluted (16.5 – 165 mg/L HS) Gorleben groundwater.

To ensure suitable conditions for pertechnetate reduction, the series containing magnetite or pyrite needed 3 days of pre-equilibration, whereas the series containing Gorleben sand needed 21 days. Subsequently, 1 ml of pertechnetate solutions with varying Tc concentrations (between 10^{-5} and 1.2×10^{-2} mol/L) in SGW were added to obtain total pertechnetate starting concentrations varying between 5×10^{-7} and 6.5×10^{-4} mol/L. The vials were turned slowly head over head to ensure good mixing.

Since pertechnetate reduction is known to be kinetically controlled (Cui and Eriksen, 1996), duplicates of some systems were studied as a function of time in order to estimate when equilibrium was reached. The systems were centrifuged (30 min, 39191×g) and the supernatant was analysed for ^{99}Tc, pH, Eh and humic substance concentration using the methodologies described in Chapter 3.

Gel permeation chromatography was performed on the supernatant solutions of nearly all experiments to verify the presence of Tc-HS, reduced free Tc species and/or pertechnetate species using the method described previously (Chapter 3). The gel permeation chromatograms of all monitored solutions showed the presence of colloidal Tc species (Tc-HS and/or reduced free Tc) and proved that pertechnetate species were absent at equilibrium.

The La-precipitation method was only applied on supernatants of the previously described systems at equilibrium. Aliquots of 5 ml of the supernatants were mixed with equal volumes of freshly prepared 0.01 Equiv./L La^{3+} solutions in polypropylene vials. This resulted in a La^{3+} concentration of 5×10^{-3} Equiv./L. The samples were gently handmixed and left to stand for 15 minutes inside the glovebox and were then centrifuged (Beckmann JA-20, 30 min, 39191×g, cut-off value 50 nm) outside the glovebox. Upon reintroduction in the box the supernatant was analysed for ^{99}Tc, pH and Absorbance. The addition of La^{3+} did precipitate all HS and Tc associated with HS ($[Tc\text{-}HS]_{La}$). The inorganic Tc(IV) concentration left in the supernatant solution after La-precipitation is called $[Tc]_{La}$.

8.3 Results and discussion

8.3.1 Quantification of the interaction between Tc(IV) and Gorleben humic substances

Table 8-1 contains the experimental conditions (S/L ratio, initial Tc dose and HS concentration) of pertechnetate reduction in the 6 studied systems together with the pH and $[Tc]_{equilibrium}$ concentration in the supernatant solution at equilibrium and after centrifugation. The Tc speciation data ($[Tc]_{La}$ and $[Tc\text{-}HS]_{La}$) measured by the La-precipitation method on the former supernatant solutions are also given in table 8-1. After centrifugation no sorption of humic substances on the solid Magnetite phase was observed. Sufficient systems were regularly controlled by gel permeation chromatography and proved the absence of pertechnetate in the equilibrium solutions.

It can be deduced from table 8-1 that a large part of the initial Tc must be present in the centrifugate either as $TcO_2.nH_2O$ precipitate or adsorbed on the inorganic surfaces (Magnetite, Pyrite and Gorleben sand). Differences are observed between these three

types of systems in their reduction kinetics and in the total Tc level at equilibrium. These differences are probably due to the different redox capacities[9] and sorption affinities of each surface (data not shown). However, in the present chapter we will only concentrate on the interaction of Tc with humic substances present in the equilibrium solution. In other words we will not focus on the distribution of Tc between the solid and solution phase. It should however be kept in mind that the presence of the reducing solid phase is absolutely necessary in order to mimic the reduction of pertechnetate in geological conditions and consequently to obtain an association between the reduced Tc(IV)-species and humic substances.

The equilibrium Tc concentration ranges from 10^{-9} mol/L to 10^{-5} mol/L and in most cases exceeds the theoretical solubility (10^{-9} – 10^{-8} mol/L) of the amorphous precipitate $TcO_2.nH_2O$, indicating that mononuclear, polynuclear or colloidal Tc species are present in the equilibrium solutions. Occasional gel permeation chromatograms showed for humic substance containing supernatants, indeed the presence of Tc-HS species and in humic free supernatants, Tc species of larger hydrodynamic size (data not shown).

It is also important to notice in table 8-1 (series 1, absence of HS) that free Tc(IV) concentrations after La precipitation ($[Tc]_{La}$) were recorded to be below and above the theoretical solubility of the Tc(IV) precipitate. All supernatant solutions after La-precipitation were clear and their Absorbances tended to zero. Hence, after La-precipitation of some supernatant solutions, still mononuclear, polynuclear or colloidal Tc(IV) species are present.

In chapter 6, the interaction of Tc(IV) species with HS was defined as:

$$\Sigma[TcO(OH)_2]_n + HS \rightleftharpoons \Sigma\,[TcO(OH)_2]_n\text{-}HS \qquad (8\text{-}1)$$

The corresponding conditional interaction constant K^{HS} reads:

$$K^{HS} = \frac{\left[\Sigma\left[TcO(OH)_2\right]_n - HS\right]}{\left[\Sigma\left[TcO(OH)_2\right]_n\right]*(HS)} \qquad (8\text{-}2)$$

This K^{HS} value was determined from a modified Schubert approach.

For the present results, the following reaction is proposed in analogy with the previous equation (8-1):

$$Tc_{La} + HS \rightleftharpoons Tc\text{-}HS_{La} \qquad (8\text{-}3)$$

$$\text{with } K^{HS} = \frac{\left[Tc - HS\right]_{La}}{\left[Tc\right]_{La}(HS)}, \qquad (8\text{-}4)$$

The experimental $[Tc]_{La}$ and $[Tc\text{-}HS]_{La}$ concentrations are therefore taken as representative for respectively the free inorganic $\Sigma[TcO(OH)_2]_n$ and the HS bound Tc(IV) concentrations. The (HS) in equations (8-3) and (8-4) stands for the amount of humic substances in solution, given in g/L. This amount can be considered equal to the free HS content since the Tc occupation is negligeable compared to the functional group capacity of the HS.

[9] The redox capacity of a surface can be quantified as the maximum amount of oxidising agent such as $[Fe(CN)_6]^{3-}$ at constant pH consumed per gram of sorbent (reducing solid phase).

$[Tc\text{-}HS]_{La}$ was calculated as the difference between half the total experimental Tc concentration ($[Tc]_{equilibrium}$) and the experimental Tc concentration after application of the La-precipitation method ($[Tc]_{La}$).:

$$[Tc\text{-}HS]_{La} = [Tc]_{equilibrium}/2 - [Tc]_{La} \quad (8\text{-}5)$$

Attention is drawn to the fact that for all further calculations half the total experimental Tc concentration ($[Tc]_{equilibrium}$) and half the (HS) concentration given in table 8-1 are taken due to the experimental set-up of the La-precipitation method (two solutions are mixed in a 1/1 ratio).

Figure 8-1 shows all measured distributions of Tc in solution between free Tc(IV) species ($[Tc]_{La}$) and the Tc species associated with the Gorleben humic substances per g HS ($[Tc\text{-}HS]_{La}/(HS)$). The results in figure 8-1 are presented as a log-log plot and correspond grossly to an adsorption isotherm of Tc on "dissolved" humic substances in solution. The slope of this isotherm can be considered as a first approximation of the aforementioned K^{HS} value in equation (8-4). Determination of the regression line (using the least-squares method) gives a value for the slope equal to 240.21 with a correlation coefficient R^2 of 0.77. The obtained Log K^{HS} value thus equals 2.4.

The experimental values of all conditional interaction constants as defined in equation (8-4) are calculated and given in table 8-1 and are also depicted in figure 8-2 versus the pH of the supernatant equilibrium solutions of the various systems studied and which were sampled for Tc speciation via La-precipitation. A spreading of about one order of magnitude on the conditional interaction constant is observed. The average K^{HS} value is equal to 2.6 ($\pm$ 0.3) and independent of the pH of the tested supernatant solution (see figure 8-2) and the equilibrium [Tc] concentration (see table 8-1). Further inspection of figure 8-2 shows that the nature of the surfaces used to create reducing conditions has no effect on the interaction of Tc with humic substances.

In figure 8-3, the conditional interaction constants are shown as a function of the Tc loading on the humic substances (mol Tc /g HS). It is clear that the conditional interaction constant remains constant with the Tc loading on the humic substances over a broad Tc loading range (10^{-3} – 10^{-6} mol Tc/g HS). Such observation is highly unusual for “normal” metal-humic substance complexation reactions. Indeed due to the heterogeneity of the functional groups in humic substances, metal complexation reactions are typically known to depend on the loading (Hummel, 1997 and 1999).

Similar results were obtained via the modified Schubert approach presented in Chapter 6 and by Maes et al. (2003) for the interaction between Tc(IV) and respectively Gorleben and Boom clay humic substances. The proposed interaction mechanism was called “inclusion of colloidal species” to distinguish it from “complex formation”.

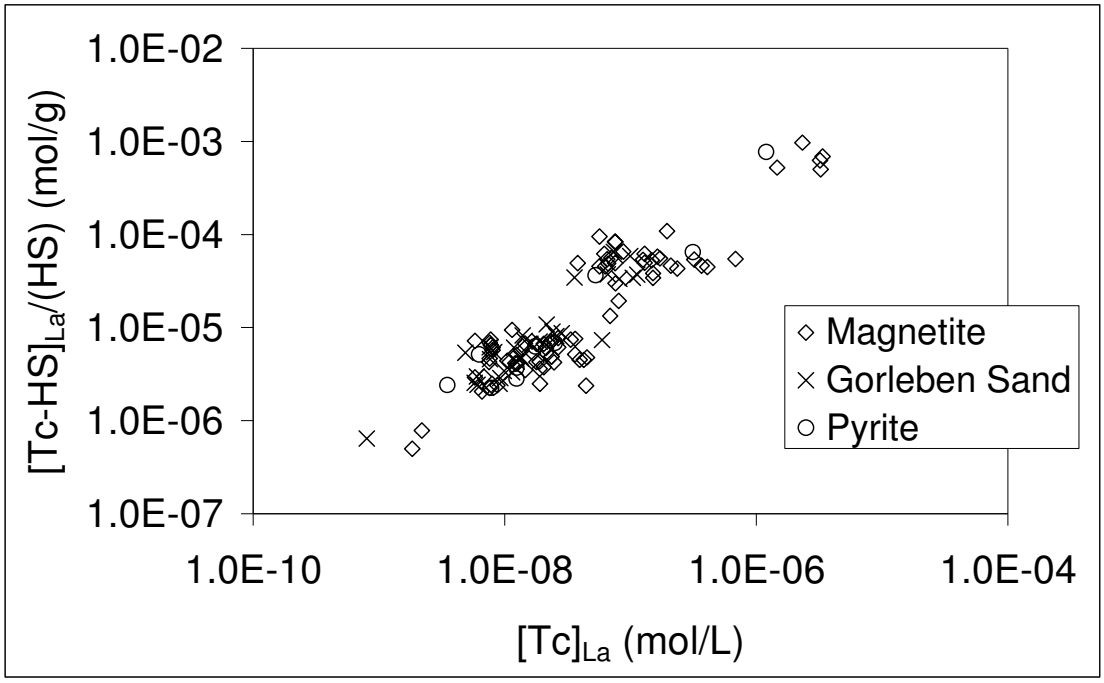

Figure 8-1. The Tc concentration associated with humic substances per gram HS (mol/g) as a function of the free inorganic Tc concentration (mol/L) as obtained via the La-precipitation method on series 2 till 6. Reduced Tc-HS species are obtained after reduction of pertechnetate in a Gorleben groundwater solution with the aid of magnetite (◊), Gorleben sand (x) and pyrite (o).

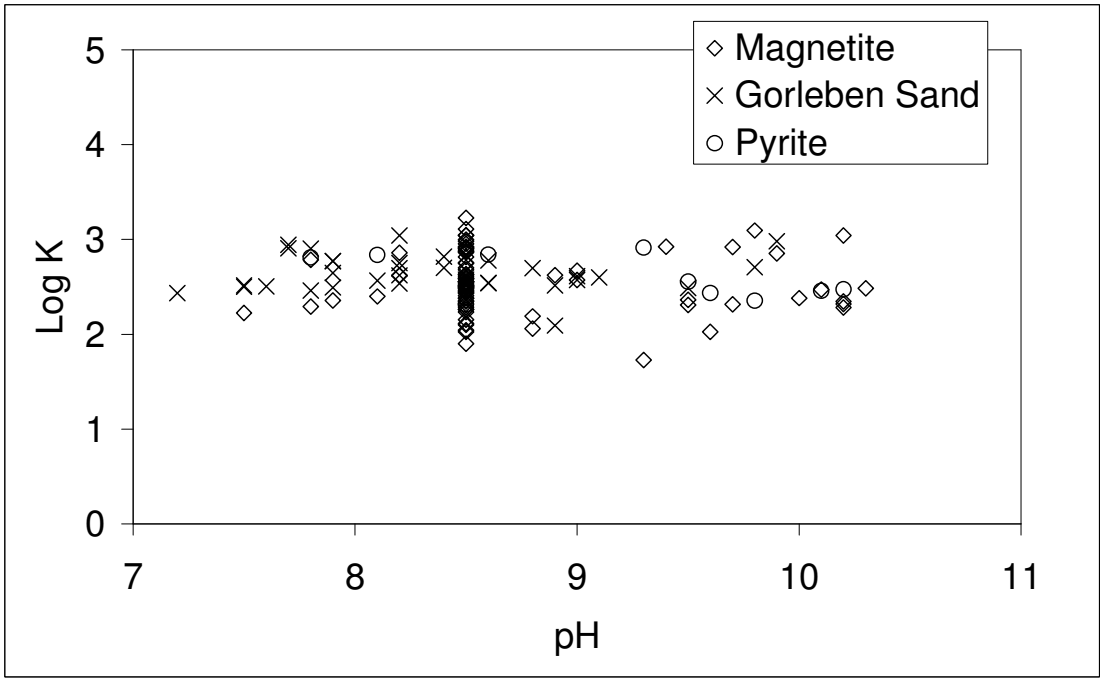

Figure 8-2. The conditional interaction constant Log KHS for the interaction between Tc(IV) and Gorleben humic substances as a function of the pH of systems 2 till 6 containing reduced Tc-HS species obtained after reduction of pertechnetate in a Gorleben groundwater solution with the aid of magnetite (◊), Gorleben sand (x) and pyrite (o).

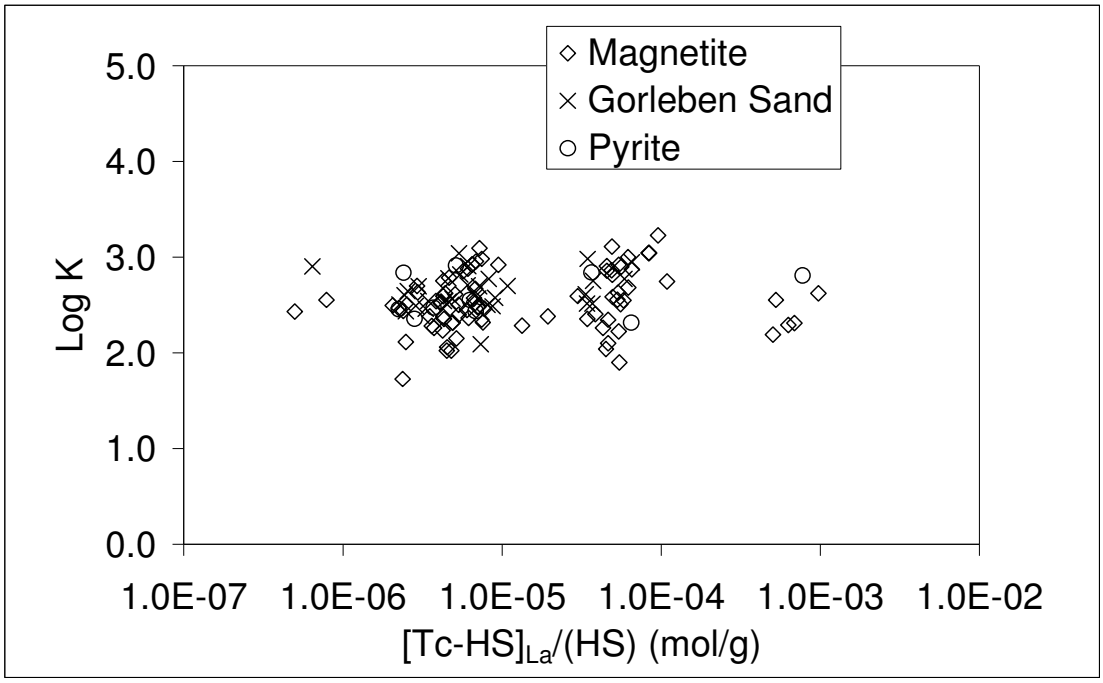

Figure 8-3. The calculated conditional interaction constant KHS as a function of Tc loading on Gorleben humic substances of systems 2 till 6 containing reduced Tc-HS species obtained after reduction of pertechnetate in a Gorleben groundwater solution with the aid of magnetite (◊), Gorleben sand (x) and pyrite (o).

8.3.2 Comparison of the conditional interaction constant with the modified Schubert approach

A conditional interaction constant for the reaction between Tc(IV) and Gorleben humic substances was previously determined via a modified Schubert approach (see chapter 6). These results were obtained on 3 series of experiments which are identical to the series 2, 3 and 4 described in the present study. Samples of the supernatants of the previous study were also used to measure the Tc speciation via the La-precipitation method.

Via the modified Schubert approach, constant conditional interaction constants Log KHS equal to 2.9 ± 0.3 (using the EQ3/6 database) or 3.0 ± 0.3 (using the NEA database) were obtained. Compared to this result, the present obtained value of 2.6 (± 0.3) is (slightly) smaller.

Therefore, the $[Tc]_{La}$ and $[Tc\text{-}HS]_{La}$ concentrations obtained from the La-precipitation method for the series 2, 3 and 4 are compared with the Tc(IV) speciation calculated from the individual K^{HS} values obtained by the modified Schubert approach. The free inorganic $\Sigma[TcO(OH)_2]_n$ and the HS bound Tc(IV) concentrations are now called respectively $[Tc]_{Schubert}$ en $[Tc\text{-}HS]_{Schubert}$.

Equation (8-2) is combined with the mass balance equation of Tc in the equilibrium test solution:

$$[Tc]_{Schubert} + [Tc\text{-}HS]_{Schubert} = [Tc]_{equilibrium}/2 \quad (8\text{-}6)$$

to calculate the $[Tc\text{-}HS]_{Schubert}$ and free inorganic $[Tc]_{Schubert}$ concentrations for the series 2, 3 and 4.

In figure 8-4, Tc-HS concentrations obtained from the proposed La-precipitation method are plotted versus Tc-HS concentrations obtained from the modified Schubert approach when using the "EQ3/6 log K^{HS} values". From figure 8-4, it is clear that Tc-HS concentrations obtained via the two methods are in very good agreement, with a correlation factor of practically one. This means that the La-precipitation speciation methodology is very accurate in describing the amount of Tc associated with humic substances. Similar results are obtained when using the NEA database, but with a slightly lower correlation factor (0.99968) (data not shown).

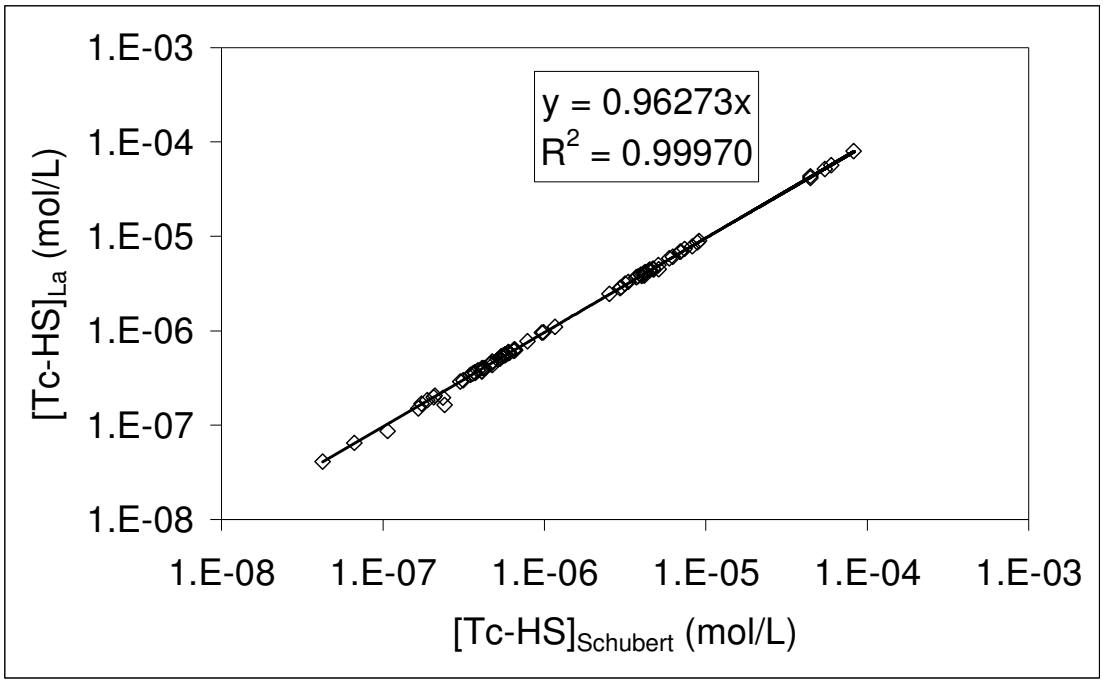

Figure 8-4. Comparison between the [Tc-HS] concentrations obtained with the La-precipitation method $[Tc\text{-}HS]_{La}$ and the modified Schubert approach $[Tc\text{-}HS]_{Schubert}$. A linear regression line is plotted on top of it.

In figure 8-5, experimental free Tc(IV) concentrations obtained from the proposed La-precipitation method are plotted versus free Tc(IV) concentrations obtained via the modified Schubert approach for the systems of series 2, 3 and 4. The scatter on the data is significantly larger than the previous comparison for Tc-HS concentrations and is mainly due to experimental errors in sampling of the supernatant solution after La precipitation. Most probably also the efficiency of La^{3+} to precipitate HS is subject to larger statistical fluctuations. No attempts were made to filter the otherwise clear supernatants before the sampling for the Tc-99 counting.

The observed Tc concentrations after La-precipitation are about a factor 5.7 higher than the free Tc(IV) concentrations obtained from the modified Schubert approach. We do not know the exact reason. A possible explanation could be the fact that a small fraction of the Tc within the Tc-HS species is subject to competition with La^{3+} and is not precipitated with the excess La present in the solutions. This small fraction of Tc(IV) species could exist in an ionic form and be associated with humic substances via a complexation mechanism. In chapter 7, it was shown that the use of higher La concentrations lead to (slightly) higher free Tc concentrations, which is also an indication for a competition effect between La^{3+} and certain Tc(IV) species for available HS sites. However, no experimental evidence is available and since it concerns only a minor fraction of the total Tc(IV) concentration, it would also be very difficult to prove such assumption through experimental methods such as EXAFS. The overwhelming part of Tc-HS species remains of course as being formed through the previous proposed interaction mechanism of colloidal inclusion of Tc(IV) species within the humic substances.

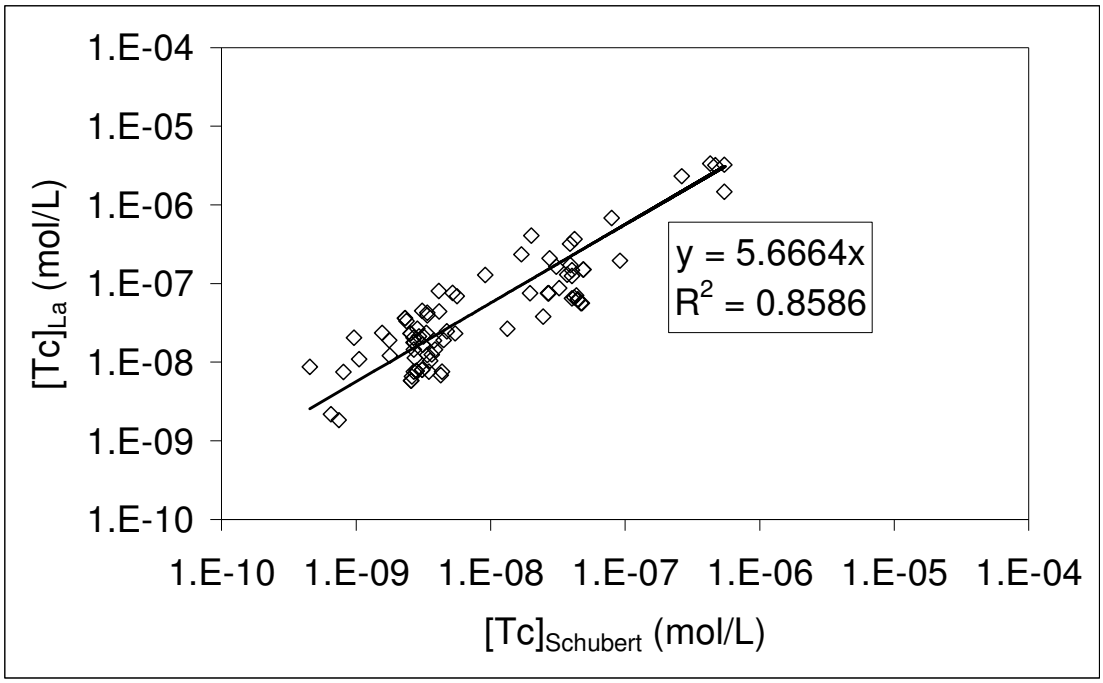

Figure 8-5. Comparison between the free [Tc] concentrations obtained with the La-precipitation method $[Tc]_{La}$ and the modified Schubert approach $[Tc]_{Schubert}$. A linear regression line is plotted on top of it.

8.3.3 La-precipation of free inorganic colloidal Tc(IV) species

It was observed in Chapter 4 that La^{3+} can also precipitate free inorganic colloidal Tc(IV) species. These findings are explored in more detail by adding La^{3+} to systems containing various amounts of reduced inorganic Tc species (series 1). The Tc concentrations found in solutions after reduction of pertechnetate in the presence of Magnetite varied between 4×10^{-9} and 2×10^{-6} mol/L and are given in table 8-1. They generally increase with increasing initial pertechnetate dose and exceed the theoretical

solubility limit of 10^{-9} – 10^{-8} mol/L. These observations demonstrate that Tc(IV) colloids were formed in line with previous results given in Chapters 4, 5 and 6.

After applying the La-precipitation method to these systems, the concentration of Tc left in solution $[Tc]_{La}$ is a linear function of the equilibrium Tc concentration in the analyte solution as shown in figure 8-6. The general trend line through the date of figure 8-6 indicates that a constant fraction of 8.8% of the Tc(IV) cannot be co-precipitated by the 0.005 Equiv./L La^{3+} solution. It is remarkable to observe that the highest $[Tc]_{La}$ concentrations exceed the theoretical solubility (10^{-8} mol/L) suggesting that part of the Tc(IV) colloids remain in equilibrium with the La^{3+} co-precipitated Tc(IV). It is at present not clear whether this trend can be extended beyond the experimental concentration range.

Based on the data in figure 8-5 free Tc(IV) colloids are present in presence of Tc-HS. Thus when applying the La^{3+} precipitation method to HS containing systems also part of the free Tc(IV) colloids should precipitate according to the relationship shown in figure 8-6. In other words the measured $[Tc]_{La}$ is in fact lower than the real concentration of free Tc(IV) colloids.

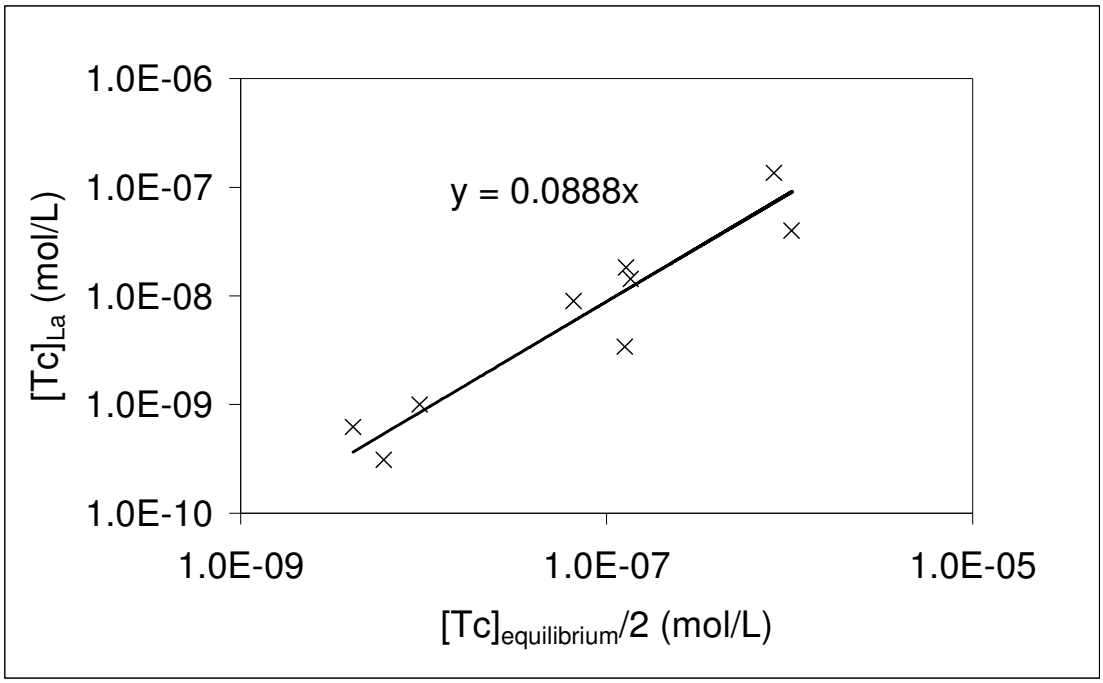

Figure 8-6. The Tc concentration (mol/L) in solution after La-precipitation of all colloids as a function of the equilibrium Tc concentration in solution (mol/L) in systems where pertechnetate was humic free solutions in the presence of magnetite. pH=8.5, S/L = 2.5.

However, using the regression line $[Tc]_{La} = 0.0888*[Tc]_{equilibrium}/2$ of figure 8-6 to calculate "$[Tc]_{La\text{-}real}$" values, results in (very) high and unrealistic values for the free inorganic [Tc] concentrations and relatively low (and sometimes impossible) "$[Tc\text{-}HS]_{La\text{-}real}$" concentrations. Applying the discussed correction leads to an average conditional interaction constant Log K^{HS} equal to 1.4 (± 0.4). This value is very unlikely if compared to the value obtained with the modified Schubert approach,

which we consider as a reference. The reason for the previous result is that the Tc La used in the calculations are concentrations in presence of HS which were already a factor 5.7 higher than the Tc Schubert values. Therefore it makes no sense to correct the Tc La concentrations in the HS containing systems.

In view of the small differences between the obtained K_{La}^{HS} and $K_{Schubert}^{HS}$ values, it is proposed that the La-precipitation method is useful for the direct speciation of Tc-HS and free Tc concentrations in solution and to quantify the interaction between Tc(IV) and humic substances when eg. the Schubert method is not applicable.

The question also arises whether the proposed La-precipitation method would be applicable for other radionuclides that interact with humic substances. Tri- and tetravalent radionuclides and analogues such as europium (Maes *et al.*, 1991, Bidoglio *et al.*, 1991), uranium (Dearlove *et al.*, 1991), americium (Maes *et al.*, 1991, Kim *et al.*, 1993), thorium (Geckeis *et al.*, 2002), terbium (Bidoglio *et al.*, 1991), curium (Kim *et al.*, 1993), neptunium (Kim *et al.*, 1991), … were all found to interact with dissolved humic and fulvic acids. For radionuclide – HS interactions occurring by way of a complexation reaction (such as Eu^{3+}), it is expected that the La-precipitation method is not useful, due to the high competition effects between La^{3+} and the metal under investigation. However, radionuclides that also easily form colloids at the near-solubility concentration (or at higher concentrations) such as Th(IV), U(IV) and Np(IV) (Fanghänel and Neck, 2002) are expected to behave in a similar way as Tc(IV) in their reaction with humic substances. Therefore, when studying the interaction between those radionuclides and humic substances, the La-precipitation method could be used as a quick and simple method to verify and quantify the interaction mechanism between those radionuclides and humic substances. It is however advisable that for such experiments, the ideal specific experimental conditions are determined before application of the method.

8.4 Conclusions

In this chapter, the interaction between Tc(IV) and Gorleben humic substances was quantified using the La-precipitation method developed in chapter 7. A constant conditional interaction constant K^{HS} equal to 2.6 (± 0.3) was found over a large range of Tc and humic substance concentrations and independent of pH (in a pH range 6 – 10) of the original supernatant solution and Tc-HS loading. These observations are in agreement with the proposed Tc - humic substance interaction mechanism of inclusion of neutral charged colloidal Tc(IV) species on the hydrophobic phramework of humic substances.

After comparison with the results obtained via a modified Schubert approach (chapter 6), it is concluded that the La-precipitation method gives an accurate description of the amount of Tc(IV) associated with humic substances but a (small) overestimation of the free inorganic Tc(IV) species is obtained. This latter observation is probably due to a slight competition effect of La.

The experimental $[Tc]_{La}$ and $[Tc\text{-}HS]_{La}$ concentrations can be taken as representative for respectively the free inorganic $\Sigma[TcO(OH)_2]_n$ and the HS bound Tc(IV) concentrations (as defined in equation (8-1)). The La-precipitation method is therefore

considered to be a useful method for the quantification of the interaction between colloidal Tc(IV) species and humic substances.

The foregoing results also indicated that the three surfaces – pyrite, magnetite and Gorleben sand - behave similarly with respect to the reduction of pertechnetate and with respect to the association between Tc and humic substances. These surfaces are only acting as electron donors in the overall redox and association reaction. They do not seem to have any specific influence on the interaction between Tc(IV) and humic substances in solution. There are only differences observed in the reduction kinetics and in the total Tc level at equilibrium for the different systems; those differences are probably due to the different redox capacity and sorption affinities of each surface.

Radionuclides – HS interactions occurring by way of a complexation reaction cannot be quantified by the La-precipitation method, due to the expected competition effects between La^{3+} and the radionuclide under investigation. However, radionuclides that also easily form colloids (even at the near-solubility concentration) such as Th(IV), U(IV) and Np(IV) are expected to behave in a similar way as Tc(IV) in their reaction with humic substances. Hence, for those radionuclides the La-precipitation method could be useful when their interaction mechanism with humic substances is investigated and quantified.

Table 8-1. Experimental conditions and results for experimental series 1 to 6 (see text).

Series	S/L	$[Tc]_{initial}$ (mol/L)	[HS] (g/L)	pH	$[Tc]_{equilibrium}$ (mol/L)	$[Tc]_{La}$ (mol/L)	$[Tc\text{-}HS]_{La}$ (mol/L)	Log K
1	2.5	2.50E-06	-	8.5	8.23E-09	6.21E-10	-	-
1	2.5	2.50E-06	-	8.5	1.21E-08	3.11E-10	-	-
1	2.5	5.00E-06	-	8.5	1.90E-08	1.00E-09	-	-
1	2.5	2.50E-05	-	8.5	1.32E-07	9.00E-09	-	-
1	2.5	2.50E-05	-	8.5	2.51E-07	3.42E-09	-	-
1	2.5	5.00E-05	-	8.5	2.55E-07	1.83E-08	-	-
1	2.5	5.00E-05	-	8.5	2.71E-07	1.43E-08	-	-
1	2.5	2.50E-04	-	8.5	1.64E-06	1.36E-07	-	-
1	2.5	2.50E-04	-	8.5	2.05E-06	4.00E-08	-	-
1	5	2.50E-06	-	8.5	4.00E-09	n.d.	-	-
1	5	2.50E-06	-	8.5	7.00E-09	4.20E-10	-	-
1	5	2.50E-05	-	8.5	6.27E-08	4.25E-08	-	-
1	5	2.50E-05	-	8.5	6.50E-08	2.89E-09	-	-
1	10	6.50E-04	-	8.5	9.40E-07	6.21E-08	-	-
1	10	6.50E-04	-	8.5	1.10E-06	5.79E-08	-	-
2	0.5	2.50E-06	0.165	8.5	1.33E-06	2.66E-08	6.37E-07	2.46
2	1.25	2.50E-06	0.165	8.5	1.20E-06	2.33E-08	5.78E-07	2.48
2	2.5	5.00E-07	0.165	8.5	1.34E-07	2.20E-09	6.49E-08	2.55
2	2.5	5.00E-07	0.165	8.5	8.59E-08	1.84E-09	4.11E-08	2.43
2	2.5	1.67E-06	0.165	8.5	7.49E-07	1.90E-08	3.56E-07	2.36
2	2.5	1.67E-06	0.165	8.5	3.52E-07	6.58E-09	1.69E-07	2.49
2	2.5	2.50E-06	0.165	8.5	1.09E-06	7.75E-09	5.36E-07	2.92
2	2.5	2.50E-06	0.165	8.5	1.03E-06	2.13E-08	4.96E-07	2.45
2	2.5	2.50E-06	0.165	8.5	1.21E-06	2.33E-08	5.83E-07	2.48
2	2.5	2.50E-06	0.165	8.5	7.05E-07	1.25E-08	3.40E-07	2.52
2	2.5	2.50E-06	0.165	8.5	1.15E-06	7.60E-09	5.66E-07	2.96
2	2.5	2.50E-06	0.165	8.5	1.15E-06	2.05E-08	5.54E-07	2.52
2	2.5	5.00E-06	0.165	8.5	2.34E-06	6.90E-08	1.10E-06	2.29
2	2.5	2.50E-05	0.165	8.5	9.07E-06	1.48E-07	4.39E-06	2.56
2	2.5	2.50E-05	0.165	8.5	9.07E-06	1.26E-07	4.41E-06	2.63
2	2.5	2.50E-05	0.165	8.5	1.39E-05	7.55E-08	6.88E-06	3.04
2	2.5	2.50E-04	0.165	8.5	8.96E-05	1.47E-06	4.33E-05	2.55
2	5	2.50E-06	0.165	8.5	8.55E-07	2.36E-08	4.04E-07	2.32
2	10	2.50E-06	0.165	8.5	7.19E-07	7.50E-09	3.52E-07	2.75
2	20	2.50E-06	0.165	8.5	4.13E-07	8.75E-09	1.98E-07	2.44
2	0.5	2.50E-05	0.165	8.5	1.83E-05	1.95E-07	8.97E-06	2.75
2	1.25	2.50E-05	0.165	8.5	1.04E-05	6.85E-07	4.50E-06	1.90
2	2.5	2.50E-05	0.165	8.5	8.40E-06	3.68E-07	3.83E-06	2.10
2	3.75	2.50E-05	0.165	8.5	8.07E-06	2.09E-07	3.83E-06	2.35

Table 8-1(continued). Experimental conditions and results for experimental series 1 to 6 (see text).

Series	S/L	$[Tc]_{initial}$ (mol/L)	[HS] (g/L)	pH	$[Tc]_{equilibrium}$ (mol/L)	$[Tc]_{La}$ (mol/L)	$[Tc\text{-}HS]_{La}$ (mol/L)	Log K
2	5	2.50E-05	0.165	8.5	8.30E-06	7.55E-08	4.08E-06	2.82
2	10	2.50E-05	0.165	8.5	8.43E-06	1.29E-07	4.09E-06	2.58
2	20	2.50E-05	0.165	8.5	5.07E-06	7.60E-08	2.46E-06	2.59
3	2.5	2.50E-06	0.017	8.5	4.90E-07	8.05E-08	1.65E-07	2.38
3	2.5	2.50E-06	0.041	8.5	2.23E-07	2.47E-08	8.69E-08	2.23
3	2.5	2.50E-06	0.116	8.5	1.12E-06	1.14E-08	5.49E-07	2.92
3	2.5	2.50E-06	0.121	8.5	3.39E-07	1.91E-08	1.51E-07	2.11
3	2.5	2.50E-06	0.14	8.5	4.27E-07	6.85E-09	2.07E-07	2.63
3	2.5	2.50E-06	0.144	8.5	1.09E-06	7.75E-09	5.36E-07	2.98
3	2.5	2.50E-06	0.154	8.5	9.55E-07	8.00E-09	4.70E-07	2.88
3	2.5	2.50E-06	0.158	8.5	8.27E-07	1.24E-08	4.01E-07	2.61
3	2.5	2.50E-06	0.17	8.5	9.39E-07	1.67E-08	4.53E-07	2.50
3	2.5	2.50E-06	0.181	8.5	9.56E-07	4.51E-08	4.33E-07	2.03
3	2.5	2.50E-06	0.242	8.5	1.32E-06	3.63E-08	6.25E-07	2.15
3	2.5	2.50E-06	0.261	8.5	1.15E-06	1.79E-08	5.58E-07	2.38
3	2.5	2.50E-06	0.375	8.5	1.57E-06	1.22E-08	7.74E-07	2.53
3	2.5	2.50E-06	0.409	8.5	1.20E-06	5.80E-09	5.97E-07	2.70
3	2.5	2.50E-06	0.446	8.5	1.93E-06	1.10E-08	9.53E-07	2.59
3	2.5	2.50E-06	0.516	8.5	1.97E-06	2.05E-08	9.65E-07	2.26
3	2.5	2.50E-05	0.066	8.5	6.42E-06	5.65E-08	3.15E-06	3.23
3	2.5	2.50E-05	0.119	8.5	7.49E-06	6.20E-08	3.68E-06	3.00
3	2.5	2.50E-05	0.14	8.5	8.00E-06	7.05E-08	3.93E-06	2.90
3	2.5	2.50E-05	0.145	8.5	6.71E-06	5.65E-08	3.30E-06	2.91
3	2.5	2.50E-05	0.15	8.5	6.07E-06	1.51E-07	2.88E-06	2.41
3	2.5	2.50E-05	0.16	8.5	1.02E-05	1.30E-07	4.97E-06	2.68
3	2.5	2.50E-05	0.172	8.5	8.50E-06	6.65E-08	4.18E-06	2.86
3	2.5	2.50E-05	0.179	8.5	1.19E-05	8.75E-08	5.86E-06	2.87
3	2.5	2.50E-05	0.21	8.5	1.25E-05	1.64E-07	6.09E-06	2.55
3	2.5	2.50E-05	0.3	8.5	1.48E-05	3.80E-08	7.36E-06	3.11
3	2.5	2.50E-05	0.349	8.5	1.65E-05	4.07E-07	7.84E-06	2.04
3	2.5	2.50E-05	0.401	8.5	1.77E-05	2.35E-07	8.62E-06	2.26
4	2.5	2.50E-06	0.165	7.8	7.81E-07	7.60E-09	3.83E-07	2.79
4	2.5	2.50E-06	0.165	8.1	9.24E-07	2.13E-08	4.41E-07	2.40
4	2.5	2.50E-06	0.165	8.8	8.24E-07	3.94E-08	3.72E-07	2.06
4	2.5	2.50E-06	0.165	8.9	7.45E-07	1.05E-08	3.62E-07	2.62
4	2.5	2.50E-06	0.165	9	1.15E-06	1.45E-08	5.59E-07	2.67
4	2.5	2.50E-06	0.165	9	1.14E-06	1.79E-08	5.50E-07	2.57
4	2.5	2.50E-06	0.165	9.3	4.79E-07	4.43E-08	1.95E-07	1.73
4	2.5	2.50E-06	0.165	9.4	1.09E-06	7.75E-09	5.36E-07	2.92

Table 8-1(continued). Experimental conditions and results for experimental series 1 to 6 (see text).

Series	S/L	$[Tc]_{initial}$ (mol/L)	[HS] (g/L)	pH	$[Tc]_{equilibrium}$ (mol/L)	$[Tc]_{La}$ (mol/L)	$[Tc\text{-}HS]_{La}$ (mol/L)	Log K
4	2.5	2.50E-06	0.165	9.5	1.07E-06	2.66E-08	5.08E-07	2.36
4	2.5	2.50E-06	0.165	9.6	8.27E-07	4.24E-08	3.71E-07	2.03
4	2.5	2.50E-06	0.165	9.7	8.52E-07	2.36E-08	4.02E-07	2.32
4	2.5	2.50E-06	0.165	9.8	1.20E-06	5.80E-09	5.94E-07	3.09
4	2.5	2.50E-06	0.165	9.9	9.55E-07	8.00E-09	4.70E-07	2.85
4	2.5	2.50E-06	0.165	10	6.08E-07	1.46E-08	2.90E-07	2.38
4	2.5	2.50E-06	0.165	10.1	3.85E-07	7.60E-09	1.85E-07	2.47
4	2.5	2.50E-06	0.165	10.2	1.32E-06	3.63E-08	6.24E-07	2.32
4	2.5	2.50E-06	0.165	10.2	6.36E-07	1.89E-08	2.99E-07	2.28
4	2.5	2.50E-06	0.165	10.2	1.29E-06	3.35E-08	6.13E-07	2.35
4	2.5	2.50E-06	0.165	10.3	1.21E-06	2.33E-08	5.83E-07	2.48
4	2.5	2.50E-05	0.165	7.5	9.54E-06	3.21E-07	4.45E-06	2.23
4	2.5	2.50E-05	0.165	7.9	5.96E-06	1.51E-07	2.83E-06	2.36
4	2.5	2.50E-05	0.165	8.2	7.65E-06	6.30E-08	3.76E-06	2.86
4	2.5	2.50E-05	0.165	8.5	9.48E-06	1.72E-07	4.57E-06	2.51
4	2.5	2.50E-05	0.165	8.5	1.40E-05	7.55E-08	6.92E-06	3.05
4	2.5	2.50E-05	0.165	9.7	9.07E-06	6.50E-08	4.47E-06	2.92
4	2.5	2.50E-05	0.165	10.2	1.39E-05	7.55E-08	6.88E-06	3.04
4	2.5	2.50E-04	0.165	7.8	1.10E-04	3.21E-06	5.18E-05	2.29
4	2.5	2.50E-04	0.165	8.2	1.65E-04	2.32E-06	8.02E-05	2.62
4	2.5	2.50E-04	0.165	8.8	8.96E-05	3.25E-06	4.16E-05	2.19
4	2.5	2.50E-04	0.165	9.5	1.20E-04	3.36E-06	5.66E-05	2.31
5	200	2.50E-06	0.114	8.9	9.56E-07	5.95E-08	4.19E-07	2.09
5	200	2.50E-06	0.121	9.5	1.11E-06	2.84E-08	5.27E-07	2.49
5	200	2.50E-06	0.157	9	1.15E-06	1.90E-08	5.56E-07	2.57
5	200	2.50E-06	0.215	8.4	1.19E-06	8.25E-09	5.87E-07	2.82
5	200	2.50E-06	0.222	9.8	1.37E-06	1.19E-08	6.73E-07	2.71
5	250	2.50E-05	0.172	9.9	6.01E-06	3.60E-08	2.97E-06	2.98
5	333	1.67E-06	0.104	8.4	1.17E-06	2.16E-08	5.63E-07	2.70
5	333	1.67E-06	0.14	7.9	1.18E-06	1.39E-08	5.76E-07	2.77
5	333	1.67E-06	0.141	8.5	1.32E-06	2.39E-08	6.36E-07	2.58
5	333	1.67E-06	0.186	9.1	4.65E-07	6.10E-09	2.26E-07	2.60
5	333	1.67E-06	0.204	8.6	7.20E-07	9.85E-09	3.50E-07	2.54
5	333	1.67E-06	0.258	8.6	1.20E-06	7.65E-09	5.92E-07	2.78
5	333	1.67E-06	0.296	8.6	1.30E-06	1.24E-08	6.38E-07	2.54
5	500	2.50E-05	0.083	7.9	2.23E-07	5.75E-09	1.06E-07	2.65
5	500	2.50E-05	0.093	8.2	3.60E-06	6.60E-08	1.73E-06	2.75
5	500	2.50E-05	0.093	7.7	5.85E-07	7.60E-09	2.85E-07	2.91
5	500	2.50E-05	0.096	7.8	6.33E-08	8.00E-10	3.09E-08	2.90

Table 8-1(continued). Experimental conditions and results for experimental series 1 to 6 (see text).

Series	S/L	$[Tc]_{initial}$ (mol/L)	[HS] (g/L)	pH	$[Tc]_{equilibrium}$ (mol/L)	$[Tc]_{La}$ (mol/L)	$[Tc\text{-}HS]_{La}$ (mol/L)	Log K
5	500	2.50E-05	0.096	7.7	6.42E-06	7.40E-08	3.14E-06	2.95
5	500	2.50E-06	0.098	7.9	5.96E-06	9.93E-08	2.88E-06	2.77
5	500	2.50E-06	0.119	7.5	4.63E-06	1.13E-07	2.20E-06	2.52
5	500	2.50E-06	0.154	7.9	4.61E-07	9.23E-09	2.21E-07	2.49
5	500	2.50E-06	0.22	9	7.52E-06	8.15E-08	3.68E-06	2.61
5	500	2.50E-06	0.234	8.8	7.10E-07	6.00E-09	3.49E-07	2.70
5	500	2.50E-05	0.256	8.9	8.93E-06	1.04E-07	4.36E-06	2.52
5	600	2.50E-06	0.23	8.2	1.57E-06	1.60E-08	7.69E-07	2.62
5	600	2.50E-06	0.265	8.2	1.93E-06	1.44E-08	9.51E-07	2.70
5	600	2.50E-06	0.345	8.2	1.86E-06	4.88E-09	9.25E-07	3.04
5	600	2.50E-06	0.42	8.2	1.97E-06	1.35E-08	9.72E-07	2.53
5	1000	2.50E-06	0.038	7.5	3.59E-07	2.56E-08	1.54E-07	2.50
5	1000	2.50E-06	0.078	7.8	2.81E-07	1.14E-08	1.29E-07	2.46
5	1000	2.50E-06	0.103	8.1	5.31E-07	1.33E-08	2.52E-07	2.57
5	1000	2.50E-06	0.15	7.2	3.91E-07	9.10E-09	1.86E-07	2.44
5	1000	2.50E-06	0.294	7.6	6.81E-07	7.10E-09	3.33E-07	2.50
6	2.5	1.00E-06	0.165	10.1	3.85E-07	7.80E-09	1.85E-07	2.46
6	2.5	1.00E-06	0.125	9.8	3.77E-07	1.24E-08	1.76E-07	2.36
6	2.5	1.00E-06	0.088	9.6	6.51E-07	2.50E-08	3.01E-07	2.44
6	2.5	1.00E-06	0.041	9.3	2.23E-07	6.25E-09	1.05E-07	2.91
6	2.5	1.00E-06	0.016	8.6	6.90E-07	5.28E-08	2.92E-07	2.84
6	2.5	1.60E-06	0.165	10.2	6.36E-07	1.24E-08	3.06E-07	2.47
6	2.5	1.60E-06	0.165	8.1	4.04E-07	3.50E-09	1.99E-07	2.84
6	2.5	2.50E-06	0.165	9.5	1.07E-06	1.75E-08	5.18E-07	2.55
6	2.5	1.60E-05	0.165	8.5	1.13E-05	3.13E-07	5.34E-06	2.32
6	2.5	1.60E-04	0.165	7.8	1.30E-04	1.20E-06	6.38E-05	2.81

GENERAL CONCLUSIONS

In order to perform a sound safety assessment study for a geological disposal site and/or the overlaying aquifers, the geochemical behaviour of the radionuclides under variable geochemical conditions should be known. This implies knowledge on redox, solubilities, interaction with complexing components and solids, as these interactions will determine their potential availability in solution. For most of the radioactive elements, their properties and behaviour under various conditions have been studied intensively over the past 25 years, but even until today their (geo)chemical behaviour has not been understood in sufficient detail. Especially, in the case of technetium, a fission product of ^{235}U and ^{239}Pu, great gaps on the knowledge of its geochemical behaviour are to be filled. The study of the interactions between Tc and various geochemical components presumably present in the repository and the overlaying aquifer systems are therefore primordial.

It is generally accepted that the most stable occurring valence states of Tc in aqueous solutions (in the absence of complexing agents) under oxidising and reducing conditions comparable to natural conditions are respectively Tc(VII) (pertechnetate) and Tc(IV) species. Only at low pH and under reducing conditions, Tc(III) species can occur. For the reduction of pertechnetate under circumstances comparable to natural conditions, suitable reducing conditions must be present, among them the necessity of a reducing solid phase. Upon reduction of pertechnetate in the absence of complexing ligands, an amorphous precipitate $TcO_2.nH_2O$ with a low solubility (10^{-9} – 10^{-8} mol/L) is formed. Reduced Tc species are able to form complexes or to associate with (immobile and mobile) humic substances. In natural groundwaters containing high amounts of dissolved humic substances, this could lead to an enhanced solubility of the formed amorphous precipitate $TcO_2.nH_2O$.

In a first attempt to quantify the interaction between reduced Tc species and humic substances, Maes *et al.* (2003) concluded that the interaction of Tc with dissolved HS should not be described by a conventional complexation mechanism but by the interaction between non-ionic Tc(IV) species (monomeric and dimeric $TcO(OH)_2$ - $(TcO(OH)_2)_2$) and dissolved HS:

$$\Sigma[TcO(OH)]_{n=1,2} + HS \rightleftharpoons [TcO(OH)]_{n=1,2}\text{-}HS \qquad (1)$$

A conditional interaction constant $LogK^{HS}$ = 2.6 (± 0.3) was calculated when expressing the humic substances on a g/L basis. However, this study gave no spectroscopic proof on the valence state of Tc within the humic substances nor the proposed Tc(IV) species involved.

The purpose of the present work was to study the behaviour of Tc under reducing conditions relevant for underground storage conditions. These conditions were gradually approached by investigating:

(i) the general conditions to reduce Tc(VII) to lower oxidation states *in casu* Tc(IV) by reducing solid phases,
(ii) the behaviour of pertechnetate (Tc(VII)) in well defined synthetic reducing systems containing a solid (Magnetite, Pyrite, Siderite and FeS) in

synthetic Gorleben groundwater (absence of humic substances) and natural Gorleben groundwater, and

(iii) the behaviour of pertechnetate in labscale natural systems containing natural Gorleben sand and natural Gorleben groundwater.

Gorleben humic substances were chosen because the Gorleben site, containing considerable amounts of dissolved humic substances, located in Germany has been investigated for many years. In addition, these humic substances are easily available in groundwater of the aquifers overlaying the salt dome.

The following conclusions were drawn throughout the study:

There is no interaction between pertechnetate and humic substances.

In agreement with literature results, pertechnetate was not found to form complexes or to associate with humic substances. In addition, it is impossible to directly reduce pertechnetate by dissolved humic substances (at least not in the short time scale – four weeks – of the experiments).

The reduction of pertechnetate is kinetically controlled and occurs only via a surface catalysed reaction.

Upon introduction of pertechnetate to a suspension containing a reducing solid phase (Magnetite and Pyrite) in either synthetic Gorleben groundwater or natural Gorleben groundwater, it was observed that the pertechnetate concentration only gradually decreased with time. The three-electron reduction process is kinetically controlled (with sorption of the pertechnetate ions via a ligand-exchange mechanism on the solid phase being the rate-determining step) and depends on the available specific surface are of the reducing surface, the nature of the reducing solid phase and the presence of humic substances. Iron(II) containing surfaces such as Pyrite and Magnetite, commonly present in natural repositories and aquifer systems, are suitable electron donors for this purpose. Ion exchanged Fe^{2+} on illite or Fe^{2+} solutions do not reduce pertechnetate to lower oxidation states. In addition, sufficiently pre-equilibrated lab scale natural systems containing Gorleben sand and Gorleben humic substances provide a suitable reducing environment for pertechnetate reduction. The presence of charcoal particles was identified as being necessary for pertechnetate reduction in these latter systems.

Upon reduction of pertechnetate in solutions containing Tc concentrations above 10^{-7} mol/L, the Tc solution concentration is controlled by colloidal Tc species both in the presence and absence of humic substances.

When pertechnetate concentrations beyond 10^{-7} mol/L are reduced in suspensions containing a reducing solid phase (Magnetite and Pyrite), the following observations were made:

(i) in the *absence of humic substances* and at equilibrium, enhanced total Tc solution concentrations (concentrations between 10^{-8} and 10^{-5} mol/L), compared to the aforementioned literature values are observed. These

enhanced Tc concentrations were ascribed to the formation of colloidal or polynuclear Tc species. Gel permeation chromatograms of the supernatant solution at equilibrium showed the absence of pertechnetate and the presence of other Tc species of a relatively large hydrodynamic size in solution confirming the presence of colloidal Tc species.

(ii) in the *presence of humic substances*, enhanced Tc solution concentrations are observed that were almost a factor 100 higher compared to the observed solution concentration in the absence of humic substances. This enhanced concentration is interpreted as a formation of Tc-humic substance species. The existence of Tc-humic substance species in the supernatant solution is proven by gel permeation chromatography.

(iii) Due to the limitations of the experimental methods used, it could not be concluded whether polymeric or colloidal Tc species also occur at the theoretical solubility level of 10^{-9} – 10^{-8} mol/L.

The valence state of reduced technetium species associated with humic substances is Tc(IV).

In most literature studies, it was "assumed" that under natural conditions either Tc(III) or Tc(IV) species associate with humic substances. In this work, it is demonstrated for the first time by XANES spectroscopy that tetravalent Tc species are associated with humic substances present in supernatant solutions of labscale natural systems (Gorleben sand and natural Gorleben groundwater) or in systems mimicking natural conditions (eg. Magnetite and natural Gorleben groundwater). In all cases, gel permation chromatography indicated an association between these Tc(IV) species and Gorleben (and the Boom clay) humic substances. Therefore, the existence of Tc(IV)-humic substance species was proven.

The observed Tc species on the reducing solid phases are mono-, di- and polynuclear (or colloidal) Tc(IV) species

Straightforward EXAFS spectroscopic evidence was obtained on the chemical environment of ^{99}Tc(IV) atoms formed upon introduction of TcO_4^- to 4 types of systems which gradually mimic *in situ* natural reducing conditions in humic rich geochemical environments: a) magnetite/pyrite in synthetic groundwater in the absence of humic substances (HS), b) magnetite/pyrite in natural Gorleben groundwater in the presence of humic substances, c) Boom clay (BC) sediment mixed with synthetic groundwater, and d) Gorleben sand mixed with natural Gorleben groundwater.

All the investigated systems refer to pH 8-9 conditions and in a first step, the Tc phases on all the solid phases (magnetite, pyrite, Boom clay and Gorleben sand) were examined. All measured samples show similar EXAFS spectra for Tc which could be fitted by a hydrated $TcO_2.nH_2O$ phase. These hydrated $TcO_2.nH_2O$ phase are considered to be mono-, di- and polynuclear (or colloidal) Tc(IV) species.

The association of Tc(IV) species and humic substances occurs by way of a colloidal inclusion of mono-, di- and polynuclear (or colloidal) Tc(IV) species within the humic substances.

EXAFS spectra of Tc phases associated with supernatant humic substances could be fitted by the same hydrated $TcO_2.nH_2O$ phase observed on the various reducing solid surfaces. The following reaction mechanism was therefore proposed: upon introduction of TcO_4^- to chemically reducing environments, small Tc(IV) oxidic polymers are formed which either may aggregate into larger units (colloids) and finally precipitate or associate with the solid phases, or may interact in their polymeric form with (dissolved and immobile) humic substances. The previously established mechanism (equation (1)) can therefore be rewritten to incorporate the interaction of polynuclear or colloidal Tc(IV) species with humic substances:

$$\Sigma[TcO(OH)_2]_n + HS \rightleftharpoons [TcO(OH)_2]_n\text{-}HS \qquad (2)$$

This latter type of interaction seriously differs from the generally accepted metal-humate complexation and therefore offers new views on the possible pathways of metals and radionuclides in humic rich environments.

The distribution of polynuclear $TcO_2.nH_2O$ species between Magnetite and a liquid phase is both in the absence and presence of humic substances controlled by a linear sorption mechanism.

The Tc(IV) distribution data between the solid Magnetite and the liquid phase (in the absence of HS) was investigated in a Tc concentration range of 5×10^{-7} – 6.5×10^{-4} mol/L for different sorbent doses. Due to the fact that combinations of different total Magnetite (sorbent) doses with varying pertechnetate gifts lead to a unique sorption versus equilibrium concentration relationship a reductive sorption process is proposed. The surface on which sorption occurs is either a growing iron(III) precipitate and/or the unaltered Magnetite phase.

In the presence of humic substances, again a linear trend is observed for the distribution of Tc(IV) between the solid and liquid phase; a similar relationship is observed as for the data set in the absence of HS. These results indicate that the Tc(IV) solution concentration is ruled by a sorption reaction but is now combined with the constant HS concentration.

But foregoing results differ from most literature data on the geochemical behaviour of technetium. Indeed it was always assumed that the solution concentration of Tc under natural reducing conditions is determined by the amorphous precipitate $TcO_2.nH_2O$ having a low solubility equal to 10^{-9} – 10^{-8} mol/L. The difference between the present study and the literature results is the fact that for the first time the interaction between Tc and Magnetite over a wide range of Tc concentrations was studied.

Using an adapted Schubert approach, the concentration quotient for the interaction between mono-, di- and polynuclear Tc(IV) species and humic substances is quantified.

The conditional interaction constant of Tc(IV) with HS was determined by adapting Schuberts ion exchange approach. For this purpose the solid Magnetite phase is considered to act as an adsorption sink according to the following reaction:

$\Sigma[TcO(OH)_2]_n$ + Surface $\rightleftharpoons$ Surface-$[TcO(OH)_2]_n$ (3)

with concentration quotient:

$$K = \frac{\left[Surface - \left[TcO(OH)_2\right]_n\right]}{\left[\Sigma\left[TcO(OH)_2\right]_n\right] * (Surface)} \quad (4)$$

This sink competes with dissolved Gorleben humic substances for hydrated neutral Tc(IV) species according to equation (2).

The distribution coefficient K_D° in the absence of humic substances can be defined as

$$K_D^\circ = \frac{\left(molTc(IV)sorbed\right)}{\left[\Sigma\left[TcO(OH)_2\right]_n\right] * A} \quad (5)$$

and the distribution coefficient of Tc(IV) in presence of Magnetite and HS can then be written as:

$$K_D = \frac{\left(molTc(IV)sorbed\right)}{\left[\Sigma\left[TcO(OH)_2\right]_n\right] * (A + K^{HS}(HS))} \quad (6)$$

The value of the conditional interaction constant K^{HS} can be obtained via combining the two latter equations into the familiar Schubert equation:

$\log(K_D^\circ/K_D - 1) = \log K^{HS} + \log [HS] - \log A$ (7)

(with A the side reaction coefficient)

One single interaction constant $\log K^{HS}$ = 2.9 (± 0.3) (EQ3/6) or 3.0 (± 0.3) (NEA) was calculated for the interaction of a range of monomeric to colloidal Tc(IV) species with dissolved humic substances from Gorleben groundwaters. This interaction constant was found to describe the distribution of dissolved Tc(IV) species between humic substance – containing solutions and the solid Magnetite for varying conditions of humic substance concentration, Magnetite solid concentration, pH and total Tc concentration.

The derived K^{HS}-value is a global value since no detailed information can be given on the relative abundance of the different (monomeric, dimeric and polymeric) Tc(IV) species in the system nor on the detailed interaction mechanism of each component with the humic substance colloids.

Via a newly developed method, called the La precipitation method, a further proof of the proposed interaction mechanism between Tc(IV) and humic substances was given

A method for quick speciation in solution was developed that was called the La-precipitation method. The addition of a sufficient excess concentration of La^{3+} in humic substance containing solutions allows to precipitate all the humic colloids. It was found that both Tc as humic substances were removed from solution after applying 5×10^{-3} Equiv./L La^{3+} to Tc – Gorleben humic substances containing solutions. None of the investigated parameters ([Tc] concentration, (HS) concentration nor pH) has an influence on the observed [Tc] concentration after La precipitation of the humic substances.

Due to the fact that no significant competition of La^{3+} was observed on the interaction between Tc and humic substances, the observations made on the La-Tc-HS solutions, are a further proof for the previously proposed colloid – colloid interaction mechanism.

The La-precipitation method can be used for a quick and rough quantification of the interaction between Tc(IV) and humic substances.

The La precipitation method was used for the determination of humic bound Tc(IV) and free Tc(IV) which allows to quantify the interaction between Tc(IV) and Gorleben humic substances, according to the following reaction:

$$Tc(IV)_{La} + HS \rightleftharpoons Tc(IV)\text{-}HS_{La} \quad (8)$$

$$\text{With } K^{HS} = \frac{[Tc-HS]_{La}}{[Tc]_{La}(HS)}, \quad (9)$$

where (HS) is the amount of humic substances in solution before La-precipitation and given in g/L. This latter amount can be considered equal to the free HS content since the Tc occupation is relatively low. $[Tc]_{La}$ is the measured Tc concentration in solution after La precipitation of all humic substances. $[Tc\text{-}HS]_{La}$ is the concentration of Tc associated with humic substances.

A constant conditional interaction constant K^{HS} equal to 2.6 (± 0.3) was found over a large range of Tc and humic substance concentrations and was independent of pH in the pH range 6 – 10 and Tc loading on HS. After comparison with the results obtained via a modified Schubert approach, it is concluded that the La-precipitation method gives an accurate description of the amount of Tc(IV) associated with humic substances but a (small) overestimation of the free inorganic Tc(IV) species is obtained. Differences between the two values are probably explained by the large experimental scatter on the data used in both methods. Another explanation can be a slight competition effect of La.

Nevertheless, the La precipitation method is useful for a quick and rough determination of the conditional interaction constant under a variety of experimental conditions. The experimental $[Tc]_{La}$ and $[Tc\text{-}HS]_{La}$ concentrations can be taken as

representative for respectively the free inorganic $\Sigma[TcO(OH)_2]_n$ and the HS bound Tc(IV) concentrations used in the Schubert approach.

The La-precipitation method can be further used for the study of other radionuclides and humic substances.

For metal/radionuclide – HS interactions occurring by way of a complexation reaction (such as eg. Eu^{3+}, …) , it is expected that the La-precipitation method is not useful, due to the expected competition effects between La^{3+} and the metal under investigation. However, radionuclides that also easily form colloids (even at the near-solubility concentration) such as Th(IV), U(IV) are expected to behave in a similar way as Tc(IV) in their reaction with humic substances.

Although, most experimental work in this Ph. D. work is performed with Gorleben humic substances, all aforementioned conclusions contribute to a more comprehensive knowledge of the geochemical behaviour of technetium in repositories or aquifer systems containing dissolved humic substances.

The calculated conditional interaction constant K^{HS} via the Schubert approach can be used in Performance Assessment studies. Therefore, knowledge of the *in situ* $K_d°$ value is necessary. The proposed model description allows to predict the K_d of Tc(IV) species between the solid Magnetite (presumably present as back-fill material and in aquifer systems) and the liquid phase at all solid/liquid ratios using the following equation derived from the Schubert equation :

$$K_d = \frac{K_d^0}{1 + \frac{K^{HS}[HS]}{A}} \tag{10}$$

A more detailed understanding of the interaction between Tc(IV) and humic substances, and between Tc(IV) and reducing solid phases, needs measuring techniques to determine the relative abundance of the different Tc(IV) species in solution and associated with humic substances or surfaces. And this would lead to a refinement in the calculated interaction constant K^{HS}.

Another important issue for performance assessment studies is whether the interaction between Tc(IV) and HS species is reversible or not. In case of reversibility Tc would desorb from the humic substances rapidly during transport. Batch Desorption experiments under a variety of conditions can provide an answer on this matter. Additionally column experiments, where the dynamic behaviour of Tc(IV)-HS species of different ages is followed may lead to a better judgement on the behaviour and stability of Tc-HS species at longer time scales. For example, in column experiments with technetium-HS species, an enhanced mobility of the Tc-HS species and increased recovery of Tc in the effluent was observed after increasing the contact time between Tc and humic substances prior to introduction into a column. On the other hand, an increase of the migration time and residence time in the column, respectively, reduced the Tc recovery.

REFERENCES

Abdelouas A., Fattahi M., Grambow B., Vichot L., Gautier E., Precipitation of technetium by subsurface sulfate-reducing bacteria. *Radiochim. Acta* 90: 773–777 (2002)

Abdelouas A., Grambow B., Fattahi M., Andrès Y., Leclerc-Cessac E., Microbial reduction of ^{99}Tc in organic matter-rich soils. *Sci. Total Environ.* 336: 255-268 (2005)

Abram U., Kirmse R., EPR Spectroscopy on Technetium Compounds. *Radiochim. Acta* 63: 139-143 (1993)

Aiken G.R., Isolation and concentration techniques for aquatic humic substances. In: *Humic substances in soil, sediment and water: geochemistry and isolation*. Eds. Aiken G.R., McKnight D.M., Wershaw R.L., and MacCarthy P., Wiley-Interscience, New York (1985)

Allen P.G., Siemering G.S., Shuh D.K., Bucher J.J., Edelstein N.M., Langton C.A., Clark S.B., Reich T., Denecke M.A., Technetium Speciation in Cement Waste Forms Determined by X-ray Absorption Fine Structure Spectroscopy. *Radiochim. Acta* 76: 77-86 (1997)

Almahamid I., Bryan J.C., Bucher J.J., Burrell A.K., Edelstein N.M., Hudson E.A., Kaltsoyannis N., Lukens W.W., Skuh D.K., Nitsche H., Reich T., Electronic and Structural Investigations of Technetium Compounds by X-ray Absorption Spectroscopy. *Inorg. Chem.* 34: 193-198 (1995)

Ankudinov A.L., Ravel B., Rehr J.J., Conradson S.D., Real-Space Multiple-Scattering Calculation and Interpretation of X-ray Absorption Near-Edge Structure. *Phys. Rev. B* 58: 7565-7576 (1998)

Artinger R., Kienzler B., Schüβler W., Kim J.I., Sampling and Characterization of Gorleben Groundwater/Sediment Systems for Actinide Migration Experiments. In: *Effects of Humic Substances on the Migration of Radionuclides: Complexation and Transport of Actinides. 1st Technical Progress Report*. Ed. Buckau G., FZKA 6124, pp. 23-42 (1998a)

Artinger R., Kienzler B., Schüβler W., Kim J.I., Effects of Humic Substances on the ^{241}Am Migration in a Sandy Aquifer: Column Experiments with Gorleben Groundwater/Sediment Systems. *J. Contam. Hydrol.* 35: 261-275 (1998b)

Artinger R., Buckau G., Geyer S., Fritz P., Wolf M., Kim J.I., Characterization of groundwater humic substances: influence of sedimentary organic carbon. *Appl. Geochem.* 15 : 97-116 (2000)

Artinger R., Schüβler W., Schäfer T., Kim J.I., A kinetic study of Am(III)/humic colloid interactions. *Environ. Sci. Technol.* 36: 4358-4363 (2002a)

Artinger R., Rabung T., Kim J.I., Sachs S., Schmeide K., Heise K.H., Bernard G., Nitsche H., Humic Colloid-Borne Migration of Uranium in Sand Columns. *J. Contam. Hydrol.* 58: 1-12 (2002b)

Artinger R., Buckau G., Zeh P., Geraedts K., Vancluysen J., Maes A., Kim J.I., Humic Colloid Mediated Transport of Tetravalent Actinides and Technetium. *Radiochim. Acta* 91: 743-750 (2003)

Ashworth D.J., Shaw G., Soil migration and plant uptake of technetium from a fluctuating water table. *J. Environ. Radioactiv.*, 81: 155-171 (2005)

Balsley S.D., Brady P.V., Krumhansl J.M., Anderson H.L. In: *^{129}I and $^{99}TcO_4$ Scavengers for Low Level Radioactive Waste Backfills.* SAND95-2978. Sandia National Laboratories, Albuquerque, New Mexico (1997)

Balsley S.D., Brady P.V., Krumhansl J.M., Anderson H.L., Anion Scavengers for low-level Radioactive Waste Repository Backfills. *J. Soil Contam.* 7: 125-141 (1998)

Barrière P., *Chem. News* 74: 159 (1896)

Beneš P., Štamberg K., Široký L., Mizera J., Radiotracer Study of Sorption of Europium on Gorleben Sand from Aqueous Solutions Containing Humic Substances. *J. Radioanal. Nucl. Chem.* 254: 231-239 (2002)

Bennett R., Willey N., Soil availability, plant uptake and soil to plant transfer of Tc-99 - a review. *J. Environ. Radioactiv.* 65: 215-231 (2003)

Ben Said K., Fattahi M., Musikas C., Revel R., Abbe J.C., The speciation of Tc(IV) in chloride solutions. *Radiochim. Acta* 88: 567-571 (1998)

Bernard J.G., Bauer E., Richards M.P., Arterburn J.B., Chamberlin R.M., Catalytic Reduction of Pertechnetate ((TcO4-)-Tc-99) in Simulated Alkaline Nuclear Wastes. *Radiochim. Acta* 89: 59-61 (2001)

Bertha E.L., Choppin G.R., Interaction of Humic and Fulvic Acids with Eu(III) and Am(III). *Inorg. Nucl. Chem.* 40: 655-658 (1978)

Bidoglio G., Grenthe I., Qi P., Robouch P., Omonetto N., Complexation of Eu and Tb with Fulvic Acids as studied by Time-Resolved Laser-Induced Fluorescence. *Talanta* 38: 999-1008 (1991)

Bostick R.C., Fendorf S., Arsenite Sorption on Galena (PbS) and Sphalerite (ZnS). *Geochim. Cosmochim. Acta* 67: 895-907 (2003a)

Bostick R.C., Fendorf S., Differential Adsorption of Molybdate and Tetrathiomolybdate on Pyrite (FeS2). *Environ. Sci. Technol.* 37: 285-291 (2003b)

Brunauer S., Emmett P.H., Teller E., Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60: 309-319 (1938)

Bryan N.D., Jones M.N., Birkett J., Livens F.R., Aggregation of Humic Substances by Metal Ions Measured by Ultracentrifugation. *Anal. Chim. Acta* 437: 291-308 (2001)

Buckau G., Komplexierung von Americium(III) mit Huminstoffen in natürlichen Grundwässern. Dissertation, FU Berlin (1991)

Buckau G., Kim J.I., Klenze R., Rhee D.S., Wimmer H., A Comparative Spectroscopic Study on the Fulvate Complexation of Trivalent Transuranium Ions. *Radiochim. Acta* 57: 105-111 (1992)

Buckau G., In: *Effects of Humic Substances on the Migration of Radionuclides: Complexation and Transport of Actinides. 1st Technical Progress Report*. Ed. Buckau G., FZKA 6124 (1998)

Buckau G., Artinger R., Fritz P., Geyer S., Kim J. I., Wolf M., Origin and mobility of humic colloids in the Gorleben aquifer system. *Appl. Geochem.* 15: 171-179 (2000)

Burnett K.B., Campbell A.B., Jobe D.J., Lemire R.J., Taylor P., Synthesis, Characterization and Heat of Formation of the Amorphous and Crystalline Forms of TcO_2. *Radiochim. Acta* 69: 241-249 (1995)

Byegard J., Albinsson Y., Skanemark G., Skalberg M., Field and Laboratory Studies of the Reduction and Sorption of Technetium (VII). *Radiochim. Acta* 58/59: 239-244 (1992)

Carlsen L., In: *Characterization of Humic Acids; the Riso Contribution to the Coco-Club Activities*. Eur-12784 (1990)

Cartledge G.H., Pertechnetate Ion as Inhibitor of the Corrosion of Iron and Steel. *Corrosion* 11: 335-342 (1955)

Choppin G.R., Bond A.H., Borkowski M., Bronikowski M.G., Chenj J.F., Labonne-Wall N.A., Lis S., Mizera J., Moore R.C., Pokrovsky O., Xia, Y.-X., Waste Isolation Pilot Plant Actinide Source Term Test Program: Solubility Studies and Development of Modeling Parameters. Technical Report. DOE AC04-94AL85000 (2001)

Clapp C.E., Hayes M.H.B., Sizes and Shapes of Humic Substances. *Soil Sci.* 164: 777-789 (1999)

Côme B., In: *CEC project MIRAGE – Second phase on migration of radionuclides in the geosphere*. EUR 11589 (1988)

Cui D.Q., Eriksen T.E., Reduction of pertechnetate by ferrous iron in solution: Influence of sorbed and precipitated Fe(II). *Environ. Sci. Technol.* 30: 2259-2262 (1996a)

Cui D.Q., Eriksen T.E., Reduction of pertechnetate in solution by heterogeneous electron transfer from Fe(II)-containing geological material. *Environ. Sci. Technol.* 30: 2263-2269 (1996b)

Curtis D., Fabryka-Martin J., Dixon P., Cramer J., Nature's Uncommon Elements: Plutonium and Technetium. *Geochim.Cosmochim.Acta* 63: 275-285 (1999)

De Craen M., Wang L., Van Geet M., Moors H., Geochemistry of Boom Clay Pore Water at the Mol Site, Status 2004. SCK·CEN Scientific Report BLG-990 (2004)

Dalziel J., Gill N.S., Nyholm R.S., Peacock R.D., Technetium. Part I. The Preparation and Properties of Potassium Hexahalogenotechnetates. *J. Chem. Soc.* 4012-4016 (1958)

Dearlove J.P.L., Longworth G., Ivanovich M., Kim J.I., Delakowitz B., Zeh P., A Study of Groundwater-Colloids and their Geochemical Interactions with Natural Radionuclides in Gorleben Aquifer Systems. *Radiochim. Acta* 52/53: 83-89 (1991)

Del Cul G. D., Bostick W. D., Trotter D. R., Osborne P. E., Technetium-99 Removal from Process Solutions and Contaminated Groundwater. *Sep. Sci. Tech.* 28:551-564 (1993)

Dierckx, A.; Put, M.; De Cannière, P.; Wang, L.; Maes, N.; Aertsens, M.; Maes, A.; Vancluysen, J.; Verdickt, W.; Gielen, R.; Christiaens, M.; Warwick, P.; Hall, A.; van der Lee, J., *Transport of radionuclides due to complexation with organic matter in clay formations (Trancom-Clay)*; Final report EUR 19135 EN, Contract No FI4W-CT95-0013 (2000)

Dixon P., Curtis D. B., Musgrave J., Roensch F., Roach J., Rokop D., Analysis of Naturally Produced Technetium and Plutonium in Geologic Materials. *Anal. Chem.* 69: 1692-1699 (1997)

Dzomback D.A., Morel F.M.M., In: *Surface Complexation Modeling: Hydrous Ferric Oxide*. John Wiley and Sons, New York (1990)

Echevarria G., Vong P.C., Leclerc-Cessac E., Morel J.L., Bioavailability of Technetium-99 as affected by plant species and growth, application form, and soil incubation. *J. Environ. Qual.* 26: 947-956 (1997)

Fanghänel Th., Neck V., Aquatic chemistry and solubility phenomena of actinide oxides/hydroxides. *Pure Appl. Chem.* 74: 1895-1907 (2002)

Fattahi M., Vichot L., Poineau F., Houee-Levin C., Grambow B., Speciation of technetium(IV) chloride under gamma irradiation. *Radiochim. Acta* 93: 409-413 (2005)

Flint C.D., Lang P.F., Infrared and Visible Luminescence Spectra of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ in Cubic Crystals. *J. Chem. Soc. Farad. T. 2* 82: 465-472 (1986)

Gee G.W., Campbell A.C., In: *Monitoring and Physical Characterization of Unsaturated Zone Transport - Laboratory Analysis*. PNL-3304, Pacific Northwest Laboratory, Richland, Washington (1980)

Geckeis H., Rabung T., Ngo Manh T., Kim J.I., Beck H.P., Humic Colloid-Borne Natural Polyvalent Metal Ions: Dissociation Experiment. *Environ. Sci. Technol.* 36: 2946 –2952 (2002)

George, G.N.; Pickering, I.J., *EXAFSPAK, A suite of computer programs for analysis of X-ray absorption spectra*; Stanford Synchrotron Radiation Laboratory, Stanford, USA, 1995.

Grossl P.R., Inskeep W.P., Precipitation of Dicalcium Phosphate Dihydrate in the Presence of Organic-Acids. *Soil Sci. Soc. Am. J.* 55: 670-675 (1991)

Haines R. I., Owen R.I., Vandergraaf T.T., Mineral Interactions with Technetium. *Nucl. J. Can*. 1: 32–37 (1987)

Hanke K., Jahrling B., Lieser K.J., Properties and Solubilities of Technetium Dioxide. In: *Technetium in the Environment.* Eds. Desmet G., Myttenaere C., Elsevier Applied Science Publishers Ltd. p. 179-187 (1986)

Hashimoto M., Wada H., Omori T., Yoshihara K., Formation of Tc(III) Complexes with EDTA and HEDTA. *Radiochim. Acta* 63: 173-177 (1993)

Henrion P.N., Monsecour M., Fonteyne A., Put M., De Regge P., Migration of Radionuclides in Boom Clay. *Radioact.* In: *Waste Manag. and the Nucl. Fuel Cycle.* Harwood Academic Publishers: New York, 6: 313-359 (1985)

Henrot J., Bioaccumulation and Chemical Modification of Tc by Soil Bacteria*. Health Phys.* 57: 239–245 (1989)

Hummel W., Binding Models for Humic Substances. In: *Modelling in Aquatic Chemistry.* OECD Nuclear Agency: Paris. pp. 153-206 (1997)

Hummel W., Glaus M.A., Van Loon L.R., Complexation of Radionuclides with Humic Substance: The Metal Concentration Effect. *Radiochim. Acta* 84: 111-114 (1999)

Inskeep W.P., Silvertooth J.C., Inhibition of Hydroxyapatite Precipitation in the Presence of Fulvic, Humic, and Tannic Acids *Soil Sci. Soc. Am. J.* 52: 941-946 (1988)

Ito K., Kanno T., Sorption Behavior of Carrier-Free Technetium-95m on Minerals, Rocks and Backfill Materials under both Oxidizing and Reducing Conditions. *J. Nucl. Sci. Tech.* 25: 534-539 (1988)

Ito K., Akiba K., Adsorption of Pertechnetate Io on Active Carbon from Acids and their Salt Solutions. *J. Radioanal. Nucl. Chem.* 153: 381-390 (1991)

Kaplan D.J., Serne R.J., Pertechnetate Exclusion from Sediments. *Radiochim. Acta* 81: 117-124 (1998)

Kang, M. J., Rhee S. W., Moon H., Sorption of MO_4^-(M= Tc, Re) on Mg/Al Layered Double Hydroxide by Anion Exchange. *Radiochim. Acta.* 75: 169-173 (1996)

Kang, M. J., Chun K. S., Rhee S. W., Do Y., Comparison of Sorption Behavior of I^- and TcO_4^-) on Mg/Al Layered Double Hydroxide. *Radiochim. Acta.* 85: 57-63 (1999)

Kawashima M., Koyama M., Fujinaga T., Aquation of Hexahalogenotechnetium(IV). *J. Inorg. Nucl. Chem.* 38: 819-822 (1976)

Kenna B. T., Kuroda P. K., Isolation of Naturally Occurring Technetium. *J. Inorg. Nucl. Chem.* 23: 142-144 (1961)

Keith-Roach M.J., Morris K., Dahlgaard H., An investigation into technetium binding in sediments. *Marine Chemistry* 81: 149-162 (2003)

Kershaw P.J., McCubbin D., Leonard K.S., Continuing contamination of north Atlantic and Arctic waters by Sellafield radionuclides. *Sci. Total Environ.* 237/238: 119–132 (1999)

Kern S., Le nouveau métal le Davyum. *La Nature* 5: 401-402 (1877)

Kim J.I., Buckau G., Li G.H., Duschner H., Psarros N., Characterization of Humic and Fulvic-Acids from Gorleben Groundwater. *Anal. Chem.* 338: 245-252 (1990)

Kim J.I., Sekine T., Complexation of Neptunium(V) with Humic Acid. *Radiochim. Acta* 55: 187-192 (1991)

Kim J.I., Rhee D.S., Buckau G., Complexation of Am(III) with Humic Acids of Different Origin. *Radiochim. Acta* 52: 49-55 (1991a)

Kim J.I., Wimmer H., Klenze R., A Study of Curium(III) Humate Complexation by Time Resolved Laser Fluorescence Spectroscopy (TRLFS). *Radiochim. Acta* 54: 35-41 (1991b)

Kim J.I., The Chemical Behaviour of Transuranium Elements and Barrier Functions in Natural Aquifer Systems. *Mat. Res. Soc. Symp. Proc.* 294: 3-21 (1993)

Kim J.I., Rhee D.S., Wimmer H., Buckau G., Klenze R., Complexation of Trivalent Actinide Ions (Am^{3+}, Cm^{3+}) with Humic Acid – a Comparison of Different Experimental Methods. *Radiochim. Acta* 62: 35-43 (1993)

Kim J.I., Delakowitz B., Zeh P., Klotz D., Lazik D., A Column Experiment for the Study of Colloidal Radionuclide Migration in Gorleben Aquifer Systems. *Radiochim. Acta* 66: 165-171 (1994)

Kononova M. M., In: *Soil Organic Matter. Its Nature, Its Role in Soil formation and in Soil Fertility*, 2nd edition. Pergamon Press, Oxford (1966)

Kopunec R., Blazsek M., Comparative Study of Pertechnetate Reduction by Thiourea Using Spectrophotometric, Solvent-Extraction and Ion-Exchange Methods. *J. Radioanal. Nucl. Chem. Ar.* 183: 171-180 (1994)

Kunze S., Neck V., Gompper K., Fanghanel T., Studies on the immobilization of technetium under near-field geochemical conditions. *Radiochim. Acta.* 74: 159-163 (1996)

Lawson B.L., Scheifers S.M., Pinkerton T.C., The Electrochemical Reduction of Pertechnetate at Carbon Electrodes in Aqueous Non-Complexing Acid Media. *J. Electroanal. Chem.* 177: 167-181 (1984)

Lebron I., Suarez D.L., Mechanisms and precipitation rate of rhodochrosite at 25 degrees C as affected by P-CO_2 and organic ligands. *Soil Sci. Soc. Am J.* 63: 561-568 (1999)

Lee S.Y., Bondietti E.A., Technetium behavior in sulfide and ferrous iron solutions. *Mat. Res. Soc. Symp. Proc.* 15: 315-322 (1983)

Liang L. Y., Gu B. H., Yin X. P., Removal of Tc-99 from Contaminated Groundwater with Sorbents and Reductive Materials. *Sep. Tech.* 6: 111-122 (1996)

Lieser K.H., Bauscher Ch., 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: 205-213 (1987)

Lieser K.H., Bauscher Ch., Nakashima T., Dissolution of TcO_2 in Aqueous Solutions Under Various Conditions. *Radiochim. Acta* 42: 191-194 (1987)

Lieser K.H., Bauscher Ch., 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: 125-128 (1988)

Liger E., Charlet L., Van Cappellen P., Surface catalysis of uranium(VI) reduction by iron(II). *Geochim. Cosmochim. Acta* 63: 2939-2955 (1999)

Liu X.L., Poineau F., Fattahi M., Grambow B., Vichot L., Speciation of Tc(IV) in Chloride Solutions by Capillary Electrophoresis. *Radiochim. Acta* 93: 305-309 (2005)

Liu D.J., Fan X.H., Adsorption Behavior of Tc-99 on Fe, Fe_2O_3 and Fe_3O_4. *J. Radioanal. Nucl. Chem.* 264: 691-698 (2005)

Lloyd J.R., Sole V.A., Van Praagh C.V.G., Lovley D.R., Direct and Fe(II)-Mediated Reduction of Technetium by Fe(III)-Reducing Bacteria. *Appl. Environ. Microbiol.* 66: 3743-3749 (2000)

Lukens W.W., Bucher J.J., Edelstein N.M., Shuh D.K., Products of Pertechnetate Radiolysis in Highly Alkaline Solution: Structure of $TcO_2.xH_2O$ *Environ. Sci. Technol.* 36: 1124-1129 (2002)

Macaskie L.E., The Application of Biotechnology to the Treatment of Wastes Produced from the Nuclear Fuel Cycle: Biodegradation and Bioaccumulation as a Means of Treating Radionuclide-Containing Streams. *CRC Crit. Rev. Biotechnol.* 11: 41–112 (1991)

Maes A., De Brabandere J., Cremers A., Complexation of Europium(III) and Americium(III) with Humic Substances. *Radiochim. Acta* 52/53: 41-47 (1991)

Maes A., Tits J., Mermans G., Dierckx A., Measurement of the Potentially Available Charge and the Dissociation Behaviour of Humic Acid from Cobaltihexammine Adsorption. *J. Soil Sci.* 43: 669-677 (1992a)

Maes, A., van Herreweghen E., Van Elewijck F. , Cremers A., Behavior of Trace Cadmium in Boom Clay Reducing Sediment .1. Complexation with Insitu Dissolved Humic Acids. *Sci. Total Environ.* 118: 463-473 (1992b)

Maes A., Bruggeman C., Geraedts K., Vancluysen J., Quantification of the interaction of Tc with dissolved boom clay humic substances. *Environ. Sci. Technol.* 37: 747-753 (2003)

Marquardt C.M., Artinger R., Zeh P., Kim J.I., Redoxchemistry of Np(V) in a groundwater rich in humic substances. In: *Effects of Humic Substances on the Migration of Radionuclides: Complexation and Transport of Actinides. 2nd Technical Progress Report.* Ed. Buckau G., FZKA 6324, 21 (1999)

Marquardt C.M., Kim J.I., Complexation of Np(V) with Humic Acid: Intercomparison of Results from Different Laboratories. *Radiochim. Acta* 80: 129-137 (1998a)

Marquardt C.M., Kim J.I., Complexation of Np(V) with Fulvic Acid. *Radiochim. Acta* 81: 143-148 (1998b)

Maslennikov A.G., Courson O., Peretroukhine V.F., David F., Masson M., Technetium electrochemical reduction in nitric solutions at mercury and carbon electrodes 78: 123-129 (1997)

Mattigod S.V., Serne R.J., Fryxell G.E., Selection and Testing of "Getters" for Adsorption of Iodine-129 and Technetium-99: a Review. PNNL-14208. Prepared for the U.S. Department of Energy under Contract DE-AC06-76RL01830 (2003)

McCullough J., Hazen T.C., Benson S.M., Metting F.B., Palmisano A.C., In: *Bioremediation of metals and radionuclides... what is it and how it works*. Lawrence Berkeley National Laboratory, Berkeley, Calif. p. 5-7 (1999)

McKeown D.A., Hagans P.L., Carette L.P.L., Russel A.E., Swider K.E., Rolison D.R., Structure of Hydrous Ruthenium Oxides: Implications for Charge Storage. *J. Phys. Chem. B* 103: 4825-4832 (1999)

Means J.L., Grerar D.A., Duguid J.O., Migration of Radioactive Wastes: Radionuclide Mobilization by Complexing Agents. *Science* 200: 1477-1481 (1978)

Meyer R.E., Arnold W.D., Case F.I., O'Kelley G.D., Solubilities of Tc(IV) Oxides. *Radiochim. Acta* 55: 11-18 (1991)

Münze R., Abram U., Mixed-ligand complexes of technetium XII. Synthesis, characterization and X-ray crystal structure of (*o*-mercaptophenolato)bis[1,2-bis-(dimethylphosphino)ethane] technetium(III) tetraphenylboranate, [Tc(meph)-$(DMPE)_2$](BPh_4). *Inorg. Chim. Acta* 186: 151-154 (1991)

Münze, R., Polynuclear Technetium(IV)-99-Citrate Complex. *Radiochemical and Radioanalytical Letters* 48: 281-287 (1981)

Murphy C.E., Johnson T.L., Vegetative Uptake of Tc-99 from Buried, Solidified, Low-Level Radioactive Waste. *J. Environ. Qual.* 22: 793-799 (1993)

Naito S., Sekine T., Kino Y., Kudo H., Formation of Tc(IV) colloids and coagulation processes. *Radiochim. Acta* 82: 129-132 (1998)

Nguyen-Trung, C.; Palmer, D.A.; Giffaut, E., *Abstracts of the Seventh International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere (Migration '99)* UCRL-ID-135626 (1999)

Nightingale, **E.R., Jr**. Poised oxidation-reduction systems. *Anal. Chem.* 30: 267-272 (1958)

Noddack W., Tacke I., Berg O., Die Ekamangane, *Naturwiss.* 13: 567-574 (1925)

Noll B., Seifert S., Münze R., Preparation and Characterization of Technetium(IV)-Complexes with Diethylenetriaminepentaacetic Acid and Ethylenediamine-tetraacetic Acid as Ligands. *Int. J. Appl. Radiat. Isot.* 34: 581-584 (1983)

Ogawa M., *J. Coll. Sci. Imp. U. Tok.* 25 (1908)

Palmer D. A., Meyer R. E., Adsorption of Technetium on Selected Inorganic Ion-Exchange Materials and on a range of naturally occurring Minerals under Oxic Conditions. *J. Inorg. Nucl. Chem.* 43: 2979-2984 (1981)

Penrose W.R., Polzer W.L., Essington E.M., Nelson D.M., Orlandi K.A., Mobility of Plutonium and Am through a shallow Aquifer in a Semiarid Region. *Environ. Sci. Technol.* 24: 228-234 (1990)

Pepper S.E., Bunker D.J., Bryan N.D., Livens F.R., Charnock J.M., Pattrick R.A.D., Collison D., Treatment of Radioactive Wastes: An X-ray Absorption Spectroscopy Study of the Reaction of Technetium with Green Rust. *J. Colloid Interf. Sci.* 268: 408-412 (2003)

Perrier C., Segré E., Some Chemical Properties of Element 43, *J. Chem. Phys.*, **5:** 712-716 (1937)

Poineau F., Fattahi M., Montavon G., Grambow B., Condensation mechanisms of tetravalent technetium in chloride media. *Radiochim. Acta* 94: 291-299 (2006)

Potapova Z.M., Krylova A.Y., Kharlamov V.T., Reduction of Pertechnetate, Sodium Technetium-99m, by Stannous Chloride. *Khimiko-Farmatsevitcheskii Zhurnal* 23: 243-245 (1989)

Pourbaix M., In: *Atlas of Electrochemical Equilibria in Aqueous Solutions.* Oxford: Pergamon Press (1966)

Rard J.A., In: *Critical review of the chemistry and thermodynamics of technetium and some of its inorganic compounds and aqueous species.* UCRL-53440. Lawrence Livermore National Laboratory, Livermore, Calif. (1983)

Rard J.A., Rand M.H., Anderegg G., Wanner H., In: *Chemical Thermodynamics of Technetium.* Eds. Sandino M.C.A. and Östhols E. Chemical Thermodynamics, vol. 3. Elsevier Science, North-Holland, New York (1999)

Rard J.A., Current Status of the Thermodynamic Data for Technetium and Its Compounds and Aqueous Species. *J. Nucl. Radiochem. Sci.* 6: 197-204 (2005)

Röβler D., Franke K., Süβ R., Becker E., Kupsch H., Synthesis and chromatographic characterization of [Tc-99m]technetium-humic acid species, *Radiochim. Acta* 88: 95-100 (2000)

Routson R. C., Jansen G., Robinson A.V., ^{241}Am, ^{237}Np, and ^{99}Tc Sorption on Two United States Subsoils from Differing Weathering Intensity Areas. *Health Phys.* 33: 311-317 (1977)

Rulfs C.L., Meinke W.W., Observations on Some Chemical and Physical Properties of Technetium and its Compounds. *J. Am. Chem. Soc.* 74: 235-236 (1952)

Schnitzer A., Chemical Structure for Humic Acid. Chemical, ^{13}C-NMR, Colloid Chemical and Electron Microscopic Evidence. In: *Humic Substances in the Global environment and implications on human health.* Proceedings of the 6th International Meeting of the International Humic Substances Society, Monopoli (Bari), Italy, Eds.: Senesi N. and Miano T.N., pp. 57-70 (1994)

Schubert J., The Use of Ion Exchangers for the Determination of Physical Chemical Properties of substance Particularly Radiotracers in Solution I. Theoretical. *J. Phys. Colloid Chem.* 52: 340-356 (1948)

Schulten H.-R., A Chemical Structure for Humic Acid. Pyrolysis-Gas Chromatography/Mass Spectrometry and Pyrolysis-Soft Ionization Mass Spectrometry Evidence. In: *Humic Substances in the Global environment and implications on human health.* Proceedings of the 6th International Meeting of the International Humic Substances Society, Monopoli (Bari), Italy, Eds.: Senesi N. and Miano T.N., pp. 43-56 (1994)

Schwochau K., In: *Technetium. Chemistry and Radiopharmaceutical Applications.* Wiley-VCH Verlag GmbH: Weinheim (2000)

Seifert S., Noll B., Münze R., Studies of the Complex Formation of Technetium(IV) with Aminopolycarboxylic Acids in Aqueous Solution. *Int. J. Appl. Radiat. Isot.* 33: 1393-1398 (1982)

Sekine T., Watanabe A., Yoshihara K., Kim J.I., Complexation of Technetium with Humic Acid. *Radiochim. Acta* 63: 87-90 (1993)

Sekine T., Asai N., Muine T., Yoshihara K., Complexation of Technetium Traces with Humic Acid. *Radiochemistry* 39: 309-311 (1997)

Sekine T., Naito S., Kino. Y., Kudo H., Laser Induced Photoacoustic Spectroscopy Applied to a Study on Colloid Formation Processes. *Radiochim. Acta* 82: 135-139 (1998)

Sekine T., Narushima H., Kino Y., Kudo H., Lin M.Z., Katsumura Y., Radiolytic formation of Tc(IV) oxide colloids. *Radiochim. Acta* 90: 611-616 (2002)

Sekine T., Narushima H., Suzuki T., Takayama T., Kudo H., Lin A., Katsumura Y., Technetium(IV) oxide colloids produced by radiolytic reactions in aqueous pertechnetate solution. *Colloid Surface A* 249: 105-109 (2004)

Serne R.J., Conca J.L., LeGore V.L., Cantrell K.J., Lindenmeier C.W., Campbell J.A., Amonette J.E., Wood M.I., In: *Solid-Waste Leach Characteristics and Contaminant-Sediment Interactions. Volume 1: Batch Leach and Adsorption Tests and Sediment Characterization*. PNL-8889, Vol. 1, Pacific Northwest Laboratory, Richland, WA. (1993)

Shade J.W., Ames L.L., McGarrah J.E., Actinide and Technetium Sorption on Ironsilicate and Dispersed Clay Colloids. In: *Geochemical Behavior of Disposed Radioactive Waste*, ACS Symp. Series 246: 68-77. American Chem. Soc. Washington D.C. (1984)

Shankland R.S., In: *Atomic and Nuclear Physics*. New York, Macmillan p. 266 (1955)

Sheppard M.I., Vandergraaf T.T., Thibault D.H., Keith Reid J.A., Technetium and Uranium: Sorption by and Plant Uptake from Peat and Sand. *Health Phys.* 44: 635-643 (1983)

Sheppard S.C., Sheppard M.I., Evenden W.G., A Novel Method Used to Examine Variation in Tc Sorption among 34 Soils, Aerated and Anoxic. *J. Environ. Radioactiv.* 11: 215-233 (1990)

Sheppard M.I., Thibault D.H., Desorption and Extraction of Selected Heavy-Metals from Soils. *Soil Sci. Soc. Am. J.* 56: 415-423 (1992)

Shilov V.P., Krot N.N., Budantseva N., Yusov A., Garnov A., Perminov V., Astafurova L., In: *Investigation of Some Redox Reactions of Neptunium, Plutonium, Americium, and Technetium in Alkaline Media*, WHC-EP-0886, Richland, WA: Westinghouse Hanford Co (1996)

Shin H.S., Lee B.H., Choi J.G., Moon H., Complexation of Soil Humic Acid with Trivalent Curium and Europium Ions: a Comparative Study. *Radiochim. Acta* 69: 185-189 (1995)

Shuh K.D., Edelstein N.M., Burns C.J., Lukens W.W., Bucher J.J., Fickes M.G., Scott B.L., In: *Research program to investigate the fundamental chemistry of technetium*, Final report, Project number: EMSP-60296, U.S. Department of Energy (2000)

Spitsyn V.I., Kuzina A.F., Oblova A.A., Glinkina M.I.I., Stepovaya L.I., On the Mechanism of the Electroreduction of TcO_4^- Ion on a Platinum Cathode in Sulphuric Acid Solutions. *J. Analyt. Chem.* 30: 561-569 (1976)

Spitsyn V.I., Kryuchkov S.V., Kuzina A.F., Reduction of Pertechnetate Ions in Nitric-Acid Solutions by Hydrazine. *Soviet Radiochemistry* 25: 471-476 (1983)

Stalmans M., The behaviour of technetium in the environment, physicochemical aspects. Ph.D. thesis n. 148. Faculteit der Landbouwwetenschappen van de K. U. Leuven (1986)

Stalmans M., Maes A., Cremers A., Role of Organic Matter as a Geochemical Sink for Technetium in Soils and Sediments. In: *Technetium in the Environment.* Eds. Desmet G., Myttenaere C., Elsevier Applied Science Publishers Ltd. p. 91-113 (1986)

Stevenson F.J., In: *Humus Chemistry: Genesis, Composition, Reactions*. John Wiley and Sons (1982)

Strickert R., Friedman A.M., Fried S., The Sorption of Technetium and Iodine Radioisotopes by Various Minerals. *Nucl. Tech.* 49: 253-266 (1980)

Tagami K., Uchida S., Analysis of technetium-99 in soil and deposition samples by inductively coupled plasma mass spectrometry. Appl. Rad. Isotop. 47: 1057-1060 (1996)

Tagami K., Uchida S., Concentration of global fallout 99Tc in rice paddy soils collected in Japan. *Environ. Poll.* 95: 151-154 (1997)

Thorne M.C., Estimation of Animal Transfer Factors for Radioactive Isotopes of Iodine, Technetium, Selenium and Uranium. *J. Environ. Radioactiv.* 70: 3-20 (2003)

Tkac P., Kopunec R., Macášek F., Skrašková S., Sorption of Tc(IV) and Tc(VII) on soils: Influence of humic substances. *J. Radioanal. Nucl. Ch.* 246: 527-531 (2000)

Tkac P., Kopunec R., Preparation of Tc-HA complex by displacement of thiourea from hexakis(thiourea-S)technetium(III) complex, *J. Radioanal. Nucl. Ch.* 256: 417-423 (2003a)

Tkac P., Kopunec R., Preparation of ^{99m}Tc-humic complex by ligand exchange from hexakis(thiourea-S)technetium(III) complex, *J. Radioanal. Nucl. Ch.* 258: 215-220 (2003b)

Vandergraaf, T.T., Ticknor K.V., George I.M., Reactions Between Technetium in Solution and Iron-Containing Minerals Under Oxic and Anoxic Conditions, *Geochemical Behavior of Disposed Radioactive Waste*, Eds. Barney G.S., Narratil J.D., Schulz W., in ACS Symposium Series, Washington, D.C.: American Chemical Society 246: 25-43 (1984)

van der Lee J., CHESS, Another Speciation and Surface Complexation Computer Code. Technical Report Nr. LHM/RD/93/39, CIG-École des Mines de Paris, Fontainebleau, France (1993)

Van Loon L.R., Stalmans M., Maes A., Cremers A., Cogneau M., Soil-Humic Acid Complexes of Technetium: Synthesis and Characterization. In: *Technetium in the Environment.* Eds. Desmet G., Myttenaere C., Elsevier Applied Science Publishers Ltd. p. 143-153 (1986)

Vichot L., Ouvrard G., Montavon G., Fattahi M., Musikas C., Grambow B., XAS Study of Technetium(IV) Polymer Formation in Mixed Sulphate/Chloride Media *Radiochim. Acta* 90: 575-579 (2002)

Vichot L., Fattahi M., Musikas C., Grambow B., Tc(IV) Chemistry in Mixed Chloride/Sulphate Acidic Media. Formation of Polyoxopolymetallic Species. *Radiochim. Acta* 91: 263-271 (2003)

Vilcek S., Kalinchak M., Machan V., 99mTc-labelled compounds prepared with sodium dithionite as reducing agent. *Nuklearmedizin* 20: 283-289 (1981)

Walton F.B., Paquette J., Ross J.P.M., Lawrence W.E., Tc(IV) and Tc(VII) interactions with iron oxyhydroxides. *Nucl. Chem. Waste Man.* 6: 121-126 (1985)

Wanner H., The NEA Thermochemical Database project. *Radiochim. Acta* 44/45: 325-329 (1988)

Wharton M.J., Atkins B., Charnock J.M., Livens F.R., Pattrick R.A.D., Collison D., An X-ray Absorption Spectroscopy Study of the Coprecipitation of Tc and Re with Mackinawite (FeS). *Appl. Geochem.* 15: 347-354 (2000)

Wildung R.E., McFadden K.M., Garland T.R., Technetium sources and behavior in the environment. *J. Environ. Qual.* 8 (2): 156-161 (1979)

Wildung R.E., Gorby Y.A., Krupka K.M., Hess N.J., Li S.W., Plymale A.E., McKinley J.P., Fredrickson J.K., Effect of electron donor and solution chemistry on products of dissimilatory reduction of technetium by Shewanella putrefaciens. *Appl. Environ. Microbiol.* 66: 2451– 2460 (2000)

Winkler A., Bruhl H., Trapp C., Bock W.D., Mobility of technetium in Various Rocks and Defined Combinations of Natural Minerals. *Radiochim. Acta.* 44/45: 183-186 (1988)

Wolery T., EQ3/6: A software Package for Geochemical Modelling of Aqueous Systems: Package Overview and Installation Guide. *Technical Report UCRL-MA-110662 PT, I ed.; Lawrence Livermore National Laboratory, Berkeley, CA* (1992)

Wolfrum C., Bunzl K., Sorption and Desorption of Technetium by Humic Substances under Oxic and Anoxic Conditions. *J. Radioan. Nucl. Ch. Ar.*, 99: 315-323 (1986)

Xu Y., Schoonen M.A.A., The absolute energy positions of conduction and valence bands of selected semiconducting minerals. *Am. Mineral.*, 85: 543–556 (2000)

Zachara J.M., Heald S.M., Jeon B.-H., Kukkadapu R.K., Liu C., McKinley J.P., Dohnalkova A. C., Moore D.A., Reduction of pertechnetate [Tc(VII)] by aqueous Fe(II) and the nature of solid phase redox products *Geochim. Cosmochim. Acta*, 71: 2137-2157 (2007)

Zeh P., Czerwinski K.R., Kim J.I., Speciation of Uranium in Gorleben Groundwaters. *Radiochim. Acta* 76: 37-44 (1997)

Zhang P. C., Krumhansl J. K., Brady P.V., Boehmite Sorbs Perrhenate and Pertechnetate. *Radiochim. Acta,* 88: 369-373 (2000)

Zhuang H., Jishu Z., Lanying Z., Sorption of Radionuclides Technetium and Iodine on Minerals. *Radiochim. Acta*. 44/45: 143-145 (1988)

Zhuang H., Zheng J.S., Xia D.Y., Zhu Z.G., Retardation of Technetium and Iodine by Antimony and Mercury-Containing Minerals. *Radiochim. Acta.* 68: 245-249 (1995)