Complexation of calcium, thorium and europium by α-isosaccharinic acid under alkaline conditions

Author(s):
Vercammen, Karlien

Publication Date:
2000

Permanent Link:
https://doi.org/10.3929/ethz-a-003861976

Rights / License:
In Copyright - Non-Commercial Use Permitted

This page was generated automatically upon download from the ETH Zurich Research Collection. For more information please consult the Terms of use.
Complexation of Calcium, Thorium and Europium by \(\alpha\)-Isosaccharinic Acid under Alkaline Conditions

A dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

for the degree of

DOCTOR OF NATURAL SCIENCES

presented by

KARLIEN VERCAMMEN

Master in Engineering in Environmental Technology, KUL (Belgium)

born June 1, 1973

citizen of Belgium

accepted on the recommendation of

Prof. Dr. Hans Sticher, examiner
Dr. Martin Glaus, co-examiner
Prof. Dr. Kaspar Hegetschweiler, co-examiner
Prof. Dr. André Maes, co-examiner

January 2000
## Contents

<table>
<thead>
<tr>
<th>Acknowledgements</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary</td>
<td>VII</td>
</tr>
<tr>
<td>Zusammenfassung</td>
<td>IX</td>
</tr>
<tr>
<td>Samenvatting</td>
<td>XI</td>
</tr>
</tbody>
</table>

### 1 General introduction

1.1 L/ILW repository 2
1.2 Degradation of cellulose into isosaccharinic acid 5
1.3 Impact of isosaccharinic acid on the radionuclide mobility 7
1.4 Aim of the present work 8
1.5 Outline of the report 11

### 2 Complexation of calcium by α-isosaccharinic acid

2.1 Introduction 13
2.2 Materials and methods 16
  2.2.1 Synthesis of Ca-(α)-isosaccharinate 16
  2.2.2 Preparation of the samples 16
  2.2.3 pH measurement 17
  2.2.4 PHREEEQE and MEDUSA, the speciation codes 19
2.3 Results and discussion 20
  2.3.1 Kinetic of the solubility of Ca(ISA)_2 20
  2.3.2 Solubility of Ca(ISA)_2 at pH_{\text{calc}} = 13.3 in the presence and absence of Ca(OH)_2 23
  2.3.3 Additional experiment 24
3 Complexation of thorium by α-isosaccharinic acid

3.1 Introduction

3.2 High performance anion-exchange chromatography study
   3.2.1 Principles of high performance anion-exchange chromatography and its influence on metal complexes
   3.2.2 Materials and methods
      3.2.2.1 Preparation of samples for HPAEC analysis
      3.2.2.2 Synthesis of ISA lactone
      3.2.2.3 Radiotracers Th-234 and Ca-45
      3.2.2.4 High performance anion-exchange chromatography: experimental set-up
   3.2.3 Results and discussion
      3.2.3.1 Evidence for the existence of a Th-ISA-Ca complex
      3.2.3.2 Kinetic effects
      3.2.3.3 Stoichiometry of the Th-ISA-Ca complex
   3.2.4 Conclusions

3.3 Batch sorption study
   3.3.1 Principles of the batch sorption method
   3.3.2 Materials and methods
      3.3.2.1 Determination of the distribution coefficient $K_d$
      3.3.2.2 Preliminary conditions for applying the batch sorption method
   3.3.3 Results and discussion
      3.3.3.1 Determination of the number of ISA ligands coordinated with Th(IV)
      3.3.3.2 Determination of $\beta$ and $\beta^{\text{Ca}}$ taking into account the uncertainty of the experimental data
      3.3.3.3 Determination of the reaction stoichiometry and the stability constants $K$ and $K^{\text{Ca}}$
   3.3.4 Conclusions
4 Complexation of europium by α-isosaccharinic acid

4.1 Introduction 91

4.2 Batch sorption study 92

4.2.1 Materials and methods 95

4.2.1.1 Determination of the distribution coefficient $K_d$ 95

4.2.1.2 Preliminary conditions for applying the batch sorption method 97

4.2.2 Results and discussion 99

4.2.2.1 Determination of the number of ISA ligands coordinated with Eu(III) 99

4.2.2.2 Determination of $\beta$ taking into account the uncertainty of the experimental data 106

4.2.2.3 Determination of the reaction stoichiometry and the stability constant $K$ 109

4.2.3 Conclusions 111

5 Application 113

5.1 Introduction 113

5.2 Speciation calculations 114

5.2.1 Concentration of total ISA 114

5.2.2 Concentration of total Ca 115

5.2.3 Concentration of total Th(IV) 115

5.2.4 Concentration of total Eu(III) 116

5.2.5 pH 116

5.2.6 Complexation constants 116

5.3 Results and discussion 118

5.3.1 Speciation of Th(IV) 118

5.3.2 Speciation of Eu(III) 124

6 General conclusions 127
Appendix

A Chi-square minimisation method 129

B Calculating the uncertainty of $K_d$ 131

B.1 Uncertainty estimation process 131
B.2 The assignment of an uncertainty to the mean value of $K_d$ 136

C Spectroscopic studies 141

C.1 $^1$H- and $^{13}$C-NMR of the Ca/ISA system 141
C.2 $^1$H-NMR of the Eu/ISA/Ca system 143
C.3 $^1$H-NMR of the Th/ISA system 144
C.4 EXAFS of the Th/ISA/Ca system 145

References 147

Curriculum Vitae 157
Acknowledgements

I would like to express my gratitude to two highly talented scientists: Dr. Martin Glaus and Dr. Luc Van Loon. Both guided me through my doctoral thesis and gave me the chance to learn. I highly appreciated the fact that they always made time for me when I was popping in their office next-door with questions. In particular I value dearly their characteristic cheerful way of discussing things and of looking at chemistry.

I would like to thank Prof. Dr. Hans Sticher for being my supervisor and providing the opportunity to carry out this work, Prof. Dr. André Maes for his interest in my work and for being my co-examiner, and Prof. Dr. Kaspar Hegutschweiler for the $^1$H- and $^13$C-NMR measurements and for providing advise.

I am grateful to Dr. Jörg Hadermann and Dr. Mike Bradbury for their comments on the manuscript. I am particularly indebted to a number of people at PSI who contributed to this work by providing experimental data:

- R. Keil for ICP-AES analyses,
- Dr. André Scheidegger for EXAFS measurements,
- Dr. Ines Günther-Leopold for ICP-MS analyses,
- Dr. R. Schibli and Dr. R. Schwarzbach for $^1$H-NMR measurements.

I am much obliged to my two colleagues Salvi and Andy with whom I shared the office and the laboratory. Their readiness to help and kindness is very much appreciated.

I would like to thank all my colleagues at the Laboratory for Waste Management who made my stay in Switzerland a pleasant one.
Very special thanks also goes to Daniel for his love and endless encouragement.
Finally, I wish to thank my parents for their love and support throughout my education and especially during my stay in Switzerland.
Summary

In the planned repository for low- and intermediate level waste in Switzerland substantial amounts of organic waste are cellulose. Under the alkaline conditions of the cementitious repository, cellulose degrades into mainly erythro- and threo-isosaccharinic acid, called α-isosaccharinic acid and β-isosaccharinic acid, respectively. Isosaccharinic acid belongs to the class of polyhydroxy ligands. These are known to form stable complexes with various metal cations, especially under alkaline conditions. The formation of water soluble radionuclide complexes with isosaccharinic acid in a repository might therefore enhance the release of radionuclides to the geo- and biosphere.

In the present work, the complexation of α-isosaccharinic acid (ISA) with Ca(II), Th(IV) and Eu(III) was studied. Owing to the presence of Ca(OH)₂ in cement, the concentration of Ca²⁺ in the pore water of a cementitious repository is relatively high (in the mM range) compared to the concentration of radionuclides ( in the nM range), and, therefore, can influence the complexation of radionuclides by ISA. The complexation of Ca²⁺ by ISA was determined by measuring the solubility of Ca(ISA)₂ as a function of pH (pH 10-14). The experimental data could be explained by the formation of CaISA⁺ and CaISA₀⁻⁻⁻ complexes. The stability constants of the complexation reactions and the solubility product of Ca(ISA)₂, are: Ca²⁺ + ISA⁻ ⇌ CaISA⁺ with log K = 1.70, Ca²⁺ + ISA⁻ ⇌ CaISA⁺ + H⁺ with log K = -10.40 and Ca(ISA)₂ ⇌ Ca²⁺ + 2 ISA⁻ with log K_{sol} = -6.36, at zero ionic strength.

The complexation of Th, a representative for tetravalent actinides, by ISA was studied under alkaline conditions by two complementary techniques. Using high performance anion exchange chromatography, evidence was found for the formation of complexes between Th, Ca and ISA. In the presence of Ca, Th is assumed to coordinate with two ISA ligands and two Ca ions. The ratio between Th and ISA in this complex in the
presence of Ca was confirmed by batch sorption experiments, in which the sorption of Th was studied as a function of the concentration of ISA. Moreover, it was demonstrated in these batch sorption experiments that, in the absence of Ca, 1:1 Th:ISA complexes are formed. The different complexation reactions and corresponding constants at I = 0.3 M are: $\text{Th} + \text{ISA} \rightleftharpoons (\text{ThISA})_{\text{aq}} + 4\text{H}^+$ with $\log K = -10.1$ and $\text{Th} + 2\text{ISA} + \text{Ca} \rightleftharpoons (\text{Th(ISA)}_2\text{Ca})_{\text{aq}} + 4\text{H}^+$ with $\log K_{\text{Ca}} = -3.6$.

The complexation of Eu, an analogous for trivalent actinides, by ISA was studied in the pH range from 10.7 to 13.3 by batch sorption experiments. It was shown that 1:1 Eu:ISA complexes are formed. No effect of Ca on the complexation was observed. The complexation reaction and corresponding constant are: $\text{Eu} + \text{ISA} \rightleftharpoons (\text{EuISA})_{\text{aq}} + 4\text{H}^+$ and $\log K = -30.6$ at I = 0.3 M.

Speciation calculations showed that already low concentrations of total ISA in the cement pore water (in the μM range) may influence the distribution of Th and Eu in the repository between the pore water and the solid phase (i.e. sorption on cement and/or precipitation of the radionuclide).
Zusammenfassung


In der vorliegenden Arbeit wurde die Komplexierung von Ca(II), Th(IV) und Eu(III) durch α-Isosaccharinsäure (ISA) untersucht. Infolge der Anwesenheit von Ca(OH)$_2$ in Zement ist die Konzentration von Ca$^{2+}$ im Zementporenwasser relativ hoch (im mM Bereich) verglichen mit der Konzentration der Radionuklide (im nM Bereich). Es ist daher denkbar, dass die Anwesenheit der Ca$^{2+}$ Ionen einen Einfluss auf die Komplexierung der Radionuklide durch ISA hat. Die Wechselwirkung von ISA mit Ca$^{2+}$ wurde mit Löslichkeitsmessungen von CaISA$_2$ ermittelt (pH 10 – 14). Die experimentellen Daten konnten mit der Bildung von CaISA$^+$, sowie von CaISA$_{4+}$-Komplexen beschrieben werden. Die Stabilitätskonstanten der Komplexbildung und das Löslichkeitsprodukt von CaISA$_2$ sind: Ca$^{2+}$ + ISA$^-$ ⇌ CaISA$^+$ mit log $K = 1.70$, Ca$^{2+}$ + ISA$^-$ ⇌ CaISA$^6$ + H$^+$ mit log $K = -10.40$ und CaISA$_2$ ⇌ Ca$^{2+}$ + 2 ISA$^-$ mit log $K_{sol} = -6.36$ bei 0M Ionenstärke.

Die Komplexierung von Th(IV), einem Modellion für vierwertige Actiniden, durch ISA wurde mittels zweier sich ergänzender Messtechniken untersucht. Mit Hochleistungs-Anionenaustauschchromatographie wurden Hinweise auf die Bildung ternärer Komplexe von Th, ISA und Ca gefunden. Es wird angenommen, dass sich der Komplex aus einem
Zusammenfassung

Th-, 2 ISA- und 2 Ca-Ionen zusammensetzt. Das stöchiometrische Verhältnis zwischen ISA und Th konnte mit Gleichgewichts-Sorptionsexperimenten, in welchen die Sorption von Th unter Beigabe von ISA untersucht worden war, bestätigt werden. Ferner kann aufgrund solcher Experimente die Bildung eines 1:1 Komplexes zwischen Th und ISA in Ca freien Lösungen postuliert werden. Die Gleichgewichtsreaktionen und ihre zugehörigen Stabilitätskonstanten sind: Th + ISA $\rightleftharpoons$ (ThISA)$_4$$^{4+}$ + 4H mit log $K = -10.1$ und Th + 2ISA + Ca $\rightleftharpoons$ (Th(ISA)$_2$Ca)$_4$$^{4+}$ + 4H mit log $K_{Ca} = -3.6$ bei $I = 0.3$ M.

Die Komplexierung von Eu(III), einem Modellion für dreiwertige Actiniden, wurde ebenfalls mit Gleichgewichts-Sorptionsexperimenten im pH Bereich zwischen 10.7 und 13.3 untersucht. Es konnte gezeigt werden, dass sich ein 1:1 Komplex bildete und dass Ca keinen Einfluss auf diese Komplexbildung hat. Die Gleichgewichtsreaktionen und ihre zugehörigen Stabilitätskonstanten sind: Eu + ISA $\rightleftharpoons$ (EuISA)$_4$$^{4+}$ + 4H mit log $K = -30.6$ bei $I = 0.3$ M.

Abschliessende Speziationsrechnungen, in welchen diese neu ermittelten Komplexeffligleichgewichte berücksichtigt werden, zeigen, dass relativ geringe Konzentrationen von ISA im Porenwasser (im µM Bereich) die Verteilung (Sorptions- oder Löslichkeitsgleichgewichte) von Th(IV) und Eu(III) zwischen Zement und der Lösungsphase zu beeinflussen vermögen.
Samenvatting


In deze studie werd de complexatie van α-isosaccharinezuur (ISA) met Ca(II), Th(IV) en Eu(III) bestudeerd. Daar Ca(OH)₂ een belangrijk bestanddeel is van cement, is de Ca²⁺ concentratie in het poriënwater van een nucleaire bergplaats op basis van cement, relatief hoog (mM-bereik) in vergelijking met de concentratie van radionucliden (nM-bereik). Ca²⁺ kan bijgevolg de complexatie van radionucliden met ISA beïnvloeden. De complexatie van Ca²⁺ met ISA werd bepaald door de oplosbaarheid van Ca(ISA)₂ als functie van de pH te meten (pH 10 - 14). De experimentele gegevens konden worden verklaard a.d.h.v. CaISA⁺- en CaISA⁺⁺⁺⁺⁺-complexen. De stabiliteitsconstanten voor beide complexatiereacties en het oplosbaarheidsprodukt voor Ca(ISA)₂ zijn: Ca²⁺ + ISA⁻ ⇄ CaISA⁺ met log K = 1.70, Ca²⁺ + ISA⁻ ⇄ CaISA⁺⁺⁺⁺⁺ + H⁺ met log K = -10.40 en Ca(ISA)₂ ⇄ Ca²⁺ + 2 ISA⁻ with log K = -6.36, bij een ionische sterkte gelijk aan nul.

Om de complexatie van Th, een vertegenwoordiger van de tetravalente actiniden, met ISA te bestuderen bij alkalische pH werden twee complementaire technieken toegepast. Met behulp van anionuitwisselingschromatografie kon het bestaan van complexen tussen Th,
Ca en ISA aangetoond worden. Indien Ca aanwezig is in de oplossing, werd aangenomen
dat Th coordineert met twee ISA-liganden en twee Ca-ionen. De verhouding Th tot ISA in
dit complex in aanwezigheid van Ca werd ook bevestigd door een batch sorptie-
experiment, waarbij de sorptie van Th als functie van de ISA-concentratie werd nagegaan.
Bovendien toonden deze batch sorptie-experimenten aan dat in afwezigheid van Ca, 1:1
Th:ISA-complexen worden gevormd. De verschillende complexatiereacties en hun
constanten, bij een ionische sterkte van 0.3 M, zijn: Th + ISA ⇌ (ThISA)₄H + 4H
met log K = -10.1 en Th + 2ISA + Ca ⇌ (Th(ISA)₂Ca)₄H + 4H met log Kₐₐ = -3.6.
De complexatie van Eu, een vertegenwoordiger van de trivalente actiniden, met ISA werd
onderzocht voor het pH-gebied van 10.7 tot 13.3 d.m.v. batch sorptie-experimenten. Er
werd aangetoond dat 1:1 Eu:ISA-complexen gevormd worden en dat Ca geen invloed
heeft op de complexatiereactie. De complexatiereactie en overeenkomstige
stabiliteitsconstanten zijn: Eu + ISA ⇌ (EuISA)₄H + 4H en log K = -30.6, bij een
ionische sterkte van 0.3 M.
Speciatieberekeningen tonen aan dat in een nucleaire bergplaats op basis van cement zelfs
lange ISA-concentraties (µM-bereik) de verdeling van Th en Eu tussen het alkalische
porfenwater en de vaste fase (sorptie op cement en/of precipitatie) kunnen beïnvloeden.
1

General introduction

Radioactive wastes arise from the production of electricity in nuclear power plants, from medical and industrial applications and research. They are distinguishable from other types of toxic waste due to their emission of radiation and, in some cases, their heat output.

Radioactive wastes demand their own regulations concerning disposal. Because the quantity of radioactive wastes is small and arises in few well defined locations, it is economically and technically possible to store the wastes arising and to isolate them from the environment. A generally foreseen long-term strategy for most types of waste is disposal in geologic formations.

In Switzerland two repository types are anticipated (NAGRA\(^1\) 1993):

- a repository for low- and short-lived intermediate-level wastes (L/ILW) from the operation and decommissioning of the Swiss nuclear power plants, from reprocessing and from medicine, industry and research.
- a repository for vitrified high-level and long-lived intermediate-level wastes (HLW/TRU) mainly from the reprocessing of spent fuel as well as for possible direct disposal of spent fuel without reprocessing.

During the course of the project's progress from concept to implementation, performance assessments are made to show viability and compliance with regulatory requirements, and to help in defining necessary research and site characterisation work.

\(^1\) NAGRA = National Co-operative for the Disposal of Radioactive Wastes
Chapter 1

The present work concerns one of the numerous chemical processes taking place in the L/ILW repository. Before entering into the details, first a short description of the L/ILW repository is given, together with the important processes occurring in the underground repository. Next, the motivation of the present work is explained and the work is placed in the framework of the safety concept. Finally, the aim of this work is discussed.

1.1 L/ILW repository

Repository performance is influenced by a large number of processes and events. For the L/ILW repository two decisive factors for long-term safety are: the release of radionuclides into the deep groundwater and the exposure of the repository through erosion (NAGRA 1993). A barrier system (engineered and geological barriers) is chosen such that the release rates of nuclides to the biosphere are below prescribed limits and that the overburden above the repository is sufficiently thick that most of the nuclide inventory can decay before the repository caverns are exposed, respectively.

In Figure 1.1 the system of safety barriers for the L/ILW repository is shown. The nuclear waste is mixed with a stabilisation matrix, which allows for safe intermediate storage and, after repository closure, has the function of limiting the rate of release of radionuclides after the eventual failure of the drum. The most commonly used matrix material is cement. The function of the metal drum is to ease handling and possibly to protect the waste from groundwater for a minimum period of time. A porous material, mainly cement mortar, is distributed around the waste drums held in a concrete container. The repository caverns are backfilled with cement mortar. A porous mortar is the preferred backfill for the planned Swiss L/ILW repository. The mortar consists of quartz and cement, and is designed to ensure that gases produced in the waste do not lead to fracturing. It guarantees the escape of the gases from the wastes through the cavern roof into the excavation disturbed zone, without a large build up of overpressure. Finally, a geological barrier surrounds the repository. The main functions of the geosphere, i.e. the host rock and surrounding geological layers, are to ensure a low water flux through the
General introduction

Solidification matrix
(cement, bitumen, resins)

- Low radionuclide release rate

Container, container infill, waste drums
(concrete / cement grout / steel)

- Low solute transport rates
- Radionuclide sorption
- Chemical buffer

Emplacement cavern, lining and backfill
(concrete / special mortar)

- Limited water access
- Delay start of release
- Low solute transport rates
- Chemical buffer
- Radionuclide sorption
- Allows gas escape

Geological barriers
Repository zone:
- Low water flux
- Favourable hydrochemistry
- Mechanical stability

Geosphere:
- Retardation of radionuclides (sorption, matrix diffusion)
- Reduction of radionuclide concentration (dilution, radioactive decay)
- Physical protection of the engineered barriers (e.g. from glacial erosion)

Figure 1.1 System of barriers for the LILW repository (taken from NAGRA 1993).
repository caverns, a favourable hydrochemistry, high sorption capacity, mechanical stability and a barrier to erosion as well as to human intrusion.

Initially, oxygen is available in the repository. In the first decades following repository closure, the oxygen is consumed mainly through metal corrosion and an anoxic environment is reestablished (NAGRA, 1993).

The presence of large amounts of cement causes a highly alkaline environment in the repository. The bulk chemistry of hydrated cement is largely defined by a system containing $\text{CaO}$, $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{SiO}_2$, $\text{SO}_3$ and $\text{H}_2\text{O}$ (Berner 1990). Through the reaction with groundwater, the cement is leached, i.e. the solid phases initially available are dissolved and/or transformed into secondary phases, mainly calcite ($\text{CaCO}_3$). In the early degradation stage of cement (approximately the first 10000 years), dissolution of NaOH and KOH determines the pH of the cement pore water ($\text{pH} = 13.3$). The Ca-concentration in such water saturated with respect to $\text{Ca(OH)}_2$ is approximately 2 mM. In the second stage of cement degradation, after all the NaOH and KOH have been leached out, dissolution of $\text{Ca(OH)}_2$ determines the water chemistry of the cement pore water ($\text{pH} = 12.5$). In this stage of cement degradation, the Ca-concentration in pore water equals approximately 20 mM. After dissolution of the Ca-hydroxide phase, the remaining solid phases cause the pH to decrease further from 12.5 to approximately 10.5. The pH value of 10.5 is only reached after about one million years (Berner 1990, Neall 1994).

Inherent components of the repository for short lived L/ILW are organic compounds. They originate from decontamination processes in nuclear power plants (e.g. oxalic acid, citric acid, ethylenediaminetetraacetic acid). Further, L/ILW contains substantial amounts of organic compounds such as ion exchange resins, cellulose, bitumen which might degrade to water soluble organic ligands (Van Loon and Kopajtic 1990, Van Loon and Hummel 1995, Van Loon and Glaus 1998). A third source of organic compounds are cellulose derivates, hydroxycarboxylic acids (gluconic acid, tartaric acid), lignosulfonates

---

2 The material in the L/ILW repository consists, in terms of mass, of approximately 94% concrete, 4% steel, 1% high molecular organic waste components and, to a small extent, of further waste components (NAGRA 1993).
etc. These are added to cement to change its properties, such as the porosity and the hardening time (Franklin 1976).

Because these organic compounds may influence radionuclide mobility through the formation of aqueous radionuclide-ligand complexes, it is planned, in the present repository concept, to store wastes with a significant concentration of potential complexants separately. Therefore, the safety analyses presently assume different waste groups, which differ in type and concentration of potentially complex-forming ligands (NAGRA 1993).

As mentioned above, one important source of organic ligands is cellulose. Cellulosic materials such as cotton, wood and paper form a substantial part of the organic waste in an ILW repository. The main degradation product of cellulose under the alkaline conditions prevailing in the L/ILW repository near-field is isosaccharinic acid. The present work focuses on this organic ligand because it may have an influence on the radionuclide mobility.

1.2 Degradation of cellulose into isosaccharinic acid

Cellulose is composed of glucose monomers (Figure 1.2). The molecule has a non-reducing end and a reducing one. The alkaline degradation of cellulose under anoxic conditions starts at the reducing end group of the molecule. This reducing end group is split off from the cellulose chain (peeling off reaction) resulting in the formation of an intermediate species. This intermediate species reacts further to give the final degradation products. In the cementitious environment of the repository with large amounts of Ca present, the main degradation product is 2,4,5-trihydroxy-2-hydroxymethyl-pentanoic acid, also called isosaccharinic acid (Blears et al. 1957, Whistler and BeMiller 1958, Machell and Richards 1958, Machell and Richards 1960, Colbran and Davidson 1961, Sjöström 1977, Lai 1991). Glaus et al. (1999) analysed the degradation products of

---

3 The near-field consists of the engineered barrier system and that part of the host rock which is altered through interactions with the man-made structures.
Aldrich cellulose, degraded for one to eight months in artificial cement pore water under \( \text{N}_2 \) atmosphere at 25 °C. Isosaccharinic acid contributed approximately 85 % to the total dissolved organic carbon (DOC), while the other products such as lactic acid, formic acid etc. formed a minor part of the DOC (4%). Earlier cellulose degradation studies by Greenfield et al. (1995) and Bourbon and Toulhoat (1996) also identified isosaccharinic acid as the main degradation product.

Two diastereomers of isosaccharinic acid are formed in about equal amounts during the peeling off process: the erythro- and threo-form, called \( \alpha \)-isosaccharinic acid and \( \beta \)-isosaccharinic acid, respectively. Both diastereomers are shown in Figure 1.3.

\( \alpha \)-isosaccharinic acid (further denoted as ISA) is chosen in the present work as the representative of the degradation products of cellulose, based on the study of Van Loon and Glaus (1998). They studied the sorption of Th(IV), Eu(III) and Ni(II) on feldspar, under repository conditions. The good agreement between the reduction in sorption caused by pure ISA and by the degradation products, is an indication that ISA in the mixture of these cellulose degradation products is mainly responsible for the observed effect.
1.3 Impact of isosaccharinic acid on the radionuclide mobility

Isosaccharinic acid belongs to the class of polyhydroxy ligands. These are known to form stable complexes with various metal cations, especially under alkaline conditions (Pecsok and Sandera 1955, Sawyer 1964, Sawyer and Ambrose 1962, Saywer and Kula 1962, Motekaitis and Martell 1984, Rich et al. 1991, Tochiyama et al. 1992, Moreton 1993). The formation of water soluble radionuclide complexes with isosaccharinic acid in a repository might therefore enhance the release of radionuclides to the geo- and biosphere. There are two important chemical processes controlling the radionuclide retention capacity of the cementitious repository which can be disturbed by the presence of organic ligands. Firstly, most radionuclides sorb on the cement matrix and the alteration phases of the host rock. The presence of isosaccharinic acid, however, can cause desorption of the radionuclides. Wieland et al. (1998) found that the sorption of Th(IV) on cement in an artificial cement pore water was reduced in the presence of ISA. Secondly, because of the high alkaline environment a whole series of safety-relevant radionuclides are not dissolved to high concentrations in groundwater, but precipitate as

\[ \text{COOH} \]
\[ \text{HO} - \text{C} - \text{OH} \]
\[ \text{H} \]
\[ \text{H} \]
\[ \text{H} \]
\[ \text{CH}_2\text{OH} \]

\[ \alpha \text{-isosaccharinic acid} \]

\[ \text{COOH} \]
\[ \text{HO} - \text{C} - \text{CH}_2\text{OH} \]
\[ \text{H} \]
\[ \text{H} \]
\[ \text{H} \]
\[ \text{CH}_2\text{OH} \]

\[ \beta \text{-isosaccharinic acid} \]

Figure 1.3 The molecular structure of $\alpha$- and $\beta$-isosaccharinic acid.

4 The hyperalkaline water arising from the cementitious engineered barrier system alters the mineralogy of the host rock, e.g. calcium silicate hydrates are formed.
(hydr)oxides. These sparingly soluble phases, however, can be dissolved by complexing ligands. Moreton (1993) and Greenfield et al. (1995) observed Pu(IV) concentrations in solutions with isosaccharinic acid which were much higher than in the expected equilibrium with the tetravalent actinide oxide in the absence of the organic ligand. Also the solubilities for Cu(II), Co(II), Sm(III) and Eu(III) increase at pH 13 in the presence of cement pore water containing cellulose degradation products (Bourbon 1994, Bourbon and Toulhoat 1996).

1.4 Aim of the present work

Two important chemical phenomena controlling the radionuclide retention capacity of the cementitious repository are solubility limitations of the radionuclides and sorption on the cement matrix. Because radionuclide concentrations in LILW systems are low, the importance of solubility limitation is generally less than that of sorption (McCombie et al. 1989). Sorption retards migration of radionuclides into the environment. The safety relevant feature is that long transport times allow for the decay of larger portions of the nuclide inventory. Sorption is quantified in terms of distribution coefficients ($K_d$), which are a measure of the distribution of the radionuclides between the immobile solid, i.e. cement, and the mobile cement pore water. This $K_d$ is an important parameter in describing the source term for radionuclides and their transport. For example, in a simple model for transport in a dual porosity medium with water conducting zones and porous rock zone (matrix), one can define a retardation factor

$$R = R_f + \frac{d}{b} (\varepsilon_p + \rho_b K_d)$$

where $R_f$ is the retardation by sorption on the surface of water conducting fractures, $d$ is the width of the matrix, $b$ the half-width of the water conducting fracture, $\varepsilon_p$ the matrix porosity, $\rho_b$ the bulk density and $K_d$ the volume based distribution coefficient describing

Equation 1.1 shows that knowledge on $K_d$ is necessary for the determination of radionuclides retardation in safety assessment studies. The majority of the measured sorption data available in the literature are for cementitious materials in equilibrium with its own pore water in contact with radionuclides. However, these values are no longer valid in systems where organic ligands are present. Consequently, the value of the distribution coefficient in the presence of ligands is needed. The effect of organic ligands on $K_d$ under repository conditions has been little studied and, therefore, $K_d$ values for systems with organic ligands are rare.

In the most simple model, where one radionuclide ion is complexed by one organic ligand (L), the influence of organic ligands on the sorption is described by the following equation:

$$\frac{K_d^0}{K_d} = 1 + K \cdot [L]$$

(Equation 1.2)

$K_d^0$ and $K_d$ are the distribution coefficients in the absence and the presence of organic ligands, respectively, $K$ is the stability constant for the complexation reaction of the radionuclide by L, and $[L]$ is the concentration of L in the aqueous phase. As can be seen from equation 1.2, ligands may reduce the amount of radionuclides sorbed on the surface, depending on (i) the concentration of ligand in solution and (ii) the stability of the radionuclide-ligand complexes formed.

Equation 1.2 can be applied for the determination of $K_d$, the parameter used in the safety assessment studies (Bradbury and Sarott 1995, Bradbury and Van Loon 1998). However, for this purpose, knowledge of the complexation reactions and of the stability constants is necessary. In contrast to transition metals (Sillén and Martell 1964, Martell and Smith 1974), stability constants for actinides with organic ligands have been measured for only a few ligands. Moreover, these stability constants have mostly been determined at more or less acidic pH values, in order to prevent hydrolysis of the metal ion. This makes them rather useless for speciation calculations under the strongly alkaline
conditions prevailing in a cementitious repository. Especially for the complexation of actinides by polyhydroxy type of ligands, such as ISA, stability data based on detailed complexation studies are almost non-existent. Actually, the complexing ability of polyhydroxy ligands for actinides at alkaline pH is only demonstrated in one single study, concerning the complexation of gluconate with the uranyl ion (Sawyer and Kula 1962).

It is, therefore, in the first place, the aim of the present work to give direct evidence for the existence of complexes between ISA and the radionuclides Th(IV) and Eu(III) under highly alkaline conditions. Secondly, it is the aim to elucidate the stoichiometry of the complexation reactions between ISA and the radionuclides Th(IV) and Eu(III) and to determine their stability constants. Knowledge on the stoichiometry and the stability constants enables the determination of $K_d$ (equation 1.2) required in safety assessment studies.

For the determination of the stoichiometry of the complexation reactions, the generalised coordination-ionisation scheme postulated for polyhydroxy carboxylic acids by van Duin et al. (1989) is used. Based on literature data covering some forty cations, the structural changes of the cation complexes of polyhydroxy carboxylates as a function of the pH are discussed. Going from low to high pH, the following changes are proposed by van Duin et al. (1989): (1) bidentate coordination of the cations by the carboxylic and $\alpha$-hydroxyl groups, (2) ionisation of the carboxylic acid function, (3) ionisation of the $\alpha$-hydroxyl group and (4) coordination by two ionised hydroxyl functions. The various species formed are pictured in Figure 1.4.

![Figure 1.4](image)

*Figure 1.4* Generalised scheme for the coordination-ionisation of cation-polyhydroxy carboxylic acid systems. Taken from van Duin et al. (1989).
Figure 1.5 summarises the dominating complexes of a whole series of cations as a function of the pH. According to this scheme, under alkaline conditions, Ca(II) will be coordinated by the ionised carboxylic and α-hydroxyl groups (region 3). The lanthanide Eu(III) and the tetravalent actinide Th(IV), on the contrary, are postulated to be coordinated by an ionised diol function (region 4).

These molecular structures proposed by van Duin et al. (1989) will be tested in the present work regarding their suitability in explaining the complexations of Th(IV) and Eu(III) by ISA.

![Diagram of pH and cation complexes]

**Figure 1.5** Successive ionisations of cation complexes of polyhydroxy carboxylic acids as a function of pH. Taken from van Duin et al. (1989).

1.5 Outline of the report

Because Ca(II) is omnipresent in a cementitious repository (presence of portlandite in cement) the complexation of ISA with Ca(II) is studied. The fairly large amounts of Ca$^{2+}$ in the cement pore water may have an important influence on the speciation of trace elements. Through competition with the radionuclides for the ISA binding sites or through promotion of the binding of radionuclides by ISA, they can have a negative or positive effect, respectively, on the mobility of radionuclides.
Further, the complexation of ISA with Th(IV) and Eu(III), respectively, is studied. Eu(III) and Th(IV) are chosen as representatives for tri- and tetravalent actinides. Finally, speciation calculations were performed using the determined complexation constants for the complexations of Ca, Th and Eu by ISA.
2

Complexation of calcium by \(\alpha\)-isosaccharinic acid

2.1 Introduction

Owing to the presence of portlandite (\(\text{Ca(OH)}_2\)) in cement, the concentration of \(\text{Ca}^{2+}\) in the pore water of a cementitious repository is relatively high (mM range) compared to the concentration of radionuclides (nM range). Therefore, on the one hand, \(\text{Ca}^{2+}\) could compete with the radionuclides for complexation with ISA, even if its affinity for ISA were orders of magnitude lower than that of radionuclides. The reason is that the relative amount of Ca-ISA species or radionuclide-ISA species depend both on the equilibrium constants and the total concentration of Ca and radionuclides.

On the other hand, \(\text{Ca}^{2+}\) might promote the complexation of radionuclides by ISA through formation of ternary complexes. This was shown for complexation of \(\text{Al}^{3+}\) by structurally related polyhydroxy dicarboxylic acids in the presence of \(\text{Ca}^{2+}\) (Venema et al. 1993). The same authors have also shown in a previous study that \(\text{Al(III)}\)-tartrate solutions possess strong coordinating properties towards alkaline earth metal ions (Venema et al. 1992).

The understanding of the complexation of \(\text{Ca}^{2+}\) by ISA will contribute to the assessment of those two phenomena, i.e. competition and promotion. Therefore, in this chapter, the complexation will be studied in more detail.

In general, the complexation of multivalent metal ions by polyhydroxy carboxylates (\(L^-\)) can involve the carboxylate group and/or deprotonated hydroxo groups as ligand sites.

\(^{1}\) Part of this chapter is published in Vercammen et al. (1999a)
The stoichiometry of the formation of a 1:1 complex is represented by the following equation

\[ M^{z+} + L^- \rightleftharpoons ML_{\text{aq}}^{z-n-I} + nH^+ \]  

(2.1)

According to the generalised coordination-ionisation scheme of van Duin et al. (1989) postulated for polyhydroxy carboxylic acids, \( n \) is expected to be 0 for the binding of \( Ca^{2+} \) in the pH region 4–10, whereas at pH larger than 10, \( n \) is expected to be 1 (see General introduction). With a single exception (Makridou et al. 1977), only reactions without proton exchange (\( n = 0 \)) are described in the literature (see Table 2.5).

Almost nothing is known about the complexation of \( Ca^{2+} \) by ISA at alkaline pH. Indirect evidence for such a reaction has recently been given by Van Loon and Glaus (1998) in a study of the degradation of cellulose in artificial cement pore water (pH 13.3, 2 mM Ca) in the presence of portlandite. It was found that the total concentration of Ca in solution increased with increasing degree of degradation of cellulose, i.e. with increasing concentration of ISA (Figure 2.1, filled symbols). The small change in pH from 13.3 to 13 as the degradation proceeded and its corresponding increase of the solubility of \( Ca(OH)_2 \), were too small to explain the total concentrations of Ca observed.

In the same study, the sorption of ISA on cement was measured, and the same dependency of the total Ca concentration on the concentration of ISA was found (Figure 2.1, open symbols). The total concentrations of Ca observed were significantly larger than could be explained from the solubility of \( Ca(OH)_2 \). However, by postulating the formation of a 1:1 complex between \( Ca^{2+} \) and ISA with \( n = 1 \) (equation 2.1), the authors could satisfactorily explain the experimental data (Figure 2.1, full line with \( K_{CaISA^{0}_{H}} = -10.50 \) at \( I = 0 \) M).

The aim of the present work is to verify the existence of such an uncharged \( CaISA^{0}_{H} \) complex in a well defined system. This contrasts with the experimental conditions used by Van Loon and Glaus (1998). In their cellulose degradation experiment at pH 13.3, \( Ca(OH)_2 \) was a pure solid phase. The ligands, however, were a mixture of different organics. Although ISA was the dominant species, the influence of other degradation products could not be excluded. In their sorption studies at pH 13.3, pure ISA was used as a ligand. The solid phase was a Portland cement comprising different solid phases but
mostly Ca(OH)$_2$. Owing to the heterogeneity of the experimental systems investigated by Van Loon and Glaus (1998), alternative explanations were possible for the increased Ca concentrations. Further, all these experiments of Van Loon and Glaus (1998) were performed at a pH of 13.3. For the present study, solubility experiments with the sparingly soluble Ca(ISA)$_2$ at various alkaline pH values between 10.5 and 13.3 are performed. If a CaISA$_{2n+1}$ complex is formed, then, the total concentration of Ca is expected to be dependent on pH owing to the exchange of one proton according to equation 2.1.

**Figure 2.1** The effect of ISA on the concentration of Ca in solution at pH 13.3 for solutions in contact with Ca(OH)$_2$ (Van Loon and Glaus 1998).
2.2 Materials and methods

All the experiments were performed at 23 ± 2 °C. Bidemineralised water was used, prepared by ultrafiltration with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.2.1 Synthesis of Ca-(α)-isosaccharinate

The original procedure (Whistler and BeMiller 1963) was slightly modified. 200 g lactose monohydrate (Merck) and 54.4 g calcium hydroxide (Merck) were dissolved in 2 litres of Argon-flushed water and stored at room temperature for 3 days in a closed vessel. After this time, the mixture was boiled for 6 hours, keeping the volume constant by adding small amounts of water. The hot solution was filtered and the volume of the filtrate reduced to about 370 ml by boiling. The solution, containing a precipitate of Ca(ISA)$_2$, was stored at 4°C overnight. The precipitate was removed by filtration, washed with water and ethanol, and dried overnight in an oven at 75°C. The crude product was redissolved by boiling at a ratio of 1.2 g of the crude product to 100 g of water. After removing insoluble impurities from the hot solution by filtration, the volume was reduced to approximately 10 % of the starting volume. The white precipitate formed was washed with water and ethanol and dried overnight in a vacuum oven at 50°C. HPAEC analysis on a Carbopac PA-100 column (Dionex DX-500, pulsed amperometric detection using a gold working electrode) of the dissolved Ca(ISA)$_2$ showed the presence of only one peak for ISA, suggesting the absence of impurities.

2.2.2 Preparation of the samples

All the solubility experiments were performed in a glovebox under N$_2$ atmosphere (O$_2$, CO$_2$ < 5 ppm).
Approximately 0.5 g Ca(ISA)$_2$ was weighed into a 40 ml polyallomer centrifuge tube together with 20 ml of a stock solution. This stock solution contained NaOH and NaClO$_4$ in calculated amounts to give the desired pH in the pH range 10.8-13.3 and an ionic strength of 0.3 M, respectively. To some samples a small amount (0.05-0.15 g) of Ca(OH)$_2$ was added. The tubes were shaken end-over-end for well defined times. After shaking, the solution was filtered (0.45 μm, non-sterile Acrodisc filter, polysulfone membrane, Gelman Sciences). Centrifuging the samples (27000 g, 0.5 h), instead of filtering them, gave no significant difference. Therefore, the fastest technique, filtration, was chosen. Further, the filtrate was analysed for Ca by ICP-AES (ARL 3410 ICP with Minitorch™) and for ISA by anion exchange chromatography (Dionex DX-500, Carbopac PA-100 (4×250 mm), eluent 80 mM NaOH, flow: 1 ml/min., suppressed conductivity).

### 2.2.3 pH measurement

In most of the samples, the pH of the filtrate was measured with a solid state electrode (ORION SURE-FLOW™, model 6165). However, these measurements had to be discarded, because it was realised, later on, that the response of the electrode was not only affected by hydrogen ions but also by the calcium ions present in the samples.

After realising the deviant behaviour of the solid state electrode, the pH was measured with a glass electrode (ORION, ROSS Combination pH Electrode). Comparing the pH measured with the glass electrode after dissolution of Ca(ISA)$_2$ with the initial calculated pH of the stock solutions (pH$_{calc}$), showed that the difference between both pH’s was not more than 0.13 pH units (std. dev. = 0.11, n = 33). Because the experiments using the solid state electrode were similar as those experiments using a glass electrode, it was decided to use the calculated pH of the stock solution (pH$_{calc}$) for modelling purposes in all those cases where the pH had been measured by the solid state electrode.

A titration experiment was performed in order to calibrate the glass electrode at an ionic strength of 0.3 M. Small amounts of 0.3 M NaOH (made from 1 M NaOH, Titrisol) were added to 15 ml of a 0.3 M NaClO$_4$ solution. The experiment was executed under Argon-atmosphere. The pH of the solution during titration was calculated based on the known
amount added NaOH. For the conversion of molar OH⁻ concentration into pH, the activity coefficients $\gamma_i$ are calculated using the Davies equation (Robinson and Stokes 1959):

$$\log \gamma_i = -0.5 \cdot z_i^2 \cdot \left( \frac{\sqrt{I}}{(1 + \sqrt{I})} - 0.3 \cdot I \right)$$

(2.2)

where $z_i$ is the charge of ion i and I is the ionic strength of the solution.

Between pH 10.5 and 13, the glass electrode shows a slight deviation from linear behaviour (Figure 2.2). Therefore, the obtained titration curves were fitted by means of a second order polynomial curve, to determine the pH value corresponding with the measured potential of the samples.

As shown in figure 2.2, a shift of the titration curve was noticed within hours. This was controlled by repeating the calibration procedure after time intervals of approximately two hours.

![Figure 2.2 Calculated pH of a solution versus the potential measured with a glass electrode, at different times.](image-url)
2.2.4 PHREEQE and MEDUSA, the speciation codes

All the calculations for determining the interaction constants (see section 2.4) were done with the PHREEQE geochemical code (Parkhurst et al. 1980). With given values for the thermodynamic constants, the program determined the species and their corresponding concentration for the chosen pH and ionic strength. This means that several calculations are necessary to know the behaviour of the species of interest as a function of the pH. The activity coefficients are calculated according to the Davies equation (equation 2.2).

The following table gives an overview of chemical equilibria used in the PHREEQE database and their corresponding thermodynamic constants.

<table>
<thead>
<tr>
<th>reaction</th>
<th>log K</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)$_2$ $\rightleftharpoons$ Ca$^{2+}$ + 2 OH$^{-}$</td>
<td>-5.19</td>
<td>Baes and Mesmer (1976)</td>
</tr>
<tr>
<td>Ca$^{2+}$ + H$_2$O $\rightleftharpoons$ CaOH$^+$ + H$^+$</td>
<td>-12.78</td>
<td>Nordstrom et al. (1990)</td>
</tr>
<tr>
<td>H$_2$O $\rightleftharpoons$ H$^+$ + OH$^{-}$</td>
<td>-14.00</td>
<td>Nordstrom et al. (1990)</td>
</tr>
</tbody>
</table>

For the simulation of the experimental data, shown by the lines in the figures 2.5-2.9, the program MEDUSA (Puigdomenech, 1983) was used. This program calculates distribution diagrams based on given thermodynamic constants. The distribution of the species as a function of a chosen parameter, e.g. the pH, is calculated. The ionic strength is kept constant over the whole pH range. The equilibrium constants in the input file are given for zero ionic strength. For the ionic strength of the experiment, i.e. I = 0.3 M, the equilibrium constants are recalculated using the activity coefficients, calculated with the following equation:

$$\log \gamma_i = -z_i^2 \cdot A \cdot \frac{\sqrt{I}}{1 + B \cdot I} - \log(1 + 0.018 \cdot I) + b \cdot I$$  (2.3)
Chapter 2

with \( A = 0.509, B = 1.22, b = 0.064, z \), the charge of ion i and I the ionic strength of the solution. Equation 2.3 is an approximation to the model proposed by Helgeson (Helgeson et al. 1981, Oelkers and Helgeson 1990).

Because both programs, PHREEQE and MEDUSA, each use a different equation for calculating the activity coefficients, their output files at \( I = 0.3 \) M are slightly different. For that reason, the equilibrium constants in the input file of MEDUSA (\( I = 0 \) M) were adjusted so that they gave the same output file as PHREEQE at \( I = 0.3 \) M.

2.3 Results and discussion

2.3.1 Kinetic of the solubility of Ca(ISA)₂

Ca(ISA)₂ was equilibrated with a NaOH/NaClO₄ mixture at different alkaline pH's and a fixed ionic strength of 0.3 M. To find out the time required to equilibrate the Ca(ISA)₂–NaOH/NaClO₄ suspensions, the supernatants were analysed after times varying between 1 and 14 days. The results are summarised in Figure 2.3 and Table 2.2.

For pH values below pH 12.8, no differences in the total concentration of Ca are observed for the equilibrium times studied. Beyond pH 12.8, two different situations can be distinguished. In the short term (1–2 days), a continuous increase of the total concentration of Ca is observed with increasing pH, whereas at longer times (3–14 days) the total concentration of Ca reaches a maximum value at a pH of approximately 12.8 and decreases at higher pH values. Obviously, the system on the short term is not in equilibrium. The fact that the total concentration of Ca suddenly drops between two and three days, suggests that a new solid phase is formed which is less soluble than Ca(ISA)₂. Presumably this solid phase is portlandite (Ca(OH)₂), because the solubility of portlandite is strongly pH dependent. Portlandite starts precipitating at pH 12.8 i.e. \( K_{\text{sol(Ca(OH)₂)}} = 10^{-5.19} \) (Baes and Mesmer 1976). With increasing pH this solubility decreases owing to the reaction:
Thus, it can be hypothesised that the systems on the short term are oversaturated with respect to portlandite. Only one single data point (pH 13.2; 7 days) deviates from this behaviour. In this system, the formation of the new solid phase seems to be delayed for unknown reasons.

Figure 2.3 Concentration of total Ca in solution in equilibrium with Ca\((\text{ISA})_2\), measured after different equilibration times. (Results taken from Table 2.2 and Table 2.4 for data in the absence of Ca.)
Table 2.2 Composition of the solutions in equilibrium with Ca\((ISA)\), at different pH values and \(I = 0.3 \, \text{M} \) \((T = 25^\circ \text{C})\), equilibrated for different times.

<table>
<thead>
<tr>
<th>time (days)</th>
<th>pH(_{\text{calc}})</th>
<th>total Ca (mM)</th>
<th>total ISA (mM)</th>
<th>time (days)</th>
<th>pH(_{\text{calc}})</th>
<th>total Ca (mM)</th>
<th>total ISA (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>10.87</td>
<td>10.25</td>
<td>20.91</td>
<td>3.8</td>
<td>10.87</td>
<td>10.65</td>
<td>21.06</td>
</tr>
<tr>
<td>1.34</td>
<td>10.53</td>
<td>20.77</td>
<td>11.34</td>
<td>10.75</td>
<td>21.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.87</td>
<td>10.85</td>
<td>21.86</td>
<td>11.87</td>
<td>10.83</td>
<td>21.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.34</td>
<td>(11.75)</td>
<td>23.49</td>
<td>12.34</td>
<td>11.60</td>
<td>23.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.87</td>
<td>(14.40)</td>
<td>29.33</td>
<td>12.87</td>
<td>14.97</td>
<td>29.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.34</td>
<td>(23.28)</td>
<td>49.41</td>
<td>13.34</td>
<td>9.51</td>
<td>53.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>10.87</td>
<td>10.58</td>
<td>22.33</td>
<td>7.2</td>
<td>10.87</td>
<td>9.76</td>
<td>19.49</td>
</tr>
<tr>
<td>1.34</td>
<td>10.50</td>
<td>21.65</td>
<td>11.34</td>
<td>10.25</td>
<td>20.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.87</td>
<td>10.90</td>
<td>22.49</td>
<td>11.87</td>
<td>11.08</td>
<td>21.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.34</td>
<td>(12.23)</td>
<td>24.39</td>
<td>12.34</td>
<td>11.60</td>
<td>23.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.87</td>
<td>(13.95)</td>
<td>30.92</td>
<td>12.87</td>
<td>14.10</td>
<td>29.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.34</td>
<td>(22.51)</td>
<td>52.30</td>
<td>13.34</td>
<td>11.88</td>
<td>52.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>10.87</td>
<td>10.28</td>
<td>21.34</td>
<td>14.2</td>
<td>10.87</td>
<td>11.10</td>
<td>20.45</td>
</tr>
<tr>
<td>1.34</td>
<td>10.60</td>
<td>20.93</td>
<td>11.34</td>
<td>10.35</td>
<td>20.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.87</td>
<td>10.60</td>
<td>21.86</td>
<td>11.87</td>
<td>10.48</td>
<td>20.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.34</td>
<td>12.08</td>
<td>23.55</td>
<td>12.34</td>
<td>10.88</td>
<td>22.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.87</td>
<td>14.10</td>
<td>29.76</td>
<td>12.87</td>
<td>13.52</td>
<td>29.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.34</td>
<td>11.90</td>
<td>50.48</td>
<td>13.34</td>
<td>11.73</td>
<td>54.07</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Ca data between parentheses were not used for modelling (section 2.4) because the equilibrium state was not reached.

The increase in the total Ca concentration between pH 12 and 12.8 (shown in Figure 2.3) is an evidence for the formation of a complex between Ca\(^{2+}\) and ISA, according to equation 2.1 with \(n \geq 1\). Because the formation of such complexes involves the dissociation of protons, the degree of complexation progresses with increasing pH and,
consequently, the concentration of Ca in solution increases. If the total concentration of Ca in solution was governed only by the solubility of Ca\((\text{ISA})_2\) and \(\text{Ca(OH)}_2\), no increase in the total concentration of Ca would be expected. Up to pH 12.8 the total concentration of Ca would be constant, because it is dominated by the dissolution of \(\text{Ca(ISA)}_2\), a pH-independent process. Beyond pH 12.8, the concentration of Ca in solution will decrease because of the precipitation of \(\text{Ca(OH)}_2\), which is pH-dependent (equation 2.4).

To check this hypothesis of portlandite precipitating, \(\text{Ca(OH)}_2\) was added to the systems with a pH higher than 12.8. This experiment is discussed in the following.

### 2.3.2 Solubility of \(\text{Ca(ISA)}_2\) at pH\(_{\text{calc}} = 13.3\) in the presence and absence of \(\text{Ca(OH)}_2\)

Four different systems were studied. Two systems containing only \(\text{Ca(ISA)}_2\) equilibrated for one day and one week, respectively, and two systems of \(\text{Ca(ISA)}_2\) to which \(\text{Ca(OH)}_2\) was added, equilibrated also for one day and one week, respectively. All the solids were equilibrated with a NaOH/NaClO\(_4\) mixture at a pH\(_{\text{calc}}\) of 13.3 and with \(I = 0.3\) M.

According to the hypothesis of delayed precipitation of portlandite, it would be expected that the \(\text{Ca(OH)}_2\) initially present would be a source of nucleation cores for the precipitation of portlandite. Consequently, the total concentration of Ca on the short term should be lower than in a system without \(\text{Ca(OH)}_2\) initially present. Once the Ca concentration decreases owing to the precipitation of portlandite, the concentration of ISA concomitantly increases in order to maintain saturation of the solution with respect to \(\text{Ca(ISA)}_2\). Thus, it is to be expected that the concentration of ISA on the short term would be higher in the system with \(\text{Ca(OH)}_2\) initially present. As can be seen from Table 2.3, the results for Ca and ISA are in agreement with the hypothesis of delayed precipitation of portlandite. Furthermore, after one week of equilibration, the samples with and without initial \(\text{Ca(OH)}_2\) show only a small difference in total Ca concentrations. Considering the spread of the data points, it is likely that this small difference is within the experimental uncertainty.
Summarising, it can be concluded that the systems equilibrated for 3 days and more are at equilibrium with Ca(OH)$_2$ so that these results may be used for the thermodynamic modelling of the chemical equilibria involved (section 2.4).

Table 2.3 Composition of the solution in equilibrium with Ca(ISA)$_2$ at $pH_{calc}$ 13.3, with and without the addition of Ca(OH)$_2$ ($I = 0.3$ M, $T = 25^\circ C$).

<table>
<thead>
<tr>
<th>equilibration time: 1 day</th>
<th>equilibration time: 1 week</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)$_2$ (g)</td>
<td>total Ca (mM)</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>0</td>
<td>19.92</td>
</tr>
<tr>
<td>0</td>
<td>20.40</td>
</tr>
<tr>
<td>0</td>
<td>19.82</td>
</tr>
<tr>
<td>0</td>
<td>19.82</td>
</tr>
<tr>
<td>0</td>
<td>20.12</td>
</tr>
<tr>
<td>0.08</td>
<td>9.74</td>
</tr>
<tr>
<td>0.09</td>
<td>9.81</td>
</tr>
<tr>
<td>0.11</td>
<td>9.58</td>
</tr>
<tr>
<td>0.17</td>
<td>9.18</td>
</tr>
<tr>
<td>0.14</td>
<td>9.50</td>
</tr>
</tbody>
</table>

The underlined data were used for evaluation of the model in section 2.5, Fig. 2.7.

2.3.3 Additional experiment

In order to get enough data for the modelling, one additional experiment was performed over the whole pH range. Ca(ISA)$_2$ was equilibrated with a NaOH/NaClO$_4$ mixture at different pH values ($I = 0.3$ M). At higher pH, Ca(OH)$_2$ was added to half of the samples. The equilibrium pH after one week was measured with a glass electrode. These pH measurements are summarised in Table 2.4, together with the results of the solubility of Ca(ISA)$_2$ in the absence and the presence of Ca(OH)$_2$ after one week.
Table 2.4 Composition of the solution in equilibration with Ca(ISA)$_2$ (and Ca(OH)$_2$) after one week of equilibration ($I = 0.3\ M$, $T = 25^\circ C$).

<table>
<thead>
<tr>
<th>Ca(ISA)$_2$ in the absence of Ca(OH)$_2$</th>
<th>Ca(ISA)$_2$ in the presence of Ca(OH)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample</td>
<td>pH</td>
</tr>
<tr>
<td>A</td>
<td>10.53</td>
</tr>
<tr>
<td>B</td>
<td>10.51</td>
</tr>
<tr>
<td>C</td>
<td>10.42</td>
</tr>
<tr>
<td>A</td>
<td>11.20</td>
</tr>
<tr>
<td>B</td>
<td>11.16</td>
</tr>
<tr>
<td>C</td>
<td>11.11</td>
</tr>
<tr>
<td>A</td>
<td>11.76</td>
</tr>
<tr>
<td>B</td>
<td>11.72</td>
</tr>
<tr>
<td>C</td>
<td>11.77</td>
</tr>
<tr>
<td>A</td>
<td>12.27</td>
</tr>
<tr>
<td>B</td>
<td>12.25</td>
</tr>
<tr>
<td>C</td>
<td>12.25</td>
</tr>
<tr>
<td>A</td>
<td>12.69</td>
</tr>
<tr>
<td>B</td>
<td>12.65</td>
</tr>
<tr>
<td>C</td>
<td>12.64</td>
</tr>
</tbody>
</table>

The Ca data between parentheses were not used for modelling in section 2.4.
Chapter 2

All the results of Table 2.4 are displayed in Figure 2.4.

![Figure 2.4 Concentration of total Ca in solution in equilibrium with Ca(ISA)₂ (and Ca(OH)₂) at different pH values (I = 0.3 M, T = 25°C).](image)

**Figure 2.4** Concentration of total Ca in solution in equilibrium with Ca(ISA)₂ (and Ca(OH)₂) at different pH values (I = 0.3 M, T = 25°C).

Figure 2.4 summarises the characteristics of the Ca(ISA)₂ - Ca(OH)₂ system:

- the increase in total Ca concentration (open symbols) in the pH range 12.5 - 13, as a result of the formation of the CaISA₀⁻H complex,
- the decrease of the total Ca concentration (open symbols) above pH 13, because of the precipitation of Ca(OH)₂. (The open symbol at pH 13.21 and [Ca] = 21 mM is considered as an outlier),
- Ca(ISA)₂ systems in equilibrium with Ca(OH)₂ at pH 13.3 have a total Ca concentration of about 10 mM. If Ca(ISA)₂ was absent, the dissolution of Ca(OH)₂ alone at pH 13.3 would lead to a total Ca concentration of about 2 mM. The higher Ca concentration obtained is caused by the formation of a CaISA₀⁻H complex,
• the difference above pH 13 between systems with Ca(OH)$_2$ added and systems in the absence of Ca(OH)$_2$, possibly caused by the non-equilibrium with respect to Ca(OH)$_2$ and/or the formation of Ca(OH)$_2$ with different solubility properties,

• below pH 12.8, adding Ca(OH)$_2$ to the system (filled symbols) causes an increase in the total Ca concentration because these systems are not saturated with respect to Ca(OH)$_2$.

2.4 Modelling of the data

After having found evidence for the existence of a pH dependent complexation reaction between pH 12 and 12.8, the aim is to describe the experimental data with a minimum set of equilibrium reactions for Ca and ISA.

The equations 2.5, 2.7 and 2.9 give the complexation reactions along with their associated equilibrium constants (equations 2.6, 2.8 and 2.10):

\[
\text{Ca(ISA)}_2 (s) \rightleftharpoons \text{Ca}^{2+} + 2 \text{ISA}^- \quad (2.5)
\]

\[
K_{\text{set}}^0 = \left[ \frac{\left[\text{Ca}^{2+}\right]\left[\text{ISA}^-\right]^2}{1} \right] \quad (2.6)
\]

\[
\text{Ca}^{2+} + \text{ISA}^- \rightleftharpoons \text{CaISA}^+ \quad (2.7)
\]

\[
K_{\text{CaISA}^+}^0 = \left[ \frac{\left[\text{CaISA}^+\right]}{\left[\text{Ca}^{2+}\right]\left[\text{ISA}^-\right]} \right] \quad (2.8)
\]

\[
\text{Ca}^{2+} + \text{ISA}^- \rightleftharpoons \text{CaISA}^0 + \text{H}^+ \quad (2.9)^2
\]

\(^2\) For simplicity, the number of protons dissociated is omitted in the notation of the complex
with [ ] representing the activity of the species.

The reason for including the complexation reaction (2.7) is that for a whole series of polyhydroxy carboxylic acids, which are structurally related to ISA, such reactions have been described in literature.

In view of the structural analogy between gluconate and ISA, the complexation strength of the CalISA$^+$ complex was considered to be the same as for calciumgluconate$^+$ (the ion pair of Ca$^{2+}$ and gluconate), i.e. $K_{	ext{CalISA}^+}^0 = 1.70$ (Schubert and Lindenbaum 1952)$^1$. This value of 1.70, is comparable with the equilibrium constants of similar ligands, that also consist of a carboxyl and an $\alpha$-hydroxy group. In Table 2.5, a few structurally related ligands and their corresponding equilibrium constants are shown. The equilibrium constant ($K_i$) of these ligands (L) for the complexation with Ca$^{2+}$ (M) is defined by:

$$K_i = \frac{(ML)}{(M)(L)}$$  

(2.11)

The data are taken from the IUPAC Stability Constants Database (1993) and recalculated for ionic strength zero using the Davies equation (equation 2.2).

---

$^1$ The complexation constant $K_{	ext{CalISA}^+}^0$ was determined by Van Loon and Glaus (2000) by an ion exchange method and a method using a Ca selective electrode. For both independent experiments the value of log $K_{	ext{CalISA}^+}^0$ was found to be $1.8 \pm 0.1$. Because of the good agreement between the value used for modelling (1.70) in the present study and the determined value (1.8), no recalculation of $K_{\text{col}}^0$ and $K_{	ext{CalISA}^+}^0$ was undertaken.
### Table 2.5
(Poly)hydroxy carboxylic acids (L) and their corresponding equilibrium constants for the formation of a positively charged CaL⁺ complex

\( (I = 0 \text{ M}, \text{T} = 25^\circ \text{C}) \).

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Molecule structure</th>
<th>log K₁</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>glycolic acid</td>
<td>HO.CH₂.COOH</td>
<td>1.59</td>
<td>Davies &amp; Monk (1954a), Davies (1938)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.62ᵃ</td>
<td>Cannan &amp; Kibrick (1938)ᵇ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.65</td>
<td>Das &amp; Nair (1975)</td>
</tr>
<tr>
<td>lactic acid</td>
<td>CH₃.CH(OH).COOH</td>
<td>1.42</td>
<td>Davies &amp; Monk (1954b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.46ᵃ</td>
<td>Masone &amp; Vicedomini (1981)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.47</td>
<td>Davies (1938)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.55</td>
<td>Ghosh &amp; Nair (1970)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.57ᵃ</td>
<td>Cannan &amp; Kibrick (1938)ᵇ</td>
</tr>
<tr>
<td>glyceric acid</td>
<td>HO.CH₂.CH(OH).COOH</td>
<td>1.69ᵃ</td>
<td>Cannan &amp; Kibrick (1938)ᵇ</td>
</tr>
<tr>
<td>gluconic acid</td>
<td>HO.CH₂.(CHOH)₂.COOH</td>
<td>1.59ᵃ</td>
<td>Masone &amp; Vicedomini (1981)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.70ᵃ</td>
<td>Schubert &amp; Lindenbaum (1952)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.72ᵃ</td>
<td>Cannan &amp; Kibrick (1938)ᵇ</td>
</tr>
</tbody>
</table>

ᵃRecalculated for \( I = 0 \text{ M} \) using the Davies equation.ᵇ No temperature specified.

The data points used for the determination of the equilibrium constants \( K_{\text{sol}}^0 \) and \( K_{\text{CaISA}}^0 \) are taken from Tables 2.2 and 2.4.

With the value of \( K_{\text{CaISA}}^0 \) fixed, the solubility product of Ca(ISA)₂ was calculated using the experimental data obtained between pH 10 and 12. At a pH lower than 12, the concentration of total Ca\(^{2+}\) in solution remains constant. Therefore, the pH dependent complexation reaction (equation 2.9) plays a negligible role and, hence, the equilibrium constants \( K_{\text{sol}}^0 \) and \( K_{\text{CaISA}}^0 \) describe the solubility of Ca(ISA)₂ in this pH range. Because \( K_{\text{CaISA}}^0 \) is already fixed, the remaining variable, \( K_{\text{sol}}^0 \) could be determined. The optimal value for log \( K_{\text{sol}}^0 \) is determined as follows. For different values of \( K_{\text{sol}}^0 \), the
concentration of total Ca in solution is calculated at every measured pH. This Ca concentration is compared with the measured one. The value for $K_{sol}^0$ that leads to the minimum applying the method of least squares is chosen as the best value to describe the experimental data points. This procedure results in $\log K_{sol}^0 = -6.36 \pm 0.1$. The uncertainty ($\pm 0.1$) is not a standard deviation, but represents an uncertainty range of $\log K_{sol}^0$, by which the most important experimental points are covered.

Finally, with fixed values for $K_{CalISA}^0$ and $K_{sol}^0$, an optimal value for $K_{CalISA^0}$ can be found from the experimental data in the pH range 12 – 13.3. The value for $\log K_{CalISA^0}^0$ is determined by the same least square procedure as for $\log K_{sol}^0$ and results in $\log K_{CalISA^0}^0 = -10.4 \pm 0.2$. In Figure 2.5, the effect of the uncertainty on $\log K_{CalISA^0}^0$ is shown by the dashed lines.

A summary of the optimum values for the three equilibrium constants associated with equations 2.5, 2.7 and 2.9 is given in Table 2.6.

<table>
<thead>
<tr>
<th>reaction</th>
<th>$\log K$ average</th>
<th>std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ca}^{2+} + \text{ISA}^- \rightleftharpoons \text{CaISA}^+$</td>
<td>1.70</td>
<td>/</td>
</tr>
<tr>
<td>$\text{Ca}(\text{ISA})_2 (s) \rightleftharpoons \text{Ca}^{2+} + 2 \text{ISA}^-$</td>
<td>-6.36 $\pm$ 0.1</td>
<td></td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{ISA}^- \rightleftharpoons \text{CaISA}^0 + \text{H}^+$</td>
<td>-10.40 $\pm$ 0.2</td>
<td></td>
</tr>
</tbody>
</table>

The value for $\log K_{sol}^0$ is in good agreement with the one measured at neutral pH by Van Loon et al. (1999b) ($\log K_{sol}^0 = -6.53$). Also the value found for $\log K_{CalISA^0}^0$ agrees well with the one estimated by Van Loon and Glaus (1998) ($\log K_{CalISA^0}^0 = -10.50$) and is similar to values of Makridou et al. (1977) for the uncharged complexes between $\text{Ca}^{2+}$ and galacturonic or glucuronic acid at an ionic strength of 1 M: $\log K_{\text{CaGal}^0}^0 = -10.15$ or $\log K_{\text{CaGlc}^0}^0 = -10.40$, respectively.
Complexation of Ca

The solubility of Ca(ISA)_2 was also studied as a function of the pH (1-14) and Ca ion molality (0.03-0.52) by Rai et al. (1998). The authors used a different model to describe their data at pH > 4, given in Table 2.7.

| reaction | log K
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(ISA)_2 (c) ⇌ Ca(ISA)_2 (aq)</td>
<td>-2.22</td>
</tr>
<tr>
<td>HISA (aq) ⇌ ISA^- + H^+</td>
<td>-4.46</td>
</tr>
<tr>
<td>Ca(ISA)_2 (c) ⇌ Ca^{2+} + 2 ISA^-</td>
<td>-7.62</td>
</tr>
</tbody>
</table>

This model, however, could not describe the solubility of Ca(ISA)_2 in equilibrium with an ion exchange resin at pH 6.5-8 as determined by Van Loon et al. (1999b). In a personal communication of D. Rai, the author revised the model of Table 2.7 and used the equations 2.5 and 2.7 to describe his experimental data. The results were log K^o_{mol} = -6.2 and log K^o_{CaISA} = 1.5, which is in good agreement with the present work and the study of Van Loon and Glaus (1998).

The model proposed in the present work (Table 2.6) could perfectly describe the experimental data of Rai et al. (1998) in the pH range 10-14 (results not shown).
2.5 Evaluation of the model

The purpose of the present paragraph is to compare the experimental data with the model based on the equilibrium constants of Table 2.6. Further, also alternative models based on other equilibrium reactions will be evaluated.

A comparison between the Ca data measured between pH 10.5 and 13.3 and the model proposed (Tables 2.1 and 2.6) is shown by the solid line in Fig. 2.5. As this figure shows, the model simulates the experimental data well except for the data at pH 13.3. The data at this pH can be fit better if the value for \( \log K_{CaSA}^0 \) is changed to -10.2 (upper limit Figure 2.5). In this case, however, the model fits the data between pH 12 and 13 less well.

Figure 2.5 Comparison between the experimental Ca data and the model proposed to simulate these data. The full line represents the model based on the Tables 2.1 and 2.6. The variation of the model between the upper limit \( \log K_{CaSA}^0 = -10.2 \) and the lower limit \( \log K_{CaSA}^0 = -10.6 \) is given by the dashed lines.
The result of simulating the experimental data for ISA in solution (Tables 2.2 and 2.4) is shown in Figure 2.6. The full line represents the model proposed (Tables 2.1 and 2.6) and describes the experimental data very well.

*Figure 2.6* Comparison between the experimental ISA data and the model proposed to simulate these data. The full line represents the model based on the Tables 2.1 and 2.6.

When the Ca(ISA) system is equilibrated with a NaClO₄/NaOH solution for only a short time (< 3 days), the precipitation of Ca(OH)₂ does not seem to take place. This is expressed by the high concentration of total Ca²⁺ in solution in Figure 2.3 at a pH higher than 13 and in Table 2.3 for the samples without addition of Ca(OH)₂. To test the hypothesis of the absence of Ca(OH)₂ precipitation, these data points were simulated by omitting the Ca(OH)₂ equilibrium (Table 2.1). The result of this simulation is shown in Figure 2.7 as a full line. The points in Figure 2.7 represent data taken from the Table 2.2 and 2.3. The good agreement between the experimental data and the model, confirms the hypothesis of a system oversaturated with respect to Ca(OH)₂ and is another validity of the complexation constants shown in Table 2.6.
Figure 2.7 Concentration of total Ca in solution in equilibrium with Ca\((\text{II})\)\(_2\). The full line represents the model without taking precipitation of Ca\((\text{OH})\)\(_2\) into account.

The assumption of a pH-dependent complexation reaction with one proton being split off of the ligand \((n = 1\) in equation 2.1\) is based on the generalised coordination-ionisation scheme of van Duin et al. (1989). This scheme generally predicts the stoichiometry of the complexes formed between a polyhydroxy ligand and a given metal ion as a function of pH. For Ca\(^{2+}\) the number of protons dissociated from hydroxyl groups at a pH higher than 10 is predicted to be 1. The question arises as to whether models including complexation reactions with more than one proton being dissociated are also able to describe the experimental data. Therefore, two other complexation models were also tested: one including the complexation reaction without protons being split off (equation 2.7) (model A) and another including, in addition, a complexation reaction with two protons dissociated (model B). An overview of the complexation reactions tested is given in Table 2.8. The equilibrium constant for the complexation reaction without protons dissociated (equation 2.7) is set equal to 1.7 in accordance with the model proposed (Table 2.6). The results are shown in Figure 2.8.
Complexation of Ca

Table 2.8  Overview of alternative complexation models tested and the equilibrium constants used.

<table>
<thead>
<tr>
<th>equilibrium reactions</th>
<th>model A (log K)</th>
<th>model B (log K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(ISA)_2 ⇌ Ca^{2+} + 2 ISA^-</td>
<td>-6.36</td>
<td>-6.36</td>
</tr>
<tr>
<td>Ca^{2+} + ISA^- ⇌ CaISA^-</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Ca^{2+} + ISA^- ⇌ CaISA_{3\text{H}^+} + 2 H^+</td>
<td>-23.80</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 2.8** Comparison between the experimental Ca data and the alternative models A and B as described in Table 2.8.

In contrast to the model proposed, the alternative model A is not able to describe the increase in the total Ca concentration because a pH-dependent complexation reaction is absent.

For the alternative model B, the complexation constant $K_{CaISA^-}$ in Table 2.8 represents the value that best described a chosen reference data point (pH 12.34, 11.60 mM Ca and 23.39 ISA). With $= -23.8$, part of the experimental data can be simulated, but with no significant improvement compared to the model proposed. Small variations of log
\( K_{\text{CaISA}^-} \) between -24.2 and -23.4 are shown in Figure 2.8, but are not able to describe the experimental results at pH > 13.

### 2.6 Conclusions

A model for the complexation of Ca\(^{2+}\) with ISA at alkaline pH is postulated. At pH lower than 12, a CaISA\(^+\) complex is formed without deprotonation of a hydroxylic group. At very alkaline pH (pH > 12), a proton of a hydroxylic group is displaced by Ca\(^{2+}\) and an uncharged CaISA\(^0\) complex is formed. The complexation constant of the CaISA\(^0\) complex equaled \( K_{\text{CaISA}^0}^0 = -10.40 \) (\( I = 0 \) M, \( T = 25 ^\circ\text{C} \)).

The model proposed in the present work is in agreement with the general coordination-ionization scheme for polyhydroxy carboxylic acids as described by van Duin et al. (1989) (Figure 1.3) and is the first experimental evidence for the validity of this scheme for Ca. According to this scheme Ca\(^{2+}\) is coordinated to the carboxylate group and a deprotonated hydroxyl group, probably the \( \alpha \)-hydroxyl group. Moreover, the existence of the CaISA\(^0\)-complex is a confirmation of the model proposed by Van Loon and Glaus (1998).

Further, it is concluded that the equilibration time is an important factor in the study of the Ca(ISA)\(_2\) solubility at a pH higher than 12.8. About three days are necessary to reach equilibrium with respect to the precipitation of Ca(OH)\(_2\).
3

Complexation of thorium by α-isosaccharinic acid

3.1 Introduction

Actinides, such as Th, Pa, U, Np, Pu, Am and Cm represent an important source of radioactivity in the L/ILW and are, therefore, of special interest in safety analyses. Th(IV) was chosen for further study as it is a representative of tetravalent actinides such as U(IV) and Pu(IV). The experimental handling of Th(IV) is easier than the latter two elements because it is redox-insensitive. Further, the hydrolysis of Th(IV) is well known (Baes and Mesmer 1976, Brown et al. 1983, Grenthe and Lagerman 1991). Knowledge on the hydrolysis is an important prerequisite for a successful determination of the speciation, because the formation of hydroxy-complexes is the most important competing process to the formation of organic complexes at alkaline pH.

Indications for the complexation of Th(IV) with ISA has been given in previous studies. Wieland et al. (1998) studied the sorption of Th on cement at pH 13.3 and found that less Th was sorbed on the solid phase with increasing concentrations of ISA ($10^{-4}$ M < [ISA] < $10^{-2}$ M). Tits et al. (2000) studied the sorption of Th(IV) on calcite in cement pore water (pH 13.3, 1.7 mM Ca) and also observed a decrease of the amount of Th sorbed with increasing ISA concentrations. In both references this phenomenon was described by the formation of 1:2 Th:ISA complexes. In a study of the sorption of Th on feldspar, a significant effect of ISA in the concentration range $10^{-3}$ M < [ISA] < $10^{-1}$ M was observed.

\footnote{Part of this chapter is published in Vercammen et al. (1999b)}
by Van Loon and Glaus (1998). Although this study was performed under similar conditions to those of Wieland et al. (1998) and Tits et al. (2000), the results were explained by the formation of a 1:1 Th:ISA complex. The three former indications for the formation of complexes were obtained from batch sorption experiments through fitting of the experimental data.

Indirect evidence for complex formation between radionuclides and ISA was given by Berry et al. (1991). They showed that the degradation products from cellulosic materials had a marked impact on the sorption of uranium and plutonium on geological materials at pH ≈ 8 and pH ≈ 11. Also, for the tetravalent actinide Pu(IV), indications for the formation of complexes with ISA at pH 12 were given (Moreton, 1993), suggesting an alteration in the stoichiometry of the complex from 1:1 to 1:2 Pu:ISA with increasing ligand concentration (10^{-6} \text{ M} < [\text{ISA}] < 10^{-2} \text{ M}).

The aim of this work is to give direct evidence for the formation of complexes between Th(IV) and ISA and to determine their stoichiometry. For this purpose, in the first part (section 3.2), high performance anion-exchange chromatography (HPAEC) is applied in order to isolate the complexes formed between Th and ISA and to elucidate directly their stoichiometry. The role of Ca^{2+} in the formation of these complexes is demonstrated. Venema et al. (1993) showed in a multinuclear-magnetic-resonance study the effect of Ca on Al^{3+}-aldarate complexes in aqueous solutions at pH 11.5. Addition of Ca^{2+} to solutions of Al^{3+} and C_3 and C_6 hydroxydicarboxylates resulted in the formation of new complexes. According to this study, xylarate and mannarate form, in the presence of Al^{3+} and Ca^{2+}, 1:2 Al^{3+}-ligand complexes. The Al^{3+}-xylarate complex binds one, whereas the mannarate complex binds two Ca^{2+} ions. Arabinate and glucarate give 2:2 Al^{3+}-ligand complexes, which bind one and two Ca^{2+} ions, respectively.

In the second part of the study on the complexation of Th(IV) by ISA (section 3.3), the stoichiometry of the complexes found using HPAEC is tested by batch sorption experiments. Moreover, stability constants for the formation of complexes are calculated by studying the sorption of Th(IV) on an appropriate sorbing phase as a function of ISA.
3.2 High performance anion-exchange chromatography study

3.2.1 Principles of high performance anion-exchange chromatography and its influence on metal complexes

Liquid chromatography has been very successfully applied for the separation of ionic metal complexes for many years. Especially the usefulness of high performance liquid chromatography (HPLC) for the separation and determination of metal complexes is being recognised in many research areas (O’Laughlin 1984):

- trace metal analysis in analytical chemistry
- the separation of metal complexes in inorganic and coordination chemistry
- speciation studies in environmental chemistry
- investigation of biologically active metal-containing species in biochemistry
- preparation of organ selective reagents in nuclear medicine

For practical applications, the reader is referred to the several reviews published on the use of HPLC in the separation of metal complexes (Karger et al. 1980, Veening and Willeford 1983, O’Laughlin 1984, and references therein).

In the present work, the HPLC separation method applied is high performance anion exchange chromatography (HPAEC). HPAEC makes use of the different ionic interactions of the sample components in the mobile phase i.e. the eluent, with the positively charged functional groups \((N^+)\) of the stationary phase. In principle, the exchange of a negatively charged counter ion \((I)\) of \(N^+\) against any negatively charged sample ion \((A^-\) or \(B^-\)) is based on stoichiometric reactions:

\[
P - N^+I^- + A^- \rightleftharpoons P - N^+A^- + I^-
\]  

(3.1)

\(^2\) The name HPLC is used to distinguish the procedures using packings with particles diameters as small as 10 μm (since the late 1960s), from the classical methods.
\[
P - N^+I^- + B^- \rightleftharpoons P - N^+B^- + I^- \quad (3.2)
\]

where \(P\) stands for the inert support matrix of the anion exchanger. The separation of \(A^-\) and \(B^-\) is accomplished through their different affinities for the stationary phase, which also determine their migration rate through the column.

A detector that responds to solute concentration is placed at the end of the column. When its signal is plotted as a function of time, a series of peaks is obtained, representing the separated sample components. Such a plot, called a chromatogram, is useful for both qualitative and quantitative analysis. The positions of the peaks on the time axis can be used to identify the components of the sample; the areas under the peaks and the peak heights provide a quantitative measure of the amount of each species.

For the simple case, where 1:1 complexes are formed between a metal ion (M) and a ligand (L), the complexation reaction is given by:

\[
M + L \rightleftharpoons ML \quad (3.3)
\]

On a chromatographic column, the three species M, L and ML distribute themselves between the stationary and the mobile phases. This distribution is quantitatively characterised by the distribution constants \(K_D^{M}, K_D^{L},\) and \(K_D^{ML}:\)

\[
K_D^{ML} = \frac{ML_{\text{stat}}}{ML_{\text{mob}}} \quad (3.4)
\]

\[
K_D^{L} = \frac{L_{\text{stat}}}{L_{\text{mob}}} \quad (3.5)
\]

\[
K_D^{M} = \frac{M_{\text{stat}}}{M_{\text{mob}}} \quad (3.6)
\]

with \(X_{\text{stat}}\) and \(X_{\text{mob}}\) the concentration of species \(X\) in the stationary phase and the mobile phase, respectively. These distribution constants depend mainly on the charge of the species, that determines the affinity for the stationary phase. Based on differences in
charge, the species are transported through the column at different velocities and are separated.

In a solution of M and L, the complexes ML exist only in equilibrium with given concentrations of free ligand and free metal. This equilibrium is defined by the complexation constant $\beta_{ML}$:

$$\beta_{ML} = \frac{[ML]}{[M][L]} \tag{3.7}$$

An aliquot of this solution in equilibrium is injected on the chromatographic device and the injected sample is transported by the mobile phase through the column. Assuming that the ligand and the free metal ion in the injected sample move at a different speed, i.e. $K_{D(M)} \neq K_{D(L)}$, then, irrespective of the value of $K_{D(M/L)}$, the metal complexes ML are no longer exposed to the same ligand and/or metal ion concentration as in the solution before injection. The initial equilibrium is disturbed and the ML complexes will dissociate to restore equilibrium. As the injected sample traverse the column, continuously ligand molecules and/or metal ions separate and each time a new equilibrium results. Beside the ligand and metal ion concentrations, also the concentration of ML complexes decreases continuously. If the kinetic of dissociation is fast, i.e. the disturbed equilibrium is restored almost immediately, all the ML complexes can have been completely dissociated before having passed the whole column. In this case only two signals are detected at the outlet of the column: one for the free ligands and one for the free metal ions. The amount of these metal ions equals the initial total amount of metal ions in the injected solution.

If, on the contrary, the kinetic of dissociation is slow compared to the retention time of the complexes on the column, some undissociated ML complexes could traverse the column. Three peaks would be detected coming from the M, L and ML complexes.

Summarising, the thermodynamic and kinetic stability of the complexes control the dissociation of the complexes in the chromatographic system. A characteristic of chromatography is that it is a dynamic measurement. This means that the chemical system is evolving continuously as a result of the transport of chemical components through the
system and the ongoing chemical reactions. This is opposed to a static situation, where the total concentration of the chemical components are assumed to be constant.

In the following, HPAEC is used to study possible complexes formed between Th(IV) and ISA. The thermodynamic and kinetic stability of this type of complexes is unknown. It might be possible that these complexes do not dissociate (completely) on the column. In that case, they can be isolated and studied.

### 3.2.2 Materials and methods

All the experiments were performed at 23 ± 2 °C. Bidemineralised water was used, prepared by ultrafiltration with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

#### 3.2.2.1 Preparation of samples for HPAEC analysis

Samples containing ISA, Ca and Th were prepared for HPAEC analysis. Three different kinds of samples can be distinguished, depending on the kind of experiments performed. An overview of each type of sample (type I - III) is given in Table 3.1.

Either Ca(ISA)$_2$ or ISA lactone was dissolved in 80 mM NaOH (Titrisol, Merck). If Ca(ISA)$_2$ was used, then, the total Ca concentration equaled half of the total ISA concentration. If ISA lactone was used, the total Ca concentration was varied by adding Ca(NO$_3$)$_2$·4H$_2$O (Merck p.a.) from an aqueous stock solution (unless otherwise stated). The samples of type III were additionally spiked with 100 μl of Ca-45 tracer solution in water to give an activity of 7.4·10$^3$ Bq/ml. Ca-45 was purchased from Amersham. The tracer solution, after dilution, contained a total Ca concentration of 2.5·10$^{-6}$ M. Th(NO$_3$)$_4$·4H$_2$O (Merck puriss.) was added to all the samples from a stock solution in 0.1 M HCl. Next, the samples were spiked with 600-700 μl of Th-234 tracer solution in 1 M HCl to give an activity of approximately 240 Bq/ml. Th-234 was extracted from uranyl nitrate (see section 3.2.2.3). The total Th concentration of the tracer solution
Complexation of Th

equaled 2 \times 10^{11} \text{ M at most. To obtain a final background of 80 mM NaOH (pH 12.8), an appropriate amount of 1 M NaOH (Titrisol, Merck) was added. The final volume of the samples was 10 ml. The samples of type I were equilibrated for 10 min. to 8 days, whereas the samples of type II and III were equilibrated for 6 days. The formation of a white precipitate sticking to the bottom of the glass volumetric flask was observed during equilibration. The clear supernatant, however, could be directly used for injection on the column without phase separation. Only the solutions of type II were centrifuged first (94800g, 1h) to remove the precipitate.

It should be remarked that:

(i) At alkaline pH, the ISA lactone ring opens under the influence of the high NaOH concentration (Figure 3.1) and the open chain form is formed.

\[
\begin{align*}
\text{HOCH}_2\text{(OH)C-} & \quad + \text{OH}^- \quad \rightarrow \\
\text{H}_2\text{C-CH} & \quad \text{HOCH}_2\text{C-OH}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{H-C=H} \\
\text{ISA lactone ring} & \quad \text{ISA open chain form}
\end{align*}
\]

**Figure 3.1 Opening of the ISA lactone ring at alkaline pH.**

To compensate for the OH\(^-\) consumption, caused by this lactone ring opening, a stoichiometric amount of NaOH was added to the samples with ISA lactone to keep the pH at 12.8 (i.e. 80 mM NaOH).
(ii) Th(NO$_3$)$_4$ was added at once to the solution or gradually by means of a burette controlled by a titroprocessor (670 Titroprocessor, Metrohm) at a rate of 5 μl/min$^3$. Because it was not possible to perform the last procedure in a glovebox, the Th(NO$_3$)$_4$ solution was added under Ar atmosphere, by sealing the vessel with parafilm and flushing it with Ar gas, from which CO$_2$ had been previously removed using Ascarite$^4$. Simultaneously, 100 μl portions of Th-234 in 1 M HCl were added to the solution under Ar atmosphere with a pipette.

(iii) The presence of the white precipitate can be explained by the formation of a Th(hydr)oxide precipitate, in view of the high total Th concentration in the system, i.e. 0.01 - 0.1 mM (Ryan and Rai 1987, Östhols et al. 1994, Felmy et al. 1997). The formation of a Th-ISA(-Ca) solid can not be excluded. Speciation calculations showed that under the given experimental conditions, a precipitate of Ca(OH)$_2$ is not expected. The preparation of the solutions of type II was performed under Argon atmosphere. Possibly the solutions were inadequately flushed with Ar to prevent the alkaline solution from reacting with atmospheric carbon dioxide. As a consequence, a CaCO$_3$ precipitate can be formed. Because Th forms complexes with carbonates (Grenthe and Lagerman 1991, Östhols et al. 1994, Felmy et al. 1997), which may interfere with the Th-ISA complexation, speciation calculations were performed. It could be concluded that all the Th is present as Th(OH)$_3$ and less than 0.01 % of the total Th is present as Th-carbonate species. Therefore, the formation of ternary complexes containing carbonates as a ligand is very unlikely.

Because the interest of this study lies on the complexes formed in the solution, further analyses of the precipitate were not undertaken.

---

$^3$ Both techniques were applied to test their influence on the formation of a precipitate.

$^4$ Ascarite is a solid adsorbent for CO$_2$ and consists of NaOH on a non-fibrous silicate.
Table 3.1 Overview of the composition and preparation of the three types of samples used for the HPAECAE analysis.

<table>
<thead>
<tr>
<th>Composition</th>
<th>type I</th>
<th>type II</th>
<th>type III</th>
</tr>
</thead>
<tbody>
<tr>
<td>total ISA (mM)</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>total Ca (mM)</td>
<td>0 or 5</td>
<td>1.7</td>
<td>5</td>
</tr>
<tr>
<td>total Th (mM)</td>
<td>0.01</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca-45 (Bq/ml)</td>
<td>/</td>
<td>/</td>
<td>7.3·10³</td>
</tr>
<tr>
<td>Th-234 (Bq/ml)</td>
<td>240</td>
<td>240</td>
<td>240</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Preparation</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>atmosphere</td>
<td>air</td>
<td>flushing with Ar</td>
<td>glove-box, N₂ (O₂, CO₂ &lt; 1 ppm)</td>
</tr>
<tr>
<td>Th(NO₃)₄ addition</td>
<td>at once</td>
<td>titroprocessor</td>
<td>at once</td>
</tr>
<tr>
<td>centrifuged</td>
<td>no</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>reaction time</td>
<td>10 min.-8 days</td>
<td>6 days</td>
<td>6 days</td>
</tr>
</tbody>
</table>

³ using Ca(ISA)₂ or ISA lactone

3.2.2.2 Synthesis of ISA lactone

The original procedure of Whistler and BeMiller (1963) was slightly modified. To a suspension of 20 g Ca(ISA)₅ in 114 ml of hot water was added a hot solution of 5.4 g oxalic acid dihydrate in 54 ml water. The mixture was filtered while hot and the filtrate was passed through a column (4.3x9 cm) of Biorad AG 50W-X2 (H⁺-form) cation-exchange resin. The column effluent and washings with water were concentrated under reduced pressure at 55 °C to a thick syrup. To this syrup, 60 ml of hot ethyl acetate were added. The system was refluxed, while stirring, for 10 min. The hot solution was then poured in a glass beaker. To the remaining syrup, another 60 ml of hot ethyl acetate was added. Again, the system was refluxed. This procedure was repeated until the syrup was

5 synthesis of Ca(ISA)₂ see section 2.2.1.
completely dissolved. While cooling the ethyl acetate fractions (3-5 fractions) to room temperature, white crystals formed. Next, the fractions were placed in a refrigerator for 6 days to promote crystal formation. The crystals were washed twice with 20 ml ethylacetate and placed overnight in a vacuum oven at 45°C. Finally, 9.3 g of crystalline α-isosaccharino-1,4-lactone were produced (m.p. 90-94°C).

C, H and O analysis of the crystals showed that the maximum difference in weight percent compared to pure ISA lactone (44.45 % C, 6.22 % H and 49.34 % O) did not exceed 0.19 % C, 0.18 % H and 0.21 % O.

3.2.2.3 Radiotracers Th-234 and Ca-45

*Extraction of Th-234*

Th-234 was prepared using the method described by Dyrssen (1950). Th-234, the first decay product of U-238, was separated from uranyl nitrate by an ether-water extraction, followed by ion-exchange.

To one gram of uranyl nitrate (\(\text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O}\), Merck), 3 drops of water and 10 ml of water-saturated ether were added. The solution was vigorously shaken for one minute. Uranium dissolves in the organic phase and thorium in the aqueous phase. The ether phase was drawn off and another 5 ml of water-saturated ether was added. Again, the ether phase was removed. The aqueous phase was diluted with 5 ml of 0.1 M HCl and passed through an ion-exchange column. This column, filled with a cation-exchange resin (Biorad AG 50W-X2, \(\varnothing = 0.8\) cm, \(h = 5\) cm in the presence of water) was previously washed with 10 ml of 4 M HCl, followed by 5 ml of water. The vial, originally containing the aqueous phase, was rinsed afterwards with 5 ml of 1 M HCl and, finally, 2 ml of water. These washings were also run through the column. The elution of uranyl and other impurities was performed by passing 5 ml of 2 M HCl through the column. After having washed the resin with 5 ml of water, Th-234 was eluted with 5 ml of 0.5 M oxalic acid (Fluka puriss. p.a.) and 5 ml of water. The two former fractions were collected in a porcelain dish. Because the whole procedure was simultaneously performed on another two ion-exchange columns, finally, three fractions with water and three fractions with oxalic acid were all collected in a porcelain dish. The dish was placed beneath a heating bulb. During this heating process, the water and the
oxalic acid disappeared through evaporation and sublimation, respectively. The residual, i.e. Th-234, was dissolved in 5 ml of 1 M HCl. The maximum Th-234 concentration in this 5 ml solution equaled \(2.10^{11}\) M and was calculated assuming that all the Th-234 was extracted from the uranyl nitrate and that the equilibrium between U-238 and its daughter, Th-234 was complete. The calculations for this maximum Th-234 concentration can be schematically presented as:

\[
\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}[g] \rightarrow \text{U}[g]^{\text{spec. act. U-238}} \rightarrow \text{U-238}[\text{Bq}] = \text{Th-234}[\text{Bq}]
\]

\[
\text{Th-234}[\text{Bq}] \rightarrow \text{Th-234}[g]^{\text{M.W. Th-234}} \rightarrow \text{Th-234}[\text{moles}]
\]

**Determination of Th-234 activity**

The total activity of Th-234 (\(t^{1/2} = 24.1\) days) was indirectly measured by the activity of its daughter, Pa-234m (\(t^{1/2} = 1.17\) min.).

Pa-234m was measured by Cerenkov counting. Cerenkov radiation is the light emitted when charged particles pass through a transparent medium at a velocity exceeding the velocity of light in that medium. The minimum energy required for a \(\beta\) particle in water is of the order of 250 keV. The energy necessary for making use of this effect through direct counting (without any scintillator to be added) is however significantly higher. Th-234, a \(\beta\) emitter with an energy of 200 keV is too weak to be measured. However, the energy of Pa-234m, a \(\beta\) emitter with an energy of 2.3 MeV, is sufficiently high.

The measurements were performed on a Canberra Packard Tri-carb 2250 CA liquid scintillation analyser.

Besides Th-234, some samples also contained Ca-45. Tests showed that this isotope did not interfere with the Th-234 radiochemical analysis.
**Determination of Ca-45 activity**

Ca-45 activities ($t^{1/2} = 163$ days, $\beta^- = 0.3$ MeV) were radiochemically determined using a Canberra Packard Tri-carb 2250 CA liquid scintillation analyser. A scintillation cocktail, Ultimagold AB™, was added to the sample at a 1:3 ratio (1 ml sample and 3 ml cocktail).

When Th-234 was present, the Ca-45 measurements were influenced due to overlapping energy bands. Therefore, the samples were first analysed for Th-234 by Cerenkov counting and, thereupon, analysed for Ca-45 by adding scintillation cocktail to the same samples. Knowing the relationship between the activity of Th-234 measured by Cerenkov counting ($cpm_{\text{Cerenkov}}^{\text{Th}}$) and its contribution ($cpm_{\text{LSC}}^{\text{Th}}$) to the liquid scintillation counting ($cpm_{\text{LSC}}^{\text{tot}}$), it was possible to calculate the count rate solely caused by Ca-45 ($cpm_{\text{LSC}}^{\text{Ca}}$):

\[
cpm_{\text{LSC}}^{\text{Ca}} = cpm_{\text{LSC}}^{\text{tot}} - cpm_{\text{LSC}}^{\text{Th}} = cpm_{\text{LSC}}^{\text{tot}} - 1.86 \cdot cpm_{\text{LSC}}^{\text{Cerenkov}}
\]  

where the factor 1.86 is the experimentally determined factor for conversion of $cpm_{\text{LSC}}^{\text{Cerenkov}}$ into $cpm_{\text{LSC}}^{\text{Th}}$.

### 3.2.2.4 High performance anion-exchange chromatography: experimental set-up

The experimental setup for the HPAEC analysis and the off-line determination of ISA, Th and Ca is represented schematically in figure 3.2.

The HPAEC analysis was performed on a 4x250 mm Carbopac PA-100 column, equipped with a 4x50 mm Carbopac PA-100 pre-column. The column was filled with sulfonated ethylvinylbenzene/divinylbenzene particles covered with quaternary amine functionalised latex (Huber and Bonn, 1995). The HPAEC system was a Dionex DX-500 device (Dionex, Switzerland) consisting of a metal-free GP 40 quaternary gradient pump and an AS3500 SpectraSYSTEM autosampler (Thermo Separation Products), equipped with a 9010 motor-driven Rheodyne injection valve, a 100 µl or 500 µl PEEK injection loop and a 250 µl or 2.5 ml sample syringe, respectively.
Complexation of Th

**Fractionating**

![Fractionating diagram]

**ISA determination**

![ISA determination diagram]

**Th and Ca determination**

![Th and Ca determination diagram]

Figure 3.2 Experimental setup for the separation of a Th-ISA(-Ca) solution and the off-line measurement of ISA, Th and Ca.
The eluent (80 mM NaOH) was mixed from a water and a 1 M NaOH reservoir, both kept under a He atmosphere. 1 M NaOH was prepared from 50% NaOH (J.T. Baker) and degassed water. 500 µl of the sample was injected on the column and eluted at a flow rate of 1 ml/min. The eluate was collected in 2 ml fractions. In the following, this procedure is described as “fractionating”, with the first fraction, the eluate from 0-2 min., the second fraction, the eluate from 2-4 min., and so on.

In the collected fractions, the total concentrations of ISA and Th (type II, Table 3.1) and the total concentration of ISA, Th and Ca (type III, Table 3.1) were determined. The determination of the total concentrations of Th and Ca was based on the radiochemical analyses of Th-234 and Ca-45. For the determination of ISA, 100 µl or 500 µl of each fraction was injected on the column. For this analysis, an ED40 electrochemical detector in the pulsed amperometric mode, with a gold working electrode was used. Control experiments showed that the presence of Th in the samples has no effect on the determination of ISA.

3.2.3 Results and discussion

3.2.3.1 Evidence for the existence of a Th-ISA-Ca complex

The existence of complexes between Th and ISA is demonstrated by studying the elution behaviour of the main species present in samples containing Th and ISA.

First, the elution behaviour of the individual species, i.e. free ISA and hydrolysed Th(IV) is studied. The injection of a pure ISA solution on the HPAEC column results in a peak with a retention time of approximately 8.1 minutes. The corresponding chromatogram is shown in Figure 3.3.

---

6 Dissolved gases produce band broadening or multiple peaks as a result of distributed pathways in the column caused by bubble formation. Helium is sparingly soluble in water.

7 The retention time is the time it takes after sample injection for the analyte to reach the detector.
Complexation of Th

Figure 3.3 Chromatogram of 0.05 mM ISA in 80 mM NaOH (inj. vol. = 500 μl). The retention time of ISA is 8.1 min. The disturbances during the first minutes are caused by impurities of the sample matrix, i.e. NaOH (Titrisol).

The hydrolysed form of Th(IV) dominating in a 80 mM NaOH solution (pH 12.8) is Th(OH)$_4^{0+}$. When an aliquot of a Th(NO$_3$)$_4$ solution in 80 mM NaOH is injected, Th(OH)$_4^{0+}$ is completely retained by the column, using an eluent of 80 mM NaOH. However, regenerating the column with 1 M HCl quantitatively removes the Th previously injected.

In a solution of Th and ISA, the species present are Th(OH)$_4^{0+}$, free ISA and a possible Th-ISA complex. Knowing the elution behaviour of both free species, it is of interest to
see how possible Th-ISA complexes behave when an aliquot of a Th/ISA solution is injected.

In a first experiment, a Th/NaISA solution (type I, Table 3.1) with an equilibration time < 1 day, is fractionated. Th analysis of the fractions shows that no Th is eluted within 2-3 hours. All the Th is bound to the column. If Th-ISA complexes had passed the column, Th would have been detected in the fractions. Moreover, the ISA analysis of the fractions only indicates the presence of ISA in the fractions where free ISA elutes. This means that the effort to isolate Th-ISA complexes failed. It is hypothesised that complexes between Th and ISA are probably formed in solution, but they dissociate completely on the column. The results of the Th and ISA analysis of the fractions is shown in the Figure 3.4.

In a following experiment, a Th/Ca(ISA)$_2$ solution (type I, Table 3.1) with an equilibration time < 1 day, is fractionated. The main difference from the former experiment is the presence of Ca. This time, Th is detected in the first two fractions (0-2 min. and 2-4 min.). Apparently, the presence of Ca makes it possible to elute Th from the column. Moreover, beside the ISA signal corresponding to free ISA, a new ISA signal is detected in the same fractions where Th elutes. These results are shown in the Figure 3.5, using the results of a comparable experiment (exp. C, type II, Table 3.5). Based on these results, it is hypothesised that Th-ISA-Ca complexes are formed in solution, which are stable enough to pass the column and elute in the first two fractions. The presence of Ca, also detected in the first two fractions, confirms this hypothesis, because control experiments demonstrated that Ca is absent in the first two fractions of an injected Ca(ISA)$_2$ or Ca(NO$_3$)$_2$ or Ca(NO$_3$)$_2$/NaISA solution. Free Ca (or possible Ca-ISA complexes) only elute after four minutes.

---

*Samples for HPAEC analysis containing both Th and ISA are generally denoted as Th/ISA solutions. More specific, if the ISA originates from Ca(ISA)$_2$ or ISA lactone, the samples are denoted as Th/Ca(ISA)$_2$ or Th/NaISA, respectively. If Ca is present in the samples of Th and ISA lactone, the notation Th/NaISA/Ca(NO$_3$)$_2$ is used.*
Figure 3.4 Total concentrations of Th (A) and ISA (B) in the eluate of a fractionated Th/NaISA solution. (Results of exp. C, Table 3.5) The procedure of the calculations is given in section 3.2.3.3.

Figure 3.5 Total concentrations of Th (A) and ISA (B) in the eluate of a fractionated Th/Ca(ISA), solution. (Results of exp. C, Table 3.5) The procedure of the calculations is given in section 3.2.3.3.

The retention time of free ISA is about 8.1 min. (Figure 3.3). This means that during the first 4 min. after sample injection, theoretically no ISA is eluted. From the ISA analysis of the fractions of an injected Th/NaISA solution (type I, Table 3.1) it was determined that ISA was below the detection limit, i.e. 0.5 μM ISA, in the eluate from 0-6 min. (Figure 3.4B). However, because complexes between Ca and ISA exist at the experimental pH (see section 2), it is necessary to verify as well the ISA separation capacity of the column for a Ca(ISA), solution. A Ca(ISA), solution with a total ISA concentration of 10^{-2} M was injected. In accordance with the former experiments, this
solution was fractionated in 2 ml volumes and the fractions were analysed for ISA. In the first two fractions no ISA could be detected.

This leads to the conclusion that in the fractions from 0-2 min. and 2-4 min. of a Th/CaISA solution, the presence of ISA is not caused by band broadening of the ISA peak at 8.1 min. or by the presence of Ca-ISA complexes, but that it originates from complexes formed between Th, ISA and Ca.

A control experiment with a Th/NaISA/Ca(NO₃)₂ solution was performed. This experiment could preclude the effect of possible impurities of CaISA on the Th complexation with ISA.

An overview of the species measured in the eluate of all the different solutions is given in Table 3.2.

Table 3.2 Overview of the solutions injected and the species measured in the eluate at pH 12.8.

<table>
<thead>
<tr>
<th>Fraction (min.)</th>
<th>0-2</th>
<th>2-4</th>
<th>4-6</th>
<th>6-8</th>
<th>8-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>NaISA</td>
<td>Th(NO₃)₄</td>
<td>Th/NaISA</td>
<td>Th/CaISA</td>
<td>Th/NaISA/Ca(NO₃)₂</td>
</tr>
<tr>
<td></td>
<td>/</td>
<td>/</td>
<td>ISA</td>
<td>ISA</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>/</td>
<td>/</td>
<td>ISA</td>
<td>ISA</td>
<td>ISA</td>
</tr>
<tr>
<td></td>
<td>ISA/Th/Ca</td>
<td>ISA/Th/Ca</td>
<td>/</td>
<td>ISA</td>
<td>ISA</td>
</tr>
<tr>
<td></td>
<td>ISA/Th/Ca</td>
<td>ISA/Th/Ca</td>
<td>/</td>
<td>ISA</td>
<td>ISA</td>
</tr>
<tr>
<td></td>
<td>/</td>
<td>/</td>
<td>Ca</td>
<td>Ca</td>
<td>Ca</td>
</tr>
<tr>
<td></td>
<td>/</td>
<td>/</td>
<td>Ca</td>
<td>ISA/Ca</td>
<td>ISA/Ca</td>
</tr>
</tbody>
</table>

/: neither ISA, Th or Ca detected

3.2.3.2 Kinetic effects

Two parallel experiments were performed to study the time-dependence of the complex formation. For this purpose, 500 µl of a Th/NaISA/Ca(NO₃)₂ solution (Solution 1, Table 3.3) and a Th/CaISA solution (Solution 2, Table 3.3) were fractionated after given reaction times. Both solutions were of type I (Table 3.1).
In Table 3.3, the percentage of Th eluting during the first 4 min. (sum of the first and second fraction) is given as a function of the reaction time of the Th/ISA/Ca solution. This percentage is calculated against the total Th amount in 500 µl of the injected solution. The data in Table 3.3 indicate a difference in the formation of Th-ISA-Ca complexes when using NaISA and Ca(NO₃)₂, as compared with solution 2. However, further experiments show that the recovery of Th during the first 4 min. after injection can vary rather strongly between the different solutions to be fractionated. Although these solutions have the same ISA, Th and Ca concentrations and are prepared in the same way, differences in the Th recovery are present, independently whether Ca(ISA)₂ or NaISA is used.

**Table 3.3** The recovery of Th in the eluate during the first 4 min. after injection as a function of the reaction time of the Th/NaISA/Ca(NO₃)₂ and Th/Ca(ISA)₂ solution. Solutions are of type I.

<table>
<thead>
<tr>
<th>Solution 1</th>
<th>Th/NaISA/Ca(NO₃)₂</th>
<th>Solution 2</th>
<th>Th/Ca(ISA)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (day)</td>
<td>Th (%)</td>
<td>Time (day)</td>
<td>Th (%)</td>
</tr>
<tr>
<td>1</td>
<td>43</td>
<td>10 min.</td>
<td>63</td>
</tr>
<tr>
<td>2</td>
<td>46</td>
<td>1</td>
<td>77</td>
</tr>
<tr>
<td>5</td>
<td>49</td>
<td>2</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td>49</td>
<td>3</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>82</td>
</tr>
</tbody>
</table>

The procedure of the calculations is given in section 3.2.3.3

Because the Th-ISA-Ca complex formation is slow, at least 2 days of reaction time are needed for equilibrium. In the following experiments, Th/ISA/Ca solutions were fractionated after 6 days of reaction time.
3.2.3.3 Stoichiometry of the Th-ISA-Ca complex

To determine the stoichiometry of the Th-ISA-Ca complexes, a series of different Th/ISA/Ca solutions were fractionated and the total Th, ISA and Ca concentrations in the first two fractions were determined. The stoichiometry of the Th-ISA-Ca complexes can be directly derived from the Th:ISA:Ca ratio in the first two fractions.

Solutions of type II and type III were used, because these solutions contained ten times more Th than those of type I. This was necessary to increase the ISA concentration in the fractions from 0-2 min. and 2-4 min. and make its quantification easier. In the first series of experiments (Exps. A-E) only the total Th and ISA concentrations were determined, because the solutions were of type II and did not contain Ca-45. In the second series of experiments (Exps. F-K), the total Ca concentration was determined in addition. These solutions were of type III.

In the following, the procedure for obtaining the Th:ISA ratio is discussed in detail for experiment A (Table 3.4). A solution of Th and Ca(ISA)₂ (type II, Table 3.1) was made and equilibrated for six days. Because of the formation of a precipitate after six days, the supernatant contained less Th than was initially added. Based on the isotopic dilution technique, the Th concentration in the supernatant was determined. This technique is based on the specific activity of Th-234, according to the relationship:

$$\frac{\text{conc}_{\text{in}} \cdot \text{act}_{\text{in}}}{\text{act}_{\text{out}}} = \text{conc}_{\text{out}}$$

with conc_{in} and act_{in}, the input concentration of Th (mol/l) and input activity of Th-234 (cpm/ml), respectively, and conc_{out} and act_{out}, the concentration of Th (mol/l) and activity of Th-234 (cpm/ml), respectively, after the dilution of Th by a process such as precipitation or sorption on the chromatographic column (see later).

500 µl of the supernatant was separated on the column. Only in the first fraction (0-2 min.) Th was determined. In the second fraction (2-4 min.), the Th signal was too low to
be quantified\(^9\). This means that the Th-ISA-Ca complex is eluted principally during the first two minutes after injection.

From the moles Th present in the 500 µl injected, 75% is found in the first fraction or 2.9 \times 10^{-8} moles Th are present in the 0-2 min. fraction as a complex. This was calculated using the isotopic dilution technique (equation 3.9).

The amount of ISA in the first fraction equals 5.7 \times 10^{-8} moles. By comparing the amounts of Th and ISA, it was found that the quantity of ISA was approximately twice as high as that of Th. This is an indication for one Th ion being complexed by two ISA molecules.

**Table 3.4** Calculation for Exp. A of the amount of Th present in the fraction from 0-2 min. and comparison with the ISA amount in this fraction. The solution is of type II.

<table>
<thead>
<tr>
<th></th>
<th>cpm Th-234/ml</th>
<th>amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th initially added</td>
<td>17897</td>
<td>100 µM</td>
</tr>
<tr>
<td>Th after centrifuging</td>
<td>13875</td>
<td>77.5 µM</td>
</tr>
<tr>
<td>Th in 500 µl injected</td>
<td>13875</td>
<td>3.9 \times 10^{-8} moles</td>
</tr>
<tr>
<td>Th in fraction</td>
<td>2636</td>
<td>2.9 \times 10^{-8} moles</td>
</tr>
<tr>
<td>ISA in fraction</td>
<td></td>
<td>5.7 \times 10^{-8} moles</td>
</tr>
<tr>
<td>ISA/Th in fraction</td>
<td></td>
<td>1.9</td>
</tr>
</tbody>
</table>

The measured concentrations of Th, ISA and Ca for the experiments A-E are given in Table 3.5, whereas in Table 3.6, the ratios of ISA, Th and Ca are shown.

\(^9\) The reason for the fluctuations of the Th and ISA concentrations in the second fraction has, on the one hand, to do with the current state of the column at the different moments of fractionating (e.g. the age of the column, the state of regeneration, etc.). On the other hand, small variations in the precipitation process probably have an influence on the composition of the injected solutions.
Table 3.5  Results of fractionating solutions containing Th, ISA and a varying amount of Ca (third column) (Exps. A-E: type II, Exps. F-K: type III). The total Th, ISA and Ca concentrations in the first two fractions are determined.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Fraction</th>
<th>tot. Ca (mM)</th>
<th>ISA form</th>
<th>Th\textsubscript{fraction} (-10\textsuperscript{8} moles)</th>
<th>ISA\textsubscript{fraction} (-10\textsuperscript{8} moles)</th>
<th>Ca\textsubscript{fraction} (-10\textsuperscript{2} moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsuperscript{a}</td>
<td>0-2</td>
<td>5</td>
<td>Ca(ISA)\textsubscript{2}</td>
<td>2.9</td>
<td>5.7</td>
<td>n.d.</td>
</tr>
<tr>
<td>B\textsuperscript{a}</td>
<td>0-2</td>
<td>5</td>
<td>Ca(ISA)\textsubscript{2}</td>
<td>2.5</td>
<td>6.1</td>
<td>n.d.</td>
</tr>
<tr>
<td>C</td>
<td>0-2</td>
<td>1</td>
<td>NaISA</td>
<td>1.3</td>
<td>2.9</td>
<td>n.d.</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td></td>
<td></td>
<td>1.1</td>
<td>2.0</td>
<td>n.d.</td>
</tr>
<tr>
<td>D\textsuperscript{a}</td>
<td>0-2</td>
<td>5</td>
<td>NaISA</td>
<td>2.3</td>
<td>4.7</td>
<td>n.d.</td>
</tr>
<tr>
<td>E</td>
<td>0-2</td>
<td>7</td>
<td>NaISA</td>
<td>1.4</td>
<td>3.6</td>
<td>n.d.</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td></td>
<td></td>
<td>1.6</td>
<td>3.5</td>
<td>n.d.</td>
</tr>
<tr>
<td>F</td>
<td>0-2</td>
<td>5</td>
<td>NaISA</td>
<td>1.1</td>
<td>3.0</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td></td>
<td></td>
<td>0.7</td>
<td>2.0</td>
<td>1.8</td>
</tr>
<tr>
<td>G</td>
<td>0-2</td>
<td>5</td>
<td>NaISA</td>
<td>1.3</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td></td>
<td></td>
<td>1.0</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td>H</td>
<td>0-2</td>
<td>5</td>
<td>NaISA</td>
<td>2.1</td>
<td>5.7</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td></td>
<td></td>
<td>1.8</td>
<td>5.4</td>
<td>5.8</td>
</tr>
<tr>
<td>I</td>
<td>0-2</td>
<td>5</td>
<td>NaISA</td>
<td>2.8</td>
<td>6.9</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td></td>
<td></td>
<td>1.6</td>
<td>4.3</td>
<td>4.2</td>
</tr>
<tr>
<td>J\textsuperscript{a}</td>
<td>0-2</td>
<td>5</td>
<td>Ca(ISA)\textsubscript{2}</td>
<td>3.0</td>
<td>5.3</td>
<td>4.5</td>
</tr>
<tr>
<td>K</td>
<td>0-2</td>
<td>5</td>
<td>Ca(ISA)\textsubscript{2}</td>
<td>3.2</td>
<td>4.9</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td></td>
<td></td>
<td>1.9</td>
<td>3.2</td>
<td>3.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The amount of Th was too low to be quantified in the 2-4 ml fraction.

Experiment A was repeated a second time. The results (exp. B) are comparable with exp. A. In the experiments A and B, Th(NO\textsubscript{3})\textsubscript{4} was equilibrated with Ca(ISA)\textsubscript{2} and evidence for a 1:2:n Th:ISA:Ca complex was found. When equilibrating Th(NO\textsubscript{3})\textsubscript{4} with NaISA and Ca(NO\textsubscript{3})\textsubscript{2}, the same Th:ISA ratio was obtained (Exps C, D and E, Table 3.6). In these experiments C-E, the total Ca concentration was varied in the range that can
be expected in the porewater of a cementitious repository, by adding different amounts of Ca(NO$_3$)$_2$.

To elucidate how many Ca ions participate in the Th-ISA-Ca complex, similar experiments to those in Exps. A-E were performed, but with a radiotracer of Ca-45 added (Exps. F-K). The radiochemical detection of Ca-45 makes it possible to quantify Ca in the collected fractions, according to equation 3.9. From the experiments F-K, there is no clear evidence for a 1:2:n Th:ISA:Ca complex, as it was the case for the experiments A-E. The existence of a 1:3:n Th:ISA:Ca complex cannot be excluded. The difference in the ratio ISA to Th between solutions containing Ca(ISA)$_2$ or NaISA cannot be explained at the moment.

The interest of experiments F-K lies largely in the comparison of the total Ca concentration with the total Th and ISA concentrations. As shown in Table 3.6, the ISA to Ca ratio clearly equals 1.0 and the ISA to Th ratio, based on all the experiments (A-K) equals 2.3 (std. dev. = 0.4). Therefore, it is hypothesised that a 1:2:2 Th:ISA:Ca complex exists at pH 12.8. The hypothesis of one Th ion coordinated by two ISA ligands is in agreement with the observations of Th sorption on cement in the presence of ISA (Wieland et al. 1998) and on calcite (Tits et al. 2000). These sorption experiments performed in an artificial cement pore water with a total Ca concentration of 1.7 mM were modeled with a 1:2 Th:ISA complex. In spite of the presence of the same concentration of Ca in the study of Th on feldspar (Van Loon and Glaus 1998), a 1:1 Th:ISA complex was proposed in this study. However, a closer look of these data shows that the data points scatter quite strongly, in such a way that the existence of a 1:2 Th:ISA complex can not be excluded.

The participation of Ca ions in the complex between Th and ISA is comparable with the Al-hydroxydicarboxylate-Ca complexes (Venema et al. 1993). However, it should be mentioned that ISA is a hydroxymono carboxylate ligand and, therefore, probably forms complexes with a different structure than a dicarboxylate ligand does.
Table 3.6 Calculation of the ISA to Th, Ca to Th and ISA to Ca ratio in the first and second fraction. (The calculations are based on Table 3.5.)

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Fraction</th>
<th>ISA/Th</th>
<th>Ca/Th</th>
<th>ISA/Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(min.)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A\textsuperscript{a}</td>
<td>0-2</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B\textsuperscript{a}</td>
<td>0-2</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0-2</td>
<td>2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D\textsuperscript{a}</td>
<td>0-2</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0-2</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>0-2</td>
<td>2.7</td>
<td>2.7</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td>3.0</td>
<td>2.7</td>
<td>1.1</td>
</tr>
<tr>
<td>G</td>
<td>0-2</td>
<td>2.7</td>
<td>2.7</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td>2.7</td>
<td>2.6</td>
<td>1.1</td>
</tr>
<tr>
<td>H</td>
<td>0-2</td>
<td>2.7</td>
<td>2.0</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td>2.9</td>
<td>3.1</td>
<td>0.9</td>
</tr>
<tr>
<td>I</td>
<td>0-2</td>
<td>2.5</td>
<td>2.6</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td>2.7</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>J\textsuperscript{a}</td>
<td>0-2</td>
<td>1.8</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>K</td>
<td>0-2</td>
<td>1.5</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>2-4</td>
<td>1.7</td>
<td>2.0</td>
<td>0.8</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td>2.3</td>
<td>2.4</td>
<td>1.0</td>
</tr>
<tr>
<td>std. dev.</td>
<td></td>
<td>0.4</td>
<td>0.5</td>
<td>0.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The amount of Th was too low to be quantified in the 2-4 ml fraction.
3.2.4 Conclusions

The existence of Th-ISA-Ca complexes was demonstrated in solutions containing Th, ISA and Ca at pH 12.8. The complexes between Th, ISA and Ca were found to be eluted in HPAEC during the first four minutes after injection of the solution. They could be isolated, because they did not completely dissociate when passing the anion exchange column. Consequently, the Th:ISA:Ca ratio could be determined. It was concluded that one Th ion is coordinated presumably by two ISA ligands and that these Th-ISA complexes bind two Ca ions. Thus, at pH 12.8, 1:2:2 Th:ISA:Ca complexes are postulated to be dominant in the presence of Ca.

The formation of Th-ISA-Ca complexes was found to be time dependent. At least two days of equilibration were necessary to reach the maximum amount of complexes formed.

It was not possible to isolate complexes formed between Th and ISA in the absence of Ca. If such complexes exist, they are hypothesised to be thermodynamically and/or kinetically less stable than the Th-ISA-Ca complexes and to dissociate completely when passing the anion exchange column.
3.3 Batch sorption study

3.3.1 Principles of the batch sorption method

The batch sorption method (Schubert 1948) is often used to derive stability constants of metal ion complexes with organic acids (Schubert and Lindenbaum 1952) or dissolved organic matter (Maes et al. 1992, Luster et al. 1994). The method is based on the distribution of a metal ion M between a solid and a liquid phase. This distribution is described by the distribution coefficient $K_d$:

$$ K_d = \frac{M_{\text{ssorb}}}{(M)_{\text{sol}}} $$

where $M_{\text{ssorb}}$ is the amount (mol/g) of metal ion sorbed on the solid phase and $(M)_{\text{sol}}$ is the concentration (mol/l) of metal ion in the liquid phase.

When a ligand that forms aqueous complexes with the metal ion is added to the system, metal ions will go into solution. Consequently, a new equilibrium is established and the value of $K_d$ changes.

Based on the results of the HPAEC study (section 3.2), two tentative general reactions for the complexation between Th(IV) and ISA can be postulated: one in the absence of Ca (equation 3.11) and the other in the presence of Ca (equation 3.12). In the following equations, ISA denotes the $\alpha$-isosaccharinate ion, i.e. with a deprotonated carboxylic group. The charges are omitted for simplicity.

$$ \text{Th} + n\text{ISA} \rightleftharpoons (\text{Th}(\text{ISA})_n)_{-m\text{H}} + m\text{H} \quad (3.11) $$

$$ \text{Th} + n\text{ISA} + k\text{Ca} \rightleftharpoons (\text{Th}(\text{ISA})_n\text{Ca}_k)_{-m\text{H}} + m\text{H} \quad (3.12) $$

The values for $n$ and $m$ are not necessarily the same in both equations. The reasons for including protons in the reactions are the hydrolysis of Th(IV) (and Ca(II)) and the observation that the coordination of polyhydroxy ligands with charged cations at alkaline
pH is accompanied by deprotonation of the coordinating hydroxyl groups (Escandar et al. 1995, Frutos et al. 1997, Hedinger et al. 1998, Gajda et al. 1998, Vercammen et al. 1999a). The stability constants associated with equations 3.11 and 3.12 are:

\[
K = \frac{\langle(\text{Th(ISA)}n)_a - n\text{H}\rangle(H)^m}{\langle\text{Th}(\text{ISA})a\rangle}
\] (3.13)

\[
K^{Ca} = \frac{\langle(\text{Th(ISA)}n \text{Ca}_k)_a - n\text{H}\rangle(H)^m}{\langle\text{Th}(\text{ISA})a (\text{Ca})^k\rangle}
\] (3.14)

Parentheses denote molar concentrations of the species. In view of the constant concentrations of protons and Ca used in each single batch sorption experiment, the following apparent stability constants are defined:

\[
\beta = \frac{K}{(H)^m}
\] (3.15)

\[
\beta^{Ca} = \frac{K^{Ca} (\text{Ca})^k}{(H)^m}
\] (3.16)

for the experiments performed in the absence and presence of Ca, respectively.

The concentration of free uncomplexed ISA in the equations 3.13 and 3.14 can be approximated by the total ISA concentration ($\text{ISA}_{tot}$), because (i) the total concentration of Th is much smaller than the total concentration of ISA, (ii) the concentration of CaISA-species is negligible with respect to the total ISA concentration (speciation calculations using the stability constants of section 2) and (iii) the deprotonation of the hydroxyl groups is estimated to occur only at very high pH ($\text{pK}_a \approx 13-15$, Coccioli and Vicedomini 1978). The combination of the equations 3.13 and 3.15 and the equations 3.14 and 3.16 yields:
$$\beta = \frac{(\text{Th}(\text{ISA})_n - m\text{H})}{(\text{Th})(\text{ISA}_{\text{tot}})^n}$$  \hspace{1cm} (3.17)$$

$$\beta^{Ca} = \frac{(\text{Th}(\text{ISA})_n\text{Ca}_k - m\text{H})}{(\text{Th})(\text{ISA}_{\text{tot}})^g}$$  \hspace{1cm} (3.18)$$

Under alkaline conditions, hydroxy-ligands also act as complexing agents and hydrolysed species of the Th ion are formed. Under the experimental conditions of the present study (pH $\geq$ 10.7, $1.6 \cdot 10^{-13}$ M Th) the dominating species is Th(OH)$_4^-$, as shown in Figure 3.6.

Figure 3.6 Th speciation as a function of pH (total Th = $1.6 \cdot 10^{-13}$ M, $I = 0.3$ M).

Thermodynamic data are taken from Östhols (1995).
Taking into account the formation of \((\text{Th(ISA)}_n\text{Ca}_k\text{)}_{m\text{H}}\) complexes and \(\text{Th(OH)}_4^0\) species, equation 3.10 is written as:

\[
K_d = \frac{\text{Th}_{\text{sorb}}}{(\text{Th}) + (\text{Th(OH)}_4) + ((\text{Th(ISA)}_n\text{)}_\text{mH})}
\]

(3.19)

for the complexation in the absence of Ca, and as:

\[
K_d = \frac{\text{Th}_{\text{sorb}}}{(\text{Th}) + (\text{Th(OH)}_4) + ((\text{Th(ISA)}_n\text{Ca}_k\text{)}_{m\text{H}})}
\]

(3.20)

for the complexation in the presence of Ca, with \(\text{Th}_{\text{sorb}}\) the amount (mol/g) of Th sorbed on the solid phase.

The hydrolysis constant of \(\text{Th(OH)}_4^0\) is defined as:

\[
\beta_{\text{Th(OH)}_4^0} = \frac{\left(\text{Th(OH)}_4\right)}{(\text{Th}) \cdot (\text{OH})^4}
\]

(3.21)

The combination of the equations 3.17, 3.19 and 3.21 leads to:

\[
K_d = \frac{\text{Th}_{\text{sorb}}}{(\text{Th})\left\{1 + \beta_{\text{Th(OH)}_4^0} (\text{OH})^4 + \beta_{\text{ISA}_\text{tot}}^n\right\}}
\]

(3.22)

for the complexation in the absence of Ca, and the combination of the equations 3.18, 3.20 and 3.21 leads to:

\[
K_d = \frac{\text{Th}_{\text{sorb}}}{(\text{Th})\left\{1 + \beta_{\text{Th(OH)}_4^0} (\text{OH})^4 + \beta_{\text{Ca}^0}^n (\text{ISA}_\text{tot})^n\right\}}
\]

(3.23)

for the complexation in the presence of Ca.
$K_d^0$ is the distribution coefficient measured in the absence of the ligand under investigation and is defined as:

$$K_d^0 = \frac{Th_{\text{surf}}}{(Th^0)\{1 + \beta_{Th/OH}^0(\text{OH})^4\}} \quad (3.24)$$

with $Th_{\text{surf}}$ the amount (mol/g) of metal ion sorbed on the solid phase and $(Th^0)$ the concentration (mol/l) of free metal ion in the liquid phase, for the system without ISA.

Under the condition of a linear sorption, the following equation is valid:

$$\frac{Th_{\text{surf}}}{(Th^0)} = \frac{Th_{\text{surf}}}{(Th)} \quad (3.25)$$

with $(Th)$ the concentration of free metal ion in solution for the system with ISA.

Then, the equations 3.22 and 3.24 combine to give:

$$\frac{K_d^0}{K_d} - 1 = \frac{\beta(ISA_{\text{tot}})^n}{A} \quad (3.26)$$

for the complexation in the absence of Ca, and the equations 3.23 and 3.24 combine to give:

$$\frac{K_d^0}{K_d} - 1 = \frac{\beta_{\text{Ca}}(ISA_{\text{tot}})^n}{A} \quad (3.27)$$

for the complexation in the presence of Ca, with $A$, the side reaction coefficient, defined as:

$$A = 1 + \beta_{Th(OH)}^+(\text{OH})^4 \quad (3.28)$$

$A$ is constant for a given pH and ionic strength.

Taking the logarithm, equations 3.26 and 3.27 finally lead to the general relationships:
Complexation of Th

\[
\log K_d = \log K_d^0 - \log \left(1 + \frac{\beta}{A} \cdot (ISA_{\text{tot}})^n\right)
\]  

(3.29)

for the complexation in the absence of Ca, and

\[
\log K_d = \log K_d^0 - \log \left(1 + \frac{\beta^{\text{Ca}}}{A} \cdot (ISA_{\text{tot}})^n\right)
\]  

(3.30)

for the complexation in the presence of Ca.

When plotting \(\log K_d\) against \(\log (ISA_{\text{tot}})\) and fitting the experimental results by equations 3.29 or 3.30, the intercept of the fitting curve with the Y-axis equals \(\log K_d^0\). The number of ligands, \(n\), participating in the Th-ISA complexes is derived from the slope of the fitting curve in the region where \(\log K_d\) is dependent on the ISA concentration. \(\beta/A\) and \(\beta^{\text{Ca}}/A\) are adjustable parameters. Because \(A\) is a known constant, the values of \(\beta\) and \(\beta^{\text{Ca}}\) can be calculated.

Finally, to determine the values of \(K\), \(K^{\text{Ca}}\), \(m\) and \(k\), experiments at different pH’s and different Ca concentrations need to be performed, according to the equations 3.15 and 3.16.
3.3.2 Materials and methods

All experiments were performed at 23 ± 2 °C in a glovebox under N₂ atmosphere (O₂, CO₂ < 1 ppm). Bidemineralised water was used, prepared by ultrafiltration with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

3.3.2.1 Determination of the distribution coefficient \( K_d \)

The distribution coefficient \( K_d \) for Th(IV) was measured as a function of the concentration of total ISA. Experiments were performed at three different pH's: 10.7, 12.0 and 13.3 and at different Ca concentrations to determine the stoichiometry of the complexation reactions.

The experiments were performed in polyallomer centrifuge tubes. Depending on the pH, different solid phases were used to obtain sufficiently large \( K_d \) values.

(i) In the experiments performed at pH 13.3, 100 mg of a BioRad 50W-X2 resin was used. The resin was pretreated first to remove impurities by washing successively with 1 M NaOH, water, 1 M HCl and water. Next, the resin was converted to the Na⁺-form by washing the resin three times with 0.3 M NaOH. The solution after the third NaOH-washing was analysed for Si, Al, Mg, Ca, Sr, Ba and K, but their concentrations were negligible, as well as the NPOC (non-purgeable organic carbon) content. After the resin was air-dried on the air or in an oven at about 40°C, it was ground in a mortar.

(ii) At pH 12.0, the sorption of Th on the polyallomer centrifuge tube was so strong that no solid phase was added to the system. The sorption equilibrium of Th between the tube wall and the solution was studied, instead of between an added solid phase and solution.

(iii) At pH 10.7, 50-60 mg of feldspar (orthoclase KAlSi₃O₈, Fronland, Norway, 63 μm) was used as solid phase.

For the experiments performed in the absence of Ca, 15 ml aliquots of a stock solution were added to the solid phase (or to the empty polyallomer tubes, pH 12.0). The stock solution contained ISA in the concentration range from 10⁻⁸ to 10⁻² M. ISA was supplied
Complexation of Th

as ISA lactone\(^\text{10}\), which hydrolyses in the presence of NaOH to form the open chain form of ISA. The pH and ionic strength of the stock solution were adjusted to the desired values with 1 M NaOH and 1 M NaClO\(_4\), respectively (I = 0.3 M). Finally, the solution was spiked with Th-234 to give an activity of the stock solution of 200 Bq/ml and a total Th concentration of 1.2–1.6\(\times\)10\(^\text{-13}\) M. At this concentration no Th colloids are present in solution (Tits et al. 2000). Th-234 was extracted from uranyl nitrate (see section 3.2.2.3).

The preparation of the samples for the experiments performed in the presence of Ca was the same as described above except that Ca was added before spiking the stock solution with Th-234. For the experiments at pH 12.0 and 10.7, Ca was supplied as Ca(NO\(_3\))\(_2\) to give total Ca concentrations of 0.7 mM and 10 mM. For experiments performed at pH 13.3, however, the stock solution was made starting from a 0.3 M NaOH solution saturated with Ca(OH)\(_2\) (solubility of Ca(OH)\(_2\) at pH 13.3 is 1.8 mM Ca). After equilibration with the resin at pH 13.3, the concentration of total Ca in solution was about 0.35 mM. This decrease was caused by the sorption of Ca on the resin. It is important to notice that at pH 13.3 only one total Ca concentration was studied because of restrictions by precipitation of Ca(OH)\(_2\) and sorption on the resin. Table 3.7 gives an overview of the eight different experiments performed.

After equilibrating the samples for 3 days on an end-over-end shaker, the tubes were centrifuged (48360g, 30 min.) (except for the tubes at pH 12.0). The total concentration of Ca in the supernatant was determined by ICP-AES (ARL 3410 ICP with Minitorch\(^\text{13}\)). The activity of Th-234 in the supernatant was determined according to section 3.2.2.3. For some experiments the pH was monitored using a glass electrode (ORION, ROSS Combination pH Electrode) and found to remain unchanged.

Next, the tubes were emptied, rinsed with water and filled with 15 ml of a 0.2 M HNO\(_3\) solution to desorb Th from the wall of the tubes (except for the tubes at pH 12.0). After one day of end-over-end shaking, the Th-234 activity in the supernatant was analysed.

The distribution of Th between the solid phase and the solution could then be calculated as follows:

---

\(^{10}\) Synthesis of ISA lactone (see section 3.2.2.2).
\[ K_d = \left( \frac{\text{Act}_{\text{input}} - \text{Act}_{\text{sol}} - \text{Act}_{\text{wall}}}{\text{Act}_{\text{sol}}} \right) \left( \frac{V}{m} \right) \]  \hspace{1cm} (3.31)

with \( \text{Act}_{\text{input}} \) = activity of the radionuclide added to the system (cpm/ml),

\( \text{Act}_{\text{sol}} \) = activity of the radionuclide in the equilibrium solution (cpm/ml),

\( \text{Act}_{\text{wall}} \) = activity of the radionuclide sorbed on the tube wall (cpm/ml),

\( V \) = volume of the suspension (ml),

\( m \) = mass of resin (g).

It is important to notice that for the experiments performed at pH 12.0, the parameter \( \text{Act}_{\text{wall}} \) is absent in equation 3.31.

**Table 3.7** Overview of the experiments performed with Th at different pH's and different total Ca concentrations.

<table>
<thead>
<tr>
<th>pH</th>
<th>[Ca\text{sol}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.3</td>
<td>\pm 10^{-4} M</td>
</tr>
<tr>
<td>12.0</td>
<td>\pm 10^{-5} M</td>
</tr>
<tr>
<td>10.7</td>
<td>\pm 10^{-5} M</td>
</tr>
</tbody>
</table>

*background concentration of Ca, these experiments are designated "experiments in the absence of Ca"*

### 3.3.2.2 Preliminary conditions for applying the batch sorption method

Several preliminary conditions must be fulfilled for applying the batch sorption method.

(i) The final relationships given by the equations 3.29 and 3.30 are limited to experimental conditions which lead to linear reference sorption isotherms for Th (equation 3.25). A test experiment was performed at pH 13.3. An ion exchange resin was brought in equilibrium with solutions containing different concentrations of inactive Th, i.e. Th(NO\text{3})_4 (10^{-6} M - 10^{-10} M) and spiked with Th-234. Based on the distribution
of Th-234 between solid and liquid phase, the concentration of inactive Th in the equilibrium solution and the amount sorbed on the ion exchange was calculated. The results are given in Figure 3.6 by the closed symbols. Also the distribution of a trace amount of Th-234 between the ion exchange resin and the liquid phase without Ca was determined at pH 13.3. Assuming that the stock solution contained 1.2-1.6$\times10^{-13}$ M Th-234, the distribution of Th-234 was calculated. The results are given by the open symbols in Figure 3.7. The combination of both data sets gives rise to a rather linear reference sorption isotherm.

![Figure 3.7 Sorption isotherm of Th(IV) on the ion exchange resin at pH 13.3.](image)

Because all the batch sorption experiments with Th are performed with stock solutions having a total Th concentration of $\pm 1.2-1.6\times10^{-13}$ M (all Th present as Th-234), the condition of a linear sorption isotherm is fulfilled according to Figure 3.7 for the experiments with the ion exchange resin as solid phase. Generally, at very low metal ion concentrations, the sorption isotherms are linear (Brouwer et al. 1983, Bradbury and Baeyens 1995, Tits et al. 2000). Based on this general experience and the test experiment, it is justified to assume that the other solid phases (feldspar, polyallomer wall) show the same linear sorption behaviour for Th.
(ii) The sorption of Th on the solid phase or the wall has to be reversible. This condition is fulfilled, because at increasing ISA concentrations, the amount of Th in solution increases as well.

(iii) The solid phase has to be chemically stable under the experimental conditions. The ion exchange resin is known to be chemically stable at pH 13.3 (manufacturer’s specifications, Van Loon and Hummel 1995). The chemical stability of feldspar was studied at the pH’s 10.7, 12 and 13.3. The alkaline solutions (15 ml) with an ionic strength of 0.3 M were equilibrated for 3.9 days with feldspar (0.01 g). To study the influence of ISA on the dissolution of feldspar, parallel experiments with $10^{-5}$ M ISA were performed at the three pH’s. The Si, Al and K content in the solution were determined by ICP-AES, but only a small increase of the three ion concentrations was observed. Therefore, the influence of this possible chemical instability of feldspar on the experimental results is assumed to be negligible.

(iv) Neither the free ISA ligand, nor the complexed Th species may sorb on the solid phase. Test experiments at pH 13.3 with $10^3$ and $10^4$ M ISA showed that no ISA sorbed on the ion-exchange resin. ISA does not sorb on feldspar at pH 13.3 (Van Loon and Glaus 1998, unpublished results). It was assumed that neither ISA, nor complexed Th species sorbed on the polyallomer tubes. This also means that blocking of the sorption sites for Th on the different solid phases by sorbed ISA could be precluded.

(v) The formation of polynuclear complexes, i.e. more than one metal ion bound by one or more ligands must be absent. This condition is fulfilled in view of the trace concentration of Th used in the experiments ($\pm 1.2\cdot 1.6\cdot 10^{-13}$ M).

(vi) A minimum equilibration time is needed to reach a constant total metal concentration in solution. In analogy with the kinetic experiment performed with Eu(III) (see section 4.2.1.2) and Th(IV) sorption on cement in the presence of ISA at pH 13.3 (Wieland et al. 1998), three days of equilibration were assumed to be sufficient.

---

11 Lower ISA concentrations were not studied because of the detection limit for ISA by HPAEC ($\pm 0.5$ μM ISA).
3.3.3 Results and discussion

3.3.3.1 Determination of the number of ISA ligands coordinated with Th(IV)

Eight batch sorption experiments were performed at different pH's and different Ca concentrations (Table 3.7). The results are shown in the Figures 3.9 - 3.16 by plotting the logarithm of the distribution coefficient $K_d$ as a function of the logarithm of the total ISA concentration. The experimental data points at “no ISA” represent the values of log $K_d^0$.

Each figure shows a decrease of log $K_d$ with increasing ISA concentrations. This behaviour is caused by the formation of aqueous complexes between Th and ISA, which increase the concentration of total Th in solution. These complexes are formed in the absence as well as in the presence of Ca.

The experimental data obtained in the absence and in the presence of Ca were fitted to the equations 3.29 and 3.30, respectively. Log $K_d^0$, $\beta/A$ or $\beta^{Ca}/A$ and $n$ were the adjustable parameters. The number of ISA ligands coordinated to one Th ion could be derived from the slope of the fitting curve. The value of the slope is represented by $n$ in the equations 3.29 and 3.30. The intercept of the fitting curve with the Y-axis represents log $K_d^0$.

For each individual data point an uncertainty was calculated (see Appendix B). This uncertainty was sometimes smaller and sometimes larger than the scatter of the data points. However, mostly the scatter of the data points was a good estimation for the uncertainty. Therefore, in the fitting procedure applied the individual experimental results were used, with their scatter being representative for their uncertainty. The uncertainty of the individual data points was not taken into account as the unweighted Chi-square minimisation method was used (see Appendix A). The results for log $K_d^0$, $\beta/A$, $\beta^{Ca}/A$ and $n$ are shown in Table 3.8.
Table 3.8 The fitted values of the free parameters \( n \), \( \log K_d^0 \) and \( \beta /A \) or \( \beta^{Ca}/A \) in equation 3.29 or 3.30, respectively, with their standard deviations. The unweighted Chi-square minimisation method was used.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>( n )</th>
<th>( \log K_d^0 )</th>
<th>( \beta /A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 13.3, no Ca</td>
<td>0.9 ± 0.1</td>
<td>3.7 ± 0.1</td>
<td>(1.7 ± 0.9)\times10^1</td>
</tr>
<tr>
<td>pH 12.0, no Ca</td>
<td>1.1 ± 0.1</td>
<td>1.7 ± 0.1</td>
<td>(6.1 ± 5.4)\times10^1</td>
</tr>
<tr>
<td>pH 10.7, no Ca</td>
<td>0.8 ± 0.1</td>
<td>4.5 ± 0.1</td>
<td>(7.1 ± 3.3)\times10^1</td>
</tr>
<tr>
<td>pH 13.3, 0.35 mM Ca</td>
<td>2.9 ± 0.3</td>
<td>4.2 ± 0.1</td>
<td>(2.1 ± 4.5)\times10^10</td>
</tr>
<tr>
<td>pH 12.0, 0.7 mM Ca</td>
<td>1.7 ± 0.1</td>
<td>1.8 ± 0.1</td>
<td>(6.2 ± 7.0)\times10^7</td>
</tr>
<tr>
<td>pH 12.0, 10 mM Ca</td>
<td>1.5 ± 0.1</td>
<td>2.5 ± 0.1</td>
<td>(2.9 ± 3.2)\times10^7</td>
</tr>
<tr>
<td>pH 10.7, 0.7 mM Ca</td>
<td>1.4 ± 0.1</td>
<td>4.2 ± 0.1</td>
<td>(2.2 ± 1.6)\times10^5</td>
</tr>
<tr>
<td>pH 10.7, 10 mM Ca</td>
<td>1.5 ± 0.1</td>
<td>5.1 ± 0.1</td>
<td>(4.4 ± 2.1)\times10^6</td>
</tr>
</tbody>
</table>

For the experiments performed in the absence of Ca, the value of \( n \) is close to one, whereas for the experiments with Ca clearly a larger value for \( n \) results. The values for \( n \) in Table 3.8 are the result of a mathematical fitting procedure. From a chemical point of view, however, \( n \) must be integer. Therefore, it was postulated that for the experiments without Ca, \( n \) equals one and for the experiments with Ca, \( n \) equals two. The model proposed for the pH range from 10.7 to 13.3 is:

in the absence of Ca, **1:1 Th:ISA complexes are dominant**

and

in the presence of Ca, **1:2:k Th:ISA:Ca complexes are dominant**.

This model describes the experimental data with a minimum number of species. The introduction of additional species would undoubtedly give a better fit to the experimental data. However, without more information on the complexes there is no benefit from such an exercise.

The justification for postulating that in the presence of Ca two ISA ligands coordinate with one Th ion is shown in Figure 3.8. This example at pH 12.0 clearly shows that a
Complexation of Th

slope with $n = 1$ is not able to describe the experimental data points. Moreover, also the HPAEC study (see section 3.2) gave evidence for one Th ion complexed by two ISA ligands in the presence of Ca. Note that a fitting curve with $n = 1.5$ describes the results of Figure 3.8 well. However, this would mean that polynuclear species are formed. In view of the very small Th concentrations used ($\text{Th} = 10^{-15}$) the formation of polynuclear complexes is precluded.

![Graph](image)

**Figure 3.8** Influence of ISA on the sorption of Th on a polyallomer tube wall at pH 12.0 in the presence of 0.7 mM Ca. The experimental data are fitted by equation 3.30 with $n = 1$ and $n = 2$.

The Figures 3.9 - 3.11 show that the fitting curves with the slope fixed at one, describe the experimental results in the absence of Ca well. In the Figures 3.12 - 3.16, the slope of the fitting curve is fixed at two and the experimental data in the presence of Ca are also well described, except for the data at pH 10.7 with 0.7 mM Ca (Figure 3.15).
Figure 3.9 Influence of ISA on the sorption of Th on an ion exchange resin at pH 13.3 in the absence of Ca. The line represents the fitting curve for a 1:1 Th:ISA complex.

Figure 3.10 Influence of ISA on the sorption of Th on a polyallomer tube wall at pH 12.0 in the absence of Ca. The line represents the fitting curve for a 1:1 Th:ISA complex.
Figure 3.11 Influence of ISA on the sorption of Th on feldspar at pH 10.7 in the absence of Ca. The line represents the fitting curve for a 1:1 Th:ISA complex.

Figure 3.12 Influence of ISA on the sorption of Th on an ion exchange resin at pH 13.3 in the presence of 0.35 mM Ca. The line represents the fitting curve for a 1:2 Th:ISA complex.
Figure 3.13 Influence of ISA on the sorption of Th on a polyallomer tube wall at pH 12.0 in the presence of 0.7 mM Ca. The line represents the fitting curve for a 1:2 Th:ISA complex.

Figure 3.14 Influence of ISA on the sorption of Th on a polyallomer tube wall at pH 12.0 in the presence of 10 mM Ca. The line represents the fitting curve for a 1:2 Th:ISA complex.
Figure 3.15 Influence of ISA on the sorption of Th on feldspar at pH 10.7 in the presence of 0.7 mM Ca. The line represents the fitting curve for a 1:2 Th:ISA complex.

Figure 3.16 Influence of ISA on the sorption of Th on feldspar at pH 10.7 in the presence of 10 mM Ca. The line represents the fitting curve for a 1:2 Th:ISA complex.
In Table 3.9 the values for $\beta/A$ and $\beta^{Ca}/A$ are shown, corresponding to the fitting curves of the Figures 3.9 - 3.16. The parameters $n$ and $\log K^0_d$ were fixed at the values indicated.

**Table 3.9** The fitted values of the free parameters $\beta/A$ and $\beta^{Ca}/A$ obtained when fixing $n$ and $\log K^0_d$ in the equations 3.29 and 3.30, respectively. The standard uncertainty of $\beta/A$ and $\beta^{Ca}/A$ are given. The unweighted Chi-square minimisation method was used.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$n$</th>
<th>$\log K^0_d$</th>
<th>$\beta/A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 13.3, no Ca</td>
<td>1</td>
<td>3.7</td>
<td>$(4.0 \pm 0.7) \times 10^5$</td>
</tr>
<tr>
<td>pH 12.0, no Ca</td>
<td>1</td>
<td>1.7</td>
<td>$(2.3 \pm 0.3) \times 10^5$</td>
</tr>
<tr>
<td>pH 10.7, no Ca</td>
<td>1</td>
<td>4.5</td>
<td>$(3.6 \pm 0.7) \times 10^4$</td>
</tr>
<tr>
<td>pH 13.3, 0.35 mM Ca</td>
<td>2</td>
<td>4.2</td>
<td>$(5.2 \pm 1.6) \times 10^7$</td>
</tr>
<tr>
<td>pH 12.0, 0.7 mM Ca</td>
<td>2</td>
<td>1.8</td>
<td>$(1.1 \pm 0.2) \times 10^8$</td>
</tr>
<tr>
<td>pH 12.0, 10 mM Ca</td>
<td>2</td>
<td>2.5</td>
<td>$(2.6 \pm 0.7) \times 10^8$</td>
</tr>
<tr>
<td>pH 10.7, 0.7 mM Ca</td>
<td>2</td>
<td>4.2</td>
<td>$(7.8 \pm 1.8) \times 10^6$</td>
</tr>
<tr>
<td>pH 10.7, 10 mM Ca</td>
<td>2</td>
<td>5.1</td>
<td>$(9.9 \pm 1.8) \times 10^7$</td>
</tr>
</tbody>
</table>

### 3.3.3.2 Determination of $\beta$ and $\beta^{Ca}$ taking into account the uncertainty of the experimental data

In this section the values of $\beta$ and $\beta^{Ca}$ are determined taking into account the uncertainty of the experimental results. In the previous section, the values of $\log \beta/A$ and $\beta^{Ca}/A$ in Table 3.9 were obtained by fitting all the experimental data points without weighting, because only the slope of the fitting curve was of interest. The uncertainty of the experimental data was less important because the obtained value for the slope was chosen to be integer. However, for the calculation of $\beta$ and $\beta^{Ca}$ it is important that data points with a large uncertainty contribute less to the value of $\beta$ and $\beta^{Ca}$ than data points with a smaller uncertainty. For this purpose, at each ISA concentration studied, the mean value
of $K_d$ was calculated, together with the uncertainty of the mean. For a detailed discussion, the reader is referred to Appendix B.

These mean values of $K_d$ were fitted to the equations 3.29 and 3.30 using the Chi-square minimisation method with instrumental weights (see Appendix A).

The value of $n$ was fixed at one for the experiments without Ca and fixed at two for the experiments with Ca. Log $K_d^0$ was fixed at the experimental mean and $A$ was fixed at the values given in Table 3.10 for the corresponding experimental hydroxyl concentration. The value of $A$ was calculated according to equation 3.28 with log $\beta_{\text{Tb(OH)}}^0 = 39.44$ at $I = 0.3$ M (Östhols 1995, $I = 0$ M). The activity coefficients were calculated using the Davies equation (equation 2.2).

**Table 3.10** The values used for the $A$ term at the experimental pH’s ($I = 0.3$ M).

<table>
<thead>
<tr>
<th>conc. OH$^-$ (mM)</th>
<th>pH</th>
<th>log A</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>13.3</td>
<td>37.35</td>
</tr>
<tr>
<td>14</td>
<td>12.0</td>
<td>32.02</td>
</tr>
<tr>
<td>0.7</td>
<td>10.7</td>
<td>26.82</td>
</tr>
</tbody>
</table>

From this fitting procedure, values for $\beta$ and $\beta^{Ca}$ resulted, together with their uncertainty (one standard deviation). In Table 3.11, the results for the fit parameters $\beta$ and $\beta^{Ca}$ at fixed values for $n$, $A$ and log $K_d^0$ are given.
Table 3.11 The fitted values of the free parameter $\beta$ or $\beta^{Ca}$, obtained when fixing $n$, $A$ and $K^0_\alpha$ in the equations 3.29 and 3.30. The uncertainty of the experimental values of $K_\alpha$ was taken into account using the Chi-square minimisation method with instrumental weights.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$n$</th>
<th>$\log K^0_\alpha$</th>
<th>$\beta$</th>
<th>$\log \beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 13.3, no Ca</td>
<td>1</td>
<td>3.7 ± 0.1</td>
<td>(1.4 ± 0.1)$\times 10^{53}$</td>
<td>43.1</td>
</tr>
<tr>
<td>pH 12.0, no Ca</td>
<td>1</td>
<td>1.7 ± 0.1</td>
<td>(2.3 ± 0.1)$\times 10^{57}$</td>
<td>37.4</td>
</tr>
<tr>
<td>pH 10.7, no Ca</td>
<td>1</td>
<td>4.5 ± 0.1</td>
<td>(8.9 ± 1.7)$\times 10^{31}$</td>
<td>32.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$n$</th>
<th>$\log K^0_\alpha$</th>
<th>$\beta^{Ca}$</th>
<th>$\log \beta^{Ca}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 13.3, 0.35 mM Ca</td>
<td>2</td>
<td>4.2 ± 0.1</td>
<td>(8.2 ± 1.9)$\times 10^{45}$</td>
<td>45.9</td>
</tr>
<tr>
<td>pH 12.0, 0.7 mM Ca</td>
<td>2</td>
<td>1.8 ± 0.1</td>
<td>(2.6 ± 0.4)$\times 10^{41}$</td>
<td>41.4</td>
</tr>
<tr>
<td>pH 12.0, 10 mM Ca</td>
<td>2</td>
<td>2.5 ± 0.1</td>
<td>(1.1 ± 0.2)$\times 10^{42}$</td>
<td>42.0</td>
</tr>
<tr>
<td>pH 10.7, 0.7 mM Ca</td>
<td>2</td>
<td>4.2 ± 0.1</td>
<td>(7.2 ± 1.6)$\times 10^{34}$</td>
<td>34.9</td>
</tr>
<tr>
<td>pH 10.7, 10 mM Ca</td>
<td>2</td>
<td>5.1 ± 0.1</td>
<td>(7.4 ± 0.9)$\times 10^{34}$</td>
<td>34.9</td>
</tr>
</tbody>
</table>

Wieland et al. (1998) determined a value for $\beta^{Cl}$/A in their study on the sorption of Th(IV) on cement (pH 13.3, 1.7 mM Ca). For $n = 2$ and $K^0_\alpha = 5\times 10^6$ ml/g, they found $\beta^{Cl}$/A $= 5\times 10^8$ M$^{-1}$. Their value is in good agreement with $\beta^{Cl}$/A at pH 13.3 and 0.35 mM Ca in Table 3.11: $\beta^{Cl}$/A $= 8.2\times 10^{45}$/10$^{57.35}$ $= 2.7\times 10^8$ M$^{-2}$. Tits et al. (2000) also determined a value for $\beta^{Cl}$/A in their study on the sorption of Th(IV) on calcite (pH 13.3, 1.7 mM Ca). For $n = 2$ and $K^0_\alpha = 6\times 10^4$ ml/g, they found $\beta^{Cl}$/A $= 3\times 10^9$ M$^{-2}$.

In Figure 3.17, as an example the result of the fitting procedure is shown for the experiment performed at pH 13.3 in the absence of Ca. Symmetrical errors for $K_\alpha$ were used for the reasons explained in Appendix B.

Table 3.11 shows the results of the fitting procedure where the uncertainties of the experimental data points were taken into account. This in contrast with Table 3.9, where no weight was given to the experimental data points. The comparison of the $\log \beta$ and $\log \beta^{Ca}$ values of the Tables 3.8, 3.9 and 3.11, given in Table 3.12, shows only small
differences. It was preferred to use the log $\beta$ and log $\beta^{\text{Ca}}$ values of Table 3.11 for further calculations, because the uncertainty of the experimental data points was considered. At this point, it is not possible to compare the values of log $\beta$ and log $\beta^{\text{Ca}}$ in Table 3.11 with one another and to evaluate the stability of the complexes. The reason is that log $\beta$ and log $\beta^{\text{Ca}}$ are dependent on the pH and the free Ca concentration (equations 3.15 and 3.16). Therefore, in the following section, the number of protons and Ca ions involved in the complexation reactions 3.11 and 3.12 are determined.

**Figure 3.17** Influence of ISA on the sorption of Th on an ion exchange resin at pH 13.3 in the absence of Ca. The full line represents the fitting curve, which takes into account the uncertainty of the mean $K_d$.
Table 3.12 Comparison of the logarithm of the free parameters $\beta$ and $\beta^{\text{Ca}}$ of Tables 3.8, 3.9 and 3.10.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Table 3.8 n, log $K^0$ free not weighted</th>
<th>Table 3.9 n, log $K^0$ fixed not weighted</th>
<th>Table 3.11 n, log $K^0$ fixed weighted</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 13.3, no Ca</td>
<td>log $\beta$ 42.6</td>
<td>log $\beta$ 43.0</td>
<td>log $\beta$ 43.1</td>
</tr>
<tr>
<td>pH 12.0, no Ca</td>
<td>log $\beta$ 37.8</td>
<td>log $\beta$ 37.4</td>
<td>log $\beta$ 37.4</td>
</tr>
<tr>
<td>pH 10.7, no Ca</td>
<td>log $\beta$ 30.7</td>
<td>log $\beta$ 32.4</td>
<td>log $\beta$ 32.0</td>
</tr>
<tr>
<td>pH 13.3, 0.35 mM Ca</td>
<td>log $\beta^{\text{Ca}}$ 47.7</td>
<td>log $\beta^{\text{Ca}}$ 45.1</td>
<td>log $\beta^{\text{Ca}}$ 45.9</td>
</tr>
<tr>
<td>pH 12.0, 0.7 mM Ca</td>
<td>log $\beta^{\text{Ca}}$ 39.8</td>
<td>log $\beta^{\text{Ca}}$ 40.0</td>
<td>log $\beta^{\text{Ca}}$ 41.4</td>
</tr>
<tr>
<td>pH 12.0, 10 mM Ca</td>
<td>log $\beta^{\text{Ca}}$ 39.5</td>
<td>log $\beta^{\text{Ca}}$ 40.4</td>
<td>log $\beta^{\text{Ca}}$ 42.0</td>
</tr>
<tr>
<td>pH 10.7, 0.7 mM Ca</td>
<td>log $\beta^{\text{Ca}}$ 32.2</td>
<td>log $\beta^{\text{Ca}}$ 33.7</td>
<td>log $\beta^{\text{Ca}}$ 34.9</td>
</tr>
<tr>
<td>pH 10.7, 10 mM Ca</td>
<td>log $\beta^{\text{Ca}}$ 33.5</td>
<td>log $\beta^{\text{Ca}}$ 34.8</td>
<td>log $\beta^{\text{Ca}}$ 34.9</td>
</tr>
</tbody>
</table>
3.3.3.3 Determination of the reaction stoichiometry and the stability constants $K$ and $K_{Ca}$

- Complexation of Th(IV) by ISA in the absence of Ca

Three experiments at different pH's were performed in the absence of Ca, and a value for the apparent stability constant $\beta$ was determined for each experiment. The results are summarised in Table 3.13.

**Table 3.13** Experimental proton concentrations and the fitted values of $\beta$ taken from Table 3.11 ($I = 0.3\, M$).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>log (H$^+$) (mol/l)</th>
<th>log $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 13.3, no Ca</td>
<td>-13.21</td>
<td>43.13</td>
</tr>
<tr>
<td>pH 12.0, no Ca</td>
<td>-11.88</td>
<td>37.35</td>
</tr>
<tr>
<td>pH 10.7, no Ca</td>
<td>-10.58</td>
<td>31.95</td>
</tr>
</tbody>
</table>

The complexation constant $K$ and the number of protons involved in the complexation reaction were simultaneously determined. Based on equation 3.15, a value for $\log K$ and $m$ results from the following relationship:

$$\log \beta = \log K - m \cdot \log (H)$$  \hspace{1cm} (3.32)

Therefore, in figure 3.18, the logarithms of the three experimental values of $\beta$ were plotted versus the logarithms of the experimental proton concentrations.
Figure 3.18 Determination of the number of protons involved in the complexation reaction in the absence of Ca and of the stability constant $K$ by plotting the logarithm of the fit parameter $\beta$ as a function of the experimental $pH$ (The uncertainty of $\log \beta$ was not taken into account.)

The results of the fitting are $m = 4.3 \pm 0.1$ and $\log K = -13.1 \pm 0.7$. It is important to notice that $\log K$ is actually the intercept at $\log (H^+) = 1$ M, and, thus, an extrapolation over at least 11 order-of-magnitudes of $\log (H^+)$. This makes $\log K$ very sensitive for small changes of $m$, as is demonstrated in the following. From a chemical point of view, $m$ must be integer. Therefore, $m$ was fixed at four and the corresponding $\log K$ equaled $-10.1 \pm 0.2$. The uncertainty of $\log K$ became smaller because by fixing $m$ the degree of freedom decreased.
• Complexation of Th(IV) by ISA in the presence of Ca

Five experiments at different pH’s and different total Ca concentrations were performed in the presence of Ca and a value for the apparent stability constant $\beta_{Ca}$ was determined for each experiment. An overview is given in Table 3.14.

**Table 3.14** Experimental proton concentration, calculated concentration of free Ca and the fitted value of the free parameter $\beta_{Ca}$ taken from Table 3.11 ($I = 0.3 \text{ M}$).

<table>
<thead>
<tr>
<th>Experiment (pH, total Ca)</th>
<th>log (H$^+$) (mol/l)</th>
<th>log (Ca$^{2+}$) (mol/l)</th>
<th>log $\beta_{Ca}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 13.3, 0.4 mM</td>
<td>-13.21</td>
<td>-3.85</td>
<td>45.91</td>
</tr>
<tr>
<td>pH 12.0, 0.7 mM</td>
<td>-11.88</td>
<td>-3.20</td>
<td>41.42</td>
</tr>
<tr>
<td>pH 12.0, 10 mM</td>
<td>-11.88</td>
<td>-2.04</td>
<td>42.03</td>
</tr>
<tr>
<td>pH 10.7, 0.7 mM</td>
<td>-10.58</td>
<td>-3.15</td>
<td>34.96</td>
</tr>
<tr>
<td>pH 10.7, 10 mM</td>
<td>-10.58</td>
<td>-2.00</td>
<td>34.87</td>
</tr>
</tbody>
</table>

The Ca$^{2+}$ concentration is a function of the total Ca in solution ($Ca^{\text{tot}}$), the concentration of complexed Ca ($Ca_{\text{complex}}$) and the CaOH$^+$ concentration:

$$[\text{Ca}^{2+}] = [Ca^{\text{tot}}] - [Ca_{\text{complex}}] - [\text{CaOH}^+]$$  \hspace{1cm} (3.33)

Complexed Ca species are Th-ISA-Ca complexes and ISA-Ca complexes. Because the concentration of Th in the experiments is much smaller than the total concentration of Ca, the amount of Th-ISA-Ca species is negligible compared to the total Ca concentration. Speciation calculations based on the stability constants for CaISA$^+$ and CaISA$^0$ (see section 2.4) show that the concentrations of CaISA$^+$ and CaISA$^0$ are also negligible compared to the total Ca concentration. The concentration of CaOH$^+$ is, depending on pH, not always negligible. At pH 10.7 the major species is Ca$^{2+}$ and the total Ca
concentration is set equal to the free Ca concentration. However, at pH 13.3 and 12.0 the fraction of CaOH\(^+\) equals approximately 58\% and 8\% of the total Ca concentration, respectively (\(\log K_{\text{CaOH}\,+} = -12.78\), Nordstrom et al. 1990).

In accordance with equation 3.16, the logarithms of \(\beta^{\text{Ca}}\) were plotted against the logarithms of the proton and the free Ca concentrations. By fitting the plane

\[
\log \beta^{\text{Ca}} = k \cdot \log (\text{Ca}^{2+}) - m \cdot \log (\text{H}^+) + \log K^{\text{Ca}}
\]  

(3.34)

through the five experimental data points, values for (i) \(k\), the number of Ca ions participating in the complex, (ii) \(m\), the number of protons involved, and (iii) \(K^{\text{Ca}}\), the stability constant were obtained. This fitted plane is shown in Figure 3.19 and describes very well the experimental results.

\[\text{Figure 3.19 Fitting the five experiments performed in the presence of Ca by equation 3.34. (The uncertainties of log \(\beta^a\) were not taken into account.)}\]
The values of the adjustable parameters \( k \), \( m \) and \( \log K^{Ca} \) with their uncertainties are:

\[ k = 1.2 \pm 0.4, \quad m = 4.4 \pm 0.3 \quad \text{and} \quad \log K^{Ca} = -8.1 \pm 2.9, \]

respectively. These results show that approximately four protons are involved in the complexation reaction and that approximately one Ca ion participates in the complex. The latter result contrasts with the HPAEC study that rather gave evidence for two Ca ions participating in the complex. To gain more structural information, \(^1\)H-NMR experiments and EXAFS measurements were performed in the framework of the present work. However, neither the \(^1\)H-NMR experiments, nor the EXAFS measurements could give more information on the identity of the complexes in solution. In Appendix C an overview is given of the different spectroscopic experiments performed and their results.

The large uncertainty of \( \log K^{Ca} \) shows the sensitivity of \( \log K^{Ca} \) for small changes in \( k \) and \( m \). Because \( \log K^{Ca} \) is actually the intercept on the Z-axis at \( (H^+) = 1 \text{ M} \) and \( (Ca^{2+}) = 1 \text{ M} \), small changes in the angle of the plane cause a large change of the \( \log K^{Ca} \) value. With \( k \) and \( m \) being integer, the species postulated are 1:2:1 Th:ISA:Ca complexes with four protons involved in the complexation reaction. The corresponding stability constant for this model is \( \log K^{Ca} = -3.6 \pm 0.2 \) (Table 3.15).

\[ \text{Table 3.15 Value of } \log K^{Ca} \text{ for } k \text{ and } m \text{ being integer.} \]

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( k )</td>
<td>1</td>
</tr>
<tr>
<td>( m )</td>
<td>4</td>
</tr>
<tr>
<td>( \log K^{Ca} )</td>
<td>-3.6 ± 0.2</td>
</tr>
</tbody>
</table>
3.3.4 Conclusions

Batch sorption experiments were performed in the pH range 10.7 - 13.3 at different Ca concentrations. Eight data sets resulted, which were used for the determination of the stoichiometry of the complexation reactions and for the determination of the stability constants. A clear difference was demonstrated between systems without Ca and systems with Ca. In the absence of Ca, 1:1 Th:ISA complexes are formed in the pH range 10.7 - 13.3 with four protons being involved in the complexation reaction. The logarithm of the stability constant $K$ equals $-10.1 \pm 0.2$. In the presence of Ca, Th(IV) is coordinated with two ISA ligands. This is in agreement with the HPAEC study and with the results of Th sorption on cement (Wieland et al. 1998), on calcite (Tits et al. 2000) and on feldspar (Van Loon and Glaus 1998), considering the large scatter of the data points in the latter study. Based on the results of the batch sorption study, 1:2:1 Th:ISA:Ca complexes are postulated with four protons being split off from the ISA ligands and/or from the water molecules coordinated with the Th and/or Ca ion. Only one Ca ion seemed to participate in the complex. This is in contrast with the HPAEC study (section 3.2) where two Ca ions were found to participate. Additional information from spectroscopic methods is required to solve this Ca question. For the model of a 1:2:1 Th:ISA:Ca complex with four protons involved, the logarithm of the stability constant $K^{\text{Ca}}$ was found to be equal to $-3.6 \pm 0.2$. 
4

Complexation of europium by α-isosaccharinic acid

4.1 Introduction

Eu(III) is a model element for the trivalent actinides such as Pu(III) (Choppin 1999), Am(III) and Cm(III) in the L/ILW repository, and is, therefore, studied in the present work. Moreover, because Eu(III) has paramagnetic properties, NMR can be applied and could provide valuable information on the structure of the Eu-ISA complexes.

Indications for the complexation of Eu(III) by ISA have been given in earlier literature. Van Loon and Glaus (1998) studied the sorption of Eu(III) on feldspar in artificial cement pore water (pH 13.3, 1.8 mM total Ca). At ISA concentrations higher than $10^4$ M, the sorption of Eu(III) on feldspar was significantly reduced. The authors further showed that the effect of a mixture of cellulose degradation products on the sorption of Eu(III) on feldspar is the same as the effect of pure ISA. The experimental data could be described by means of a 1:1 complex between Eu(III) and ISA. Bourbon (1994) measured an enhanced solubility of Eu(III) and Sm(III) in cellulose degradation solutions in the pH range 10.5 - 12.0. It is reasonable to assume that ISA is mainly responsible for this enhanced solubility, based on the observations of Van Loon and Glaus (1998). Tits et al. (2000) studied the sorption of Eu(III) on calcite in artificial cement pore water. The decrease in $K_d$ observed for (ISA) $> 10^5$ M could be described by the formation of 1:1 Eu:ISA complexes. The influence of ISA on the sorption of Eu(III) on cement in artificial cement pore water was studied by Wieland et al. (1998). However, they found little or no significant influence of ISA on the sorption of Eu(III). A tentative explanation given by
the authors for the high affinity of Eu(III) was the formation of ternary complexes on the surface of cement.

In all of the above mentioned work, indications for the formation of complexes between Eu(III) and ISA are given and a possible stoichiometry of the complexes is derived. However, the influence of pH and the corresponding stability constants were not determined. Therefore, in the present work, batch sorption experiments in the pH range from 10.7 to 13.3 and 'H-NMR measurements at pH 13.3 were performed to determine the stoichiometry of the complexation reactions and their stability constants.

4.2 Batch sorption study

The batch sorption method was described earlier in section 3.3.1 for the complexation of Th(IV) by ISA. Analogous to the batch sorption study on Th(IV), a tentative general complexation reaction was postulated for the complexation of Eu(III) by ISA, based on the results of the HPAEC study. A similar HPAEC study to that for Th (section 3.2) was performed with Eu and ISA. Three solutions, prepared in 80 mM NaOH, were fractionated: (i) Eu(NO₃)₃, (ii) Eu(NO₃)₃ with NaISA, and (iii) Eu(NO₃)₃ with Ca(ISA)₂. However, no Eu was found in the eluate of any fractionated solution. This implied that neither ISA, nor ISA in the presence of Ca were able to elute Eu. It could not be decided from these experiments whether Eu-ISA or Eu-ISA-Ca complexes were formed in the solutions injected but dissociated on the column or that such complexes were formed at all. For simplicity, it was assumed that Eu-ISA-Ca complexes do not exist and only Eu-ISA complexes are formed. It was decided to try to describe the experimental data with one single tentative general complexation reaction:

\[
\text{Eu} + n\text{ISA} \rightleftharpoons (\text{Eu(ISA)}_n)_m + n\text{H} + m\text{H}
\] (4.1)
The charges are omitted for simplicity. The reasons for including protons in equation 4.1 are the hydrolysis of Eu(III) and the observation that the hydroxo groups of polyhydroxy ligands are deprotonated when coordinating with cations (Escandar et al. 1995, Frutos et al. 1997, Hedinger et al. 1998, Gajda et al. 1998, Vercammen et al. 1999a).

The stability constant associated with equation 4.1 is:

\[
K = \frac{(Eu(ISA)_n \cdot m^+ H)(H)^m}{(Eu)(ISA)^n} \quad (4.2)
\]

and the apparent stability constant \(\beta_i\) is defined as:

\[
\beta = \frac{K}{(H)^m} \quad (4.3)
\]

or

\[
\beta = \frac{(Eu(ISA)_n \cdot m^+)}{(Eu)(ISA)^n} \quad (4.4)
\]

Parentheses denote molar concentrations of the species. The concentration of free ISA in equation 4.2 can be approximated by the total ISA concentration (equation 4.4) for the reasons explained earlier in section 3.3.1. Thus, the general relationship describing the changes in sorption is:

\[
\log K'_d = \log K'_o - \log \left(1 + \frac{\beta}{A} \cdot (ISA_{tot})^n\right) \quad (4.5)
\]

with \(A\) the side reaction coefficient, defined as:

\[
A = 1 + \beta_{Eu(OH)_4} (OH)^+ \approx \beta_{Eu(OH)_4} \frac{K_w^4}{(H)^4} \quad (4.6)
\]
Note that the approximation in equation 4.6 is valid for the pH range covered by the experiments. In the present work, the existence of Eu(OH)$_4^-$ is assumed. Under the experimental conditions (pH $\geq 10.7$, $5 \cdot 10^{-10}$ M Eu), Eu(OH)$_4^-$ is the dominant hydrolysis species of Eu, as shown in Figure 4.1.

**Figure 4.1** Eu speciation as a function of pH (total Eu = $5 \cdot 10^{-10}$ M, $I = 0.3$ M). Thermodynamic data are taken from Haas et al. (1995).
4.2.1 Materials and methods

All experiments were performed at 23 ± 2 °C in a glovebox under N₂ atmosphere (O₂, CO₂ < 1 ppm). Bidemineralised water was used, prepared by ultrafiltration with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

4.2.1.1 Determination of the distribution coefficient Kₐ

The distribution coefficient Kₐ for Eu(III) sorption on feldspar was measured as a function of the total ISA concentration. Experiments were performed at three different pH's: 10.7, 12.0 and 13.3 and at different Ca concentrations to determine the stoichiometry of the complexation reactions.

For the experiments performed in the absence of Ca, 15 ml aliquots of a stock solution were added to 10 - 15 mg of feldspar (orthoclase KAlSi₃O₈, Fronland, Norway, 63 μm), weighed in polyallomer tubes. The stock solutions contained ISA in the concentration range from 10⁻⁵ to 10⁻¹ M. ISA was supplied as ISA lactone¹, which hydrolyses in the presence of NaOH to form the open chain form of ISA. The pH and ionic strength of the stock solutions were adjusted to the desired values with 1 M NaOH and 1 M NaClO₄, respectively (I = 0.3 M). The stock solutions were spiked with Eu-152 to give an activity of 5·10⁵ Bq/ml. The total Eu concentration equaled 5·10⁻¹⁰ M. At this total Eu concentration the formation of Eu-colloids can be excluded (Tits et al. 2000). The Eu-152 trace solution was purchased from Amersham.

The preparation of the samples for the experiments performed in the presence of Ca was the same, except that Ca was added before spiking the stock solution with Eu-152. At pH 13.3, a saturated Ca(OH)₂ solution in 0.3 M NaOH was mixed with an aliquot of ISA solution, before spiking with Eu-152. The total concentration of Ca in solution equaled 1.8 mM. The sorption of Ca on feldspar was negligible. At pH 10.7 and 12.0, Ca(NO₃)₂ solution was added to the feldspar/ISA/NaOH suspension to give total Ca concentrations of 1.8 mM and 10 mM. An overview of the eight different experiments is given in Table 4.1.

¹ Synthesis of ISA lactone (see section 3.2.2.2).
After four days of equilibration on an end-over-end shaker, the tubes were centrifuged (48360g, 30 min.). The total concentration of Ca in the supernatant was determined by ICP-AES (ARL 3410 ICP with Minitorch™). The activity of Eu-152 in the supernatant was measured on a Packard Minaxi γ AutoGamma 5000 Series counter or on a Packard Cobra Quantum Auto-Gamma counter. For some experiments the pH was checked using a glass electrode (ORION, ROSS Combination pH Electrode) and found to remain unchanged.

Next, the tubes were emptied, rinsed with water and filled with 15 ml of a 0.2 M HNO₃ solution to desorb Eu from the wall of the tubes. After one day of end-over-end shaking, the Eu-152 activity in the supernatant was analysed.

The distribution coefficient of Eu was then calculated according to equation 3.31.

<table>
<thead>
<tr>
<th>pH</th>
<th>[Ca₅₀]</th>
<th>[Ca₅₀]</th>
<th>[Ca₅₀]</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.3</td>
<td>± 10⁻³ M²</td>
<td>1.8 mM</td>
<td>/</td>
</tr>
<tr>
<td>12.0</td>
<td>± 10⁻⁴ M²</td>
<td>1.8 mM</td>
<td>10 mM</td>
</tr>
<tr>
<td>10.7</td>
<td>± 10⁻⁵ M²</td>
<td>1.8 mM</td>
<td>10 mM</td>
</tr>
</tbody>
</table>

* background concentration of Ca, these experiments are designated “experiments in the absence of Ca”
4.2.1.2 Preliminary conditions for applying the batch sorption method

Several preliminary conditions must be fulfilled for applying the batch sorption method. Analogous to section 3.3.2.2, the different conditions are discussed.

(i) The reference isotherm for Eu must be linear. The sorption isotherms are generally linear at very low metal ion concentrations (Brouwer et al. 1983, Bradbury and Baeyens 1995, Tits et al. 2000). This was demonstrated for Th sorption on an ion exchange resin at pH 13.3 (Figure 3.7). It is assumed that Eu shows also a linear sorption behaviour on feldspar at each experimental pH and Ca concentration.

(ii) The sorption of Eu on feldspar has to be reversible. This condition is fulfilled, because the experiments showed that at increasing ISA concentrations, the amount of Eu in solution increases as well.

(iii) It was demonstrated that feldspar was stable under the experimental conditions (see section 3.3.2.2).

(iv) ISA does not sorb on feldspar at pH 13.3 (Van Loon and Glaus 1998, unpublished results). It is assumed that at pH 10.7 and 12.0, neither free ISA, nor the complexed Eu-ISA species sorb on feldspar.

(v) The formation of polynuclear complexes is negligible because of the small concentrations of Eu used in the experiments (± 5·10^{-10} M).

(vi) To determine the equilibration time, two kinetic experiments were performed. The sorption of Eu on feldspar at pH 12.0 and 13.3 was studied in the presence of 10^{-4} M ISA. The results are shown in Figure 4.2 and demonstrate that, especially at pH 12.0, no equilibrium is reached after six days. However, one can clearly distinguish between a fast process (≤ one day) and a slow process (several days). The slow process might be incorporation of Eu in feldspar, slow changes of the feldspar surface, etc. The fast process represents sorption, that is known to be fast (within one day). Because the
sorption process mainly determines the $K_d$ values, the samples were only equilibrated for four days.

**Figure 4.2** Kinetics of the sorption of Eu(III) on feldspar in the presence of $10^{-4} \text{ M} \text{ ISA}$ at pH 12.0 and 13.3.
4.2.2 Results and discussion

4.2.2.1 Determination of the number of ISA ligands coordinated with Eu(III)

Eight batch sorption experiments were performed (Table 4.1). The results are shown in the Figures 4.3 - 4.10 by plotting the logarithm of the distribution coefficient $K_d$ as a function of the logarithm of the total ISA concentration. The experimental data points at "no ISA" represent the values of $\log K^0_d$.

At increasing ISA concentrations, the amount of complexes between Eu and ISA in solution increases. Consequently, the concentration of total Eu in solution becomes larger and $\log K_d$ decreases, as shown in the Figures 4.3 - 4.10.

For the determination of the number of ISA ligands participating in the complexation reaction, the experimental data points were fitted to equation 4.5. The slope of the fitting curve in the region of changing $K_d$, $n$, represents the number of ISA ligands coordinated with one Eu ion. The intercept of the curve with the Y-axis gives the fitted value of $\log K^0_d$. The results for the adjustable parameters $n$, $\log K^0_d$ and $\beta/A$ are given in Table 4.2. The uncertainty of the experimental data points was not taken into account.

The slope of the fitting curve of the experiments performed in the absence of Ca, as well as those performed in the presence of Ca, is close to one. Unlike the experiments performed with Th, no effect of Ca on the slope is noticed.

To describe the experimental results with a minimum number of species, it is postulated that in the absence as well as in the presence of Ca, 1:1 Eu:ISA complexes are dominant. It was verified whether all the experimental data points could be described as postulated by a 1:1 Eu:ISA complex, by fitting the results to equation 4.5 with $n$ fixed at one ($n$ must be integer from a chemical point of view) and $\log K^0_d$ fixed at the values of Table 4.2. The fitting curves are shown in the Figures 4.3 - 4.10. Values determined for the adjustable parameter $\beta/A$ are given in Table 4.3.
Table 4.2 The fitted values of the free parameters $n$, log $K^0_d$ and $\beta/A$ in equation 4.5, with their standard deviations. The unweighted Chi-square minimisation method was used.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$n$</th>
<th>log $K^0_d$</th>
<th>$\beta/A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 13.3, no Ca</td>
<td>0.9 ± 0.1</td>
<td>4.2 ± 0.1</td>
<td>(6.9 ± 1.9)$\times 10^3$</td>
</tr>
<tr>
<td>pH 13.3, 1.8 mM Ca</td>
<td>1.2 ± 0.2</td>
<td>5.3 ± 0.1</td>
<td>(7.2 ± 8.9)$\times 10^4$</td>
</tr>
<tr>
<td>pH 12.0, no Ca</td>
<td>0.8 ± 0.1</td>
<td>5.1 ± 0.1</td>
<td>(2.7 ± 1.3)$\times 10^4$</td>
</tr>
<tr>
<td>pH 12.0, 1.8 mM Ca</td>
<td>1.1 ± 0.1</td>
<td>5.4 ± 0.1</td>
<td>(1.5 ± 0.9)$\times 10^5$</td>
</tr>
<tr>
<td>pH 12.0, 10 mM Ca</td>
<td>1.3 ± 0.1</td>
<td>5.4 ± 0.1</td>
<td>(4.8 ± 2.5)$\times 10^4$</td>
</tr>
<tr>
<td>pH 10.7, no Ca</td>
<td>0.6 ± 0.1</td>
<td>4.6 ± 0.1</td>
<td>(8.9 ± 3.5)$\times 10^5$</td>
</tr>
<tr>
<td>pH 10.7, 1.8 mM Ca</td>
<td>1.2 ± 0.2</td>
<td>5.0 ± 0.1</td>
<td>(1.5 ± 1.7)$\times 10^5$</td>
</tr>
<tr>
<td>pH 10.7, 10 mM Ca</td>
<td>1.3 ± 0.1</td>
<td>5.1 ± 0.1</td>
<td>(4.0 ± 2.3)$\times 10^5$</td>
</tr>
</tbody>
</table>

Table 4.3 The fitted values of the free parameter $\beta/A$, obtained when fixing $n$ and log $K^0_d$ in equation 4.5. The standard uncertainty of $\beta/A$ is given. The unweighted Chi-square minimisation method was used.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$n$</th>
<th>log $K^0_d$</th>
<th>$\beta/A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 13.3, no Ca</td>
<td>1</td>
<td>4.2</td>
<td>(1.6 ± 0.1)$\times 10^4$</td>
</tr>
<tr>
<td>pH 13.3, 1.8 mM Ca</td>
<td>1</td>
<td>5.3</td>
<td>(1.6 ± 0.4)$\times 10^4$</td>
</tr>
<tr>
<td>pH 12.0, no Ca</td>
<td>1</td>
<td>5.1</td>
<td>(1.8 ± 0.4)$\times 10^5$</td>
</tr>
<tr>
<td>pH 12.0, 1.8 mM Ca</td>
<td>1</td>
<td>5.4</td>
<td>(6.5 ± 0.9)$\times 10^4$</td>
</tr>
<tr>
<td>pH 12.0, 10 mM Ca</td>
<td>1</td>
<td>5.4</td>
<td>(7.0 ± 1.1)$\times 10^4$</td>
</tr>
<tr>
<td>pH 10.7, no Ca</td>
<td>1</td>
<td>4.6</td>
<td>(9.7 ± 2.3)$\times 10^5$</td>
</tr>
<tr>
<td>pH 10.7, 1.8 mM Ca</td>
<td>1</td>
<td>5.0</td>
<td>(4.3 ± 1.2)$\times 10^4$</td>
</tr>
<tr>
<td>pH 10.7, 10 mM Ca</td>
<td>1</td>
<td>5.1</td>
<td>(6.3 ± 1.0)$\times 10^4$</td>
</tr>
</tbody>
</table>
Figure 4.3 Influence of ISA on the sorption of Eu on feldspar at pH 13.3 in the absence of Ca. The line represents the fitting curve for the formation of 1:1 Eu:ISA complexes.

Figure 4.4 Influence of ISA on the sorption of Eu on feldspar at pH 13.3 in the presence of 1.8 mM Ca. The line represents the fitting curve for the formation of 1:1 Eu:ISA complexes.
Figure 4.5 Influence of ISA on the sorption of Eu on feldspar at pH 12.0 in the absence of Ca. The line represents the fitting curve for the formation of 1:1 Eu:ISA complexes.

Figure 4.6 Influence of ISA on the sorption of Eu on feldspar at pH 12.0 in the presence of 1.8 mM Ca. The line represents the fitting curve for the formation of 1:1 Eu:ISA complexes.
Complexation of Eu

**Figure 4.7** Influence of ISA on the sorption of Eu on feldspar at pH 12.0 in the presence of 10 mM Ca. The line represents the fitting curve for the formation of 1:1 Eu:ISA complexes.

**Figure 4.8** Influence of ISA on the sorption of Eu on feldspar at pH 10.7 in the absence of Ca. The line represents the fitting curve for the formation of 1:1 Eu:ISA complexes.
Figure 4.9 Influence of ISA on the sorption of Eu on feldspar at pH 10.7 in the presence of 1.8 mM Ca. The line represents the fitting curve for the formation of 1:1 Eu:ISA complexes.

Figure 4.10 Influence of ISA on the sorption of Eu on feldspar at pH 10.7 in the presence of 10 mM Ca. The line represents the fitting curve for the formation of 1:1 Eu:ISA complexes.
The experiments in the absence of Ca at pH 12.0 (Figure 4.5) and pH 13.3 (Figure 4.3) are well described by a 1:1 Eu:ISA complex. However, at pH 10.7 (Figure 4.8), \( n = 0.5 \) better describes the data points than \( n = 1 \). This would mean that 2:1 Eu:ISA complexes are formed. At the low Eu concentrations used \((5 \times 10^{-10} \text{ M})\) the formation of polynuclear complexes is rather unlikely. Therefore, in view of the scatter of the experimental data points, the postulated model of 1:1 Eu:ISA complexes was maintained.

The experiment in the presence of Ca at pH 13.3 (Figure 4.4) can also be described by a fitting curve with a slope set equal to two. This would mean that 1:2 Eu:ISA complexes are formed. But, because of (i) the large scatter of the data points and (ii) the two references in the literature (Van Loon and Glaus 1998, Tits et al. 2000) which both gave evidence for the formation of 1:1 Eu:ISA complexes, it was postulated that in this system 1:1 Eu:ISA complexes dominate.

The experiments in the presence of Ca at pH 12.0 (Figure 4.6 and 4.7) and pH 10.7 (Figure 4.9 and 4.10) are well described by a fitting curve with slope one. It is important to note that the experiment at pH 10.7, 1.8 mM Ca (Figure 4.9) could also be fitted by \( n = 2 \). However, the scatter of the data points at \((\text{ISA}_{\text{tot}}) > 10^{-3} \text{ M}\) is so large, that the importance of these data points is small. Therefore, the data points at \((\text{ISA}_{\text{tot}}) \leq 10^{-3} \text{ M}\) are better described by a fitting curve with \( n = 1 \).
4.2.2.2 Determination of $\beta$ taking into account the uncertainty of the experimental data

In the previous paragraph, the uncertainty of the experimental data was not taken into account, because the parameter of interest, $n$, was set to an integer value by the postulated model. However, for the determination of $\beta$ and $K$ it is important to obtain values which describe the experimental data set as well as possible. This means that data points with a large uncertainty should contribute less to the values of $\beta$ and $K$. Therefore, for each data point the uncertainty was calculated. Next, for each ISA concentration, the mean value of $K_d$ and its uncertainty were determined, based on the uncertainties of the individual data points. This procedure is discussed in Appendix B.

The mean values of $K_d$ were fitted to equation 4.5 taking into account their uncertainty by using the Chi-square minimisation method with instrumental weights. The value of $n$ was fixed at one and $\log K_d^0$ was fixed at the experimental mean. The side reaction coefficient $A$ was fixed at the values given in Table 4.4 for the corresponding experimental hydroxyl concentration. The value of $A$ was calculated according to equation 4.6 with $\log \beta_{Fe(OH)_{2+}} = 19.89$ at $I = 0.3$ M (Haas et al. 1995). The activity coefficients were calculated using the Davies relation, equation 2.2.

<table>
<thead>
<tr>
<th>pH</th>
<th>conc. OH$^-$ (mmol/l)</th>
<th>log A</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.3</td>
<td>300</td>
<td>17.80</td>
</tr>
<tr>
<td>12.0</td>
<td>14</td>
<td>12.47</td>
</tr>
<tr>
<td>10.7</td>
<td>0.7</td>
<td>7.27</td>
</tr>
</tbody>
</table>

From this fitting procedure, values for $\beta$ and their uncertainties (one standard deviation) resulted. In Table 4.5 the results of the fit parameters $\beta$ at fixed values for $n$, $A$ and $\log K_d^0$ are given.
Complexation of Eu

Table 4.5 The fitted values of the free parameter $\beta$ obtained when fixing $n$, $A$ and $K^0_\infty$ in the equation 4.5. The uncertainty of the experimental values of $K_i$ was taken into account using the Chi-square minimisation method with instrumental weights.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$n$</th>
<th>$\log K^0_\infty$</th>
<th>$\beta$</th>
<th>$\log \beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 13.3, no Ca</td>
<td>1</td>
<td>4.2</td>
<td>$(2.1 \pm 0.2) \times 10^{22}$</td>
<td>22.3</td>
</tr>
<tr>
<td>pH 13.3, 1.8 mM Ca</td>
<td>1</td>
<td>5.3</td>
<td>$(3.2 \pm 2.5) \times 10^{21}$</td>
<td>21.5</td>
</tr>
<tr>
<td>pH 12.0, no Ca</td>
<td>1</td>
<td>5.1</td>
<td>$(1.1 \pm 0.1) \times 10^{18}$</td>
<td>18.0</td>
</tr>
<tr>
<td>pH 12.0, 1.8 mM Ca</td>
<td>1</td>
<td>5.4</td>
<td>$(0.5 \pm 1.2) \times 10^{17}$</td>
<td>16.7</td>
</tr>
<tr>
<td>pH 12.0, 10 mM Ca</td>
<td>1</td>
<td>5.4</td>
<td>$(2.2 \pm 1.1) \times 10^{17}$</td>
<td>17.3</td>
</tr>
<tr>
<td>pH 10.7, no Ca</td>
<td>1</td>
<td>4.6</td>
<td>$(3.8 \pm 2.2) \times 10^{11}$</td>
<td>11.6</td>
</tr>
<tr>
<td>pH 10.7, 1.8 mM Ca</td>
<td>1</td>
<td>5.0</td>
<td>$(1.6 \pm 2.7) \times 10^{11}$</td>
<td>11.2</td>
</tr>
<tr>
<td>pH 10.7, 10 mM Ca</td>
<td>1</td>
<td>5.1</td>
<td>$(1.0 \pm 5.0) \times 10^{12}$</td>
<td>12.0</td>
</tr>
</tbody>
</table>

The values obtained for $\log \beta$ are dependent on pH (see Equation 4.3). As shown in Table 4.5, at a given pH, $\log \beta$ values do not differ by more than approximately one order of magnitude, irrespective of the presence of Ca. This is an indication that systems without and with Ca can be described by the same complexation reaction. If 1:1:k Eu:ISA:Ca complexes were to be dominant in systems with Ca, then, it would be reasonable to assume that the stability constant of these Eu:ISA:Ca complexes would differ from the stability constant of Eu:ISA complexes. This would mean that for a given pH, the value of $\log \beta$ for a system without Ca should be different from the values of $\beta$ for the systems with Ca. However, the systems without Ca, as well as the systems with Ca have roughly the same value for $\beta$ at a given pH. This indicates that only Eu:ISA complexes are formed, as postulated before.

In their study on the Eu(III) sorption on feldspar in artificial cement pore water, Van Loon and Glaus (1998) determined $\log K = -18.6 \pm 0.2$ (equation 4.3) for $m = 3$ (equation 4.1) and $\log A = 17$ (equation 4.6), at $I = 0.3$ M. To be able to compare their value with the one of the present study, the value of $\beta/A$ was calculated:
\( \beta / A = 10^{-18.6} / (6.2 \cdot 10^{-14})^3 (10^{17}) = 1.1 \cdot 10^4 \). This value is in good agreement with the one of the present study: \( \beta / A = 3.2 \cdot 10^{21} / 10^{17.8} = 5.1 \cdot 10^3 \). In the study on the sorption of Eu(III) on calcite, Tits et al. (2000) found for the formation of 1:1 Eu:ISA complexes that \( \beta / A \) was equal to \( 3.7 \pm 1.3 \cdot 10^7 \).

As a comparison, the values of \( \log \beta \) from Tables 4.2, 4.3 and 4.5 are summarised in Table 4.6. Only small differences exist between the different fitting procedures. This also indicates that the calculated uncertainties play a relatively minor role in the determination of \( \beta \) (Table 4.5).

**Table 4.6** Comparison of the logarithm of the free parameter \( \beta \) of Tables 4.2, 4.3 and 4.5.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Table 4.2</th>
<th>Table 4.3</th>
<th>Table 4.5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n, log K^0_free</td>
<td>n, log K^0_fixed</td>
<td>n, log K^0_fixed</td>
</tr>
<tr>
<td></td>
<td>not weighted</td>
<td>not weighted</td>
<td>weighted</td>
</tr>
<tr>
<td>pH 13.3, no Ca</td>
<td>21.6</td>
<td>22.0</td>
<td>22.3</td>
</tr>
<tr>
<td>pH 13.3, 1.8 mM Ca</td>
<td>22.7</td>
<td>22.0</td>
<td>21.5</td>
</tr>
<tr>
<td>pH 12.0, no Ca</td>
<td>16.9</td>
<td>17.7</td>
<td>18.0</td>
</tr>
<tr>
<td>pH 12.0, 1.8 mM Ca</td>
<td>17.6</td>
<td>17.3</td>
<td>16.7</td>
</tr>
<tr>
<td>pH 12.0, 10 mM Ca</td>
<td>18.2</td>
<td>17.3</td>
<td>17.3</td>
</tr>
<tr>
<td>pH 10.7, no Ca</td>
<td>10.2</td>
<td>11.3</td>
<td>11.6</td>
</tr>
<tr>
<td>pH 10.7, 1.8 mM Ca</td>
<td>12.4</td>
<td>11.9</td>
<td>11.2</td>
</tr>
<tr>
<td>pH 10.7, 10 mM Ca</td>
<td>12.9</td>
<td>12.1</td>
<td>12.0</td>
</tr>
</tbody>
</table>
4.2.2.3 Determination of the reaction stoichiometry and the stability constant \( K \)

Table 4.7 summarises the experimental proton concentrations and the fitted values of \( \beta \) of the eight experiments.

Table 4.7 Experimental proton concentrations and the fitted values of \( \beta \), taken from Table 4.5 (\( I = 0.3 \) M).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>log (H') (mol/l)</th>
<th>log ( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 13.3, no Ca</td>
<td>-13.21</td>
<td>22.33</td>
</tr>
<tr>
<td>pH 13.3, 1.8 mM Ca</td>
<td>-13.21</td>
<td>21.51</td>
</tr>
<tr>
<td>pH 12.0, no Ca</td>
<td>-11.88</td>
<td>18.03</td>
</tr>
<tr>
<td>pH 12.0, 1.8 mM Ca</td>
<td>-11.88</td>
<td>16.71</td>
</tr>
<tr>
<td>pH 12.0, 10 mM Ca</td>
<td>-11.88</td>
<td>17.33</td>
</tr>
<tr>
<td>pH 10.7, 1.8 mM Ca</td>
<td>-10.58</td>
<td>11.58</td>
</tr>
<tr>
<td>pH 10.7, 10 mM Ca</td>
<td>-10.58</td>
<td>11.21</td>
</tr>
<tr>
<td>pH 10.7, no Ca</td>
<td>-10.58</td>
<td>12.00</td>
</tr>
</tbody>
</table>

The complexation constant \( K \) and the number of protons involved in the complexation reaction were simultaneously determined. Based on equation 4.3, a value for \( m \) and log \( K \) results from the relationship:

\[
\log \beta = \log K - m \cdot \log(H) \tag{4.7}
\]

Plotting the logarithms of \( \beta \), versus the logarithms of the experimental proton concentrations, as shown in Figure 4.11, gives the following results: \( m = 3.96 \pm 0.21 \) and log \( K = -30.1 \pm 2.5 \) at \( I = 0.3 \) M. Because \( m \) must be integer, \( m \) was fixed at 4 and the resulted value for the complexation constant is log \( K = -30.6 \pm 0.2 \).
Note that the combination of the equations 4.3 and 4.6 leads to

\[
\frac{\beta}{A} = \frac{K \cdot (H^+)^m}{(H^+)^m \cdot \beta_{\text{Eu(OH)_{m+1}}} \cdot K_w^m}
\] (4.8)

For \( m = 4 \), the parameter \( \beta/A \) in equation 4.8 becomes constant and independent of pH, which is in agreement with the values of \( \beta/A \) in Table 4.3. However, the existence of Eu(OH)\(_4^+\) species is controversial. On the assumption that Eu(OH)\(_4^-\) species do not exist and that Eu(OH)\(_3^0\) species dominate under alkaline conditions, \( \beta/A \) is pH independent for \( m = 3 \).

![Figure 4.11](image)

**Figure 4.11** Determination of the number of protons involved in the complexation reaction and of the stability constant \( K \) by plotting the logarithm of the fit parameter \( \beta \) as a function of the experimental pH. (The uncertainty of log \( \beta \) was not taken into account.)

All the experimental results can be described by one single equation. The value obtained for log \( K \) is valid for the experiments without Ca, as well as for the experiments with Ca. As discussed before, this precludes the existence of Eu:ISA:Ca complexes.
4.2.3 Conclusions

Batch sorption experiments were performed in the pH range from 10.7 to 13.3 at different Ca concentrations. Analysis of the different data sets demonstrated that in systems without Ca, as well as in systems with Ca, one Eu ion was coordinated by one ISA ligand. Moreover, no indications were found that Ca participates in the complexes because for a given pH, the apparent stability constant $\beta$ was approximately the same for systems with and without Ca. Therefore, it was postulated that 1:1 Eu:ISA complexes are dominant in the pH range from 10.7 to 13.3, irrespective of the presence of Ca.

Further, it was demonstrated that four protons are involved in the formation of 1:1 Eu:ISA complexes and that the logarithm of the stability constant $K$ equaled $-30.6 \pm 0.2$ at $I = 0.3$ M.

Note that the involvement of four protons is only valid if Eu(OH)$_4$ species are assumed to be the dominant hydrolysis species at alkaline pH. Therefore, the stability constant $K$ can only be used in calculations taking the hydrolysis constant of Eu(OH)$_3$ into account.
Seite Leer / Blank leaf
5 Application

5.1 Introduction

It is the purpose of this chapter to show under which conditions the speciation of Th and Eu is significantly influenced by the presence of ISA. The following speciation calculations are in particular applied to a repository for L/ILW by taking into account the specific boundary conditions for such engineered system. It is important to note that the calculated concentrations of Th and Eu in solution do not represent the expected concentrations in the repository. In the repository, the concentrations of radionuclides in solution are limited, among other parameters, by their inventory and, therefore, will not be as high as the concentrations predicted by the speciation calculations. In the speciation calculations no limit for Th or Eu in solution was included. An unlimited source of Th and Eu was used, because the radionuclide inventory in the planned repository is not exactly known at the moment. The sometimes unrealistic concentrations of Th and Eu in solution obtained in the calculations at the higher ISA concentrations make that these speciation calculations may not be considered as a safety analysis. A detailed safety assessment study is beyond the scope of this work.

In a L/ILW repository, part of the total Th and Eu inventory is dissolved in the cement pore water. This is the mobile component which can be transported with the groundwater into the geo- and biosphere. The other immobile part may be sorbed on cement and/or may be present as a solid phase (amorphous, crystalline, mixed solid phase,...). In the presence of ISA, aqueous Th-ISA and Eu-ISA species are formed. Consequently, the total amount of mobile radionuclide increases.
In this chapter the effect of the total concentration of ISA in cement pore water on the speciation of Th and Eu in solution is examined. As long as the concentration of radionuclide-ISA complexes is smaller than the hydrolysed radionuclide species, ISA does not influence the distribution of mobile and immobile Th and Eu. However, if at a given total ISA concentration the concentration of complexed ISA species is substantially higher than the hydrolysed radionuclide species, the presence of ISA may enhance the mobility of the Th and Eu inventory in the repository.

5.2 Speciation calculations

The speciation calculations were performed with the program MEDUSA (Puigdomenech 1983) described in section 2.2.4. Ionic strength and temperature were fixed at 0.3 M and 25°C, respectively.

5.2.1 Concentration of total ISA

An important aspect of the speciation calculations is the concentration of ISA in the cement pore water in a L/ILW repository. The amount of ISA formed in the repository is limited by two factors: (i) the amount of cellulose present in the waste, i.e. the cellulose loading, and (ii) the extent of degradation of cellulose. Based on the cement porosity, it is possible to estimate the amount of cement pore water and, consequently, the total concentration of ISA in the pore water. Finally, the sorption of ISA on cement and the solubility of Ca(ISA), are the two processes controlling the equilibrium concentration of ISA in the cement pore water. Van Loon and Glaus (1998) calculated that for a cellulose loading of 3 - 6 %, the concentration of ISA in cement pore water is reduced by sorption on cement to about $10^4$ - $10^5$ M. Their calculations were based on the studies of ISA sorption on cement (Van Loon et al. 1997) and the kinetics of cellulose degradation (Van Loon et al. 1999a). In the latter study, they found that the concentration of ISA in
solution reaches a maximum after 13 months and thereafter remains constant. They estimated that in a first stage (first $10^4 - 10^5$ years), about 3% of cellulose will degrade (Van Loon and Glaus, 1998). However, Pavasars (1999) estimated that already after 100 years, all cellulose will have degraded.

In the following, the concentration of ISA in solution was not fixed, but varied between two boundary values. The maximum concentration of ISA was set equal to the solubility limit of Ca(ISA)$_2$, at pH 13.3, i.e. approximately $10^{-1}$ M (75 mM ISA according to Figure 2.6, 44 mM ISA according to Van Loon et al. 1999b). The reasonable value of $10^{-6}$ M ISA was chosen for the lower limit.

5.2.2 Concentration of total Ca

In a cementitious repository for LILW, the total concentration of Ca in solution is controlled by the solubility of Ca(OH)$_2$. During the first stage of cement degradation, the pH is 13.3 and the total concentration of Ca in solution equals 1.8 mM (see General Introduction). In the following speciation calculations, the solution is in contact with Ca(OH)$_2$, acting as the Ca source of the system.

5.2.3 Concentration of total Th(IV)

Under the repository conditions, Th(OH)$_4^{2-}$ is the dominating Th species. Its concentration in cement pore water is between $10^6$ and $3\cdot10^{-7}$ M (Berner 1999). In the following calculations, microcrystalline ThO$_2$ was chosen as solid phase, maintaining a constant concentration of $2.9\cdot10^{-7}$ M Th(OH)$_4^{2-}$ in solution. The sorption of Th on cement was not explicitly taken into account.
5.2.4 Concentration of total Eu(III)

The present work is based on the assumption that Eu(OH)$_7$ species exist. At highly alkaline pH, Eu(OH)$_4$ becomes the dominating Eu species. The concentration of Eu in artificial cement pore water is measured to be $2 \times 10^{-9}$ M (Ochs et al. 1998, Tits et al. 2000). For simplicity, the Eu in the solid phase (i.e. sorbed and precipitated) was assumed to be present as Eu(OH)$_3$. In the supposition that the hydrolysis constants are correct, the solubility product of Eu(OH)$_3$ as given by Baes and Mesmer (1976) overestimated the total Eu concentration in solution at alkaline pH. Therefore, for the speciation calculations, the solubility product of Eu(OH)$_3$ was adjusted to give an Eu(OH)$_7$ concentration of $2 \times 10^{-9}$ M at pH 13.3.

5.2.5 pH

The speciation was calculated in the pH range from 12.5 to 14. This range covers the pH during the first and second degradation state of cement (see General Introduction). For the speciation calculations performed as a function of the total ISA concentration in solution, the pH is fixed at 13.3, i.e. the pH of the repository during the first stage of cement degradation.

5.2.6 Complexation constants

In the present work, the complexation constants for Th with ISA (K and $K^{Ca}$) and Eu with ISA (K) were determined. The constants for the complexation reactions with the stoichiometry being integer are used in the following speciation calculations. The effect of the uncertainty of these constants on the Th and Eu speciation is demonstrated. All the thermodynamic constants used in the speciation calculations at $I = 0.3$ M are shown in Table 5.1. The constants were recalculated with the Davies equation (equation 2.2) to an ionic strength of 0.3 M.
Table 5.1  Overview of the equilibrium reactions and their equilibrium constants at $I = 0.3 \, M$ ($\log K^{n,1}$).

<table>
<thead>
<tr>
<th>Equilibrium reaction</th>
<th>$\log K^{n,1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ca}^{2+} + \text{ISA}^- \rightleftharpoons \text{CaISA}^+$</td>
<td>1.16</td>
<td>this work</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{ISA}^- \rightleftharpoons \text{CaISA}^0 + \text{H}^+$</td>
<td>-10.94</td>
<td>this work</td>
</tr>
<tr>
<td>$\text{Ca}^2\text{ISA}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{ISA}^-$</td>
<td>-5.69</td>
<td>this work</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CaOH}^+ + \text{H}^+$</td>
<td>-13.05</td>
<td>Nordstrom et al. (1990)</td>
</tr>
<tr>
<td>$\text{Ca(OH)}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$</td>
<td>-4.38</td>
<td>Baes and Mesmer (1976)</td>
</tr>
<tr>
<td>$\text{Th}^{4+} + \text{ISA}^- \rightleftharpoons \text{ThISA}^- + 4\text{H}^+$</td>
<td>-10.1</td>
<td>this work</td>
</tr>
<tr>
<td>$\text{Th}^{4+} + 2\text{ISA}^- + \text{Ca}^{2+} \rightleftharpoons \text{ThISA}_2\text{Ca}^0 + 4\text{H}^+$</td>
<td>-3.6</td>
<td>this work</td>
</tr>
<tr>
<td>$\text{Th}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{ThOH}^{3+} + \text{H}^+$</td>
<td>-3.96</td>
<td>Östhols (1995)</td>
</tr>
<tr>
<td>$\text{Th}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Th(OH)}_3^+ + 3\text{H}^+$</td>
<td>-10.69</td>
<td>Östhols (1995)</td>
</tr>
<tr>
<td>$\text{Th}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Th(OH)}_4^0 + 4\text{H}^+$</td>
<td>-15.48</td>
<td>Östhols (1995)</td>
</tr>
<tr>
<td>$\text{ThO}_2(s) + 4\text{H}^+ \rightleftharpoons \text{Th}^{4+} + 2\text{H}_2\text{O}$</td>
<td>8.92</td>
<td>Östhols et al. (1994)</td>
</tr>
<tr>
<td>$\text{Eu}^{3+} + \text{ISA}^- \rightleftharpoons \text{EuISA}^2^- + 4\text{H}^+$</td>
<td>-30.6</td>
<td>this work</td>
</tr>
<tr>
<td>$\text{Eu}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{EuOH}^{2+} + \text{H}^+$</td>
<td>-8.44</td>
<td>Haas et al. (1995)</td>
</tr>
<tr>
<td>$\text{Eu}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Eu(OH)}_2^+ + 2\text{H}^+$</td>
<td>-17.19</td>
<td>Haas et al. (1995)</td>
</tr>
<tr>
<td>$\text{Eu}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Eu(OH)}_3^0 + 3\text{H}^+$</td>
<td>-26.23</td>
<td>Haas et al. (1995)</td>
</tr>
<tr>
<td>$\text{Eu}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Eu(OH)}_4^- + 4\text{H}^+$</td>
<td>-35.07</td>
<td>Haas et al. (1995)</td>
</tr>
<tr>
<td>$\text{Eu(OH)}_2(s) + 3\text{H}^+ \rightleftharpoons \text{Eu}^{3+} + 3\text{H}_2\text{O}$</td>
<td>13.24</td>
<td>adjusted value (see text)</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$</td>
<td>-13.73</td>
<td>Nordstrom et al. (1990)</td>
</tr>
</tbody>
</table>
5.3 Results and discussion

5.3.1 Speciation of Th(IV)

Figure 5.1 shows the distribution of the Th-ISA species as a function of pH in the presence of the maximum ISA concentration: \( (ISA) = 10^{-1} \) M. Over the whole pH range, the Th-ISA species are dominant over \( \text{Th(OH)}_4^{2+} \).

Figure 5.2 shows the distribution of the Th-ISA species as a function of pH in the presence of the expected concentration of ISA (based on Van Loon and Glaus (1998)): \( (ISA) = 10^{-1.5} \) M. The total concentration of Th-ISA species is slightly larger than the concentration of \( \text{Th(OH)}_4^{2+} \).

Figure 5.3 describes the distribution of the species as a function of the total ISA concentration at pH 13.3. At total ISA concentration higher than \( 4.3 \times 10^{-6} \) M the dominant Th species in solution is Th-ISA species. This means that already at low ISA concentrations, an effect of ISA on the distribution of Th can be expected. In spite of the large concentration of Ca in the system, the excess of Ca \( (\approx 2 \times 10^{-3} \) M) causes no competition with Th for ISA. The concentration of Th-ISA complexes remains as high as in a solution without Ca (results not shown).

The uncertainty given in section 3.3.3.3 for the complexation constants is small, i.e. \( \log K, K^C_{\text{a}} \pm 0.2 \), and is possibly underestimated. In order to be on the safe side, it was decided to study the effect of uncertainties on the complexation constants by assigning an uncertainty of 0.5 log-units to the complexation constants. The results are shown in Figure 5.4, where the upper limits of the complexation constants (\( \log K = -9.6 \) and \( \log K^C_{\text{a}} = -3.1 \)) were compared with the lower limits (\( \log K = -10.6 \) and \( \log K^C_{\text{a}} = -4.1 \)). At the upper and lower limits, the ratio \( \text{Th(OH)}_4^{2+} \) over Th-ISA species equals one at \( (ISA) = 1.5 \times 10^{-6} \) M and \( 1.5 \times 10^{-4} \) M, respectively.
Figure 5.1  Distribution of the Th species in solution as a function of pH in the presence of 10^{-1} M ISA. (A discussion on the high total Th concentrations is given in the Introduction.)

Figure 5.2  Distribution of the Th species in solution as a function of pH in the presence of 10^{-2.5} M ISA.
Figure 5.3  Distribution of the Th species in solution as a function of total ISA in solution at pH 13.3. (A discussion on the high total Th concentrations is given in the Introduction.)

Figure 5.4  Variation of the total concentration of Th-ISA species in solution between the upper limit (log $K = -9.6$ and log $K^{Ca} = -3.1$) and the lower limit (log $K = -10.6$ and log $K^{Ca} = -4.1$) at pH 13.3. The limits are given by the dashed lines, the full line represents log $K = -10.1$ and log $K^{Ca} = -3.6$. (A discussion on the high total Th concentrations is given in the Introduction.)
Comparing the batch sorption experiment at pH 13.3 in the presence of Ca (Figure 3.12) with the speciation calculations at pH 13.3 (Figure 5.3) shows a discrepancy. In the batch sorption experiment, the fitting curve shows an effect of ISA on the distribution coefficient $K_d$ only at approximately $(\text{ISA})_{\text{tot}} \geq 8 \cdot 10^{-5}$ M, whereas the speciation calculation indicate that already at $(\text{ISA})_{\text{tot}} = 4.3 \cdot 10^{-6}$ M the Th-ISA species start dominating over $\text{Th(OH)}_4$. A concentration of Th-ISA species equal to the concentration of $\text{Th(OH)}_4$ in the speciation calculation results in $K_d = K_0^0/2$ in the batch sorption experiment. The reason for this difference is that the fitting curve describes the behaviour of the $\text{Th(ISA)}_2\text{Ca}$ complexes only, based on the initial assumption that $\text{Th(ISA)}_2\text{Ca}$ complexes dominate over the $\text{ThISA}$ complexes in the presence of Ca. The fitting curves based on the determined values of $K$ (equation 5.1) and $K^0$ (equation 5.2) separately,

$$\log K_d = \log K_0^0 - \log \left(1 + \frac{K}{(\text{H})^4 \cdot A} (\text{ISA}_{\text{tot}})\right) \quad (5.1)$$

$$\log K_d = \log K_0^0 - \log \left(1 + \frac{K^0 \cdot (\text{Ca})}{(\text{H})^4 \cdot A} (\text{ISA})^2\right) \quad (5.2)$$

and the fitting curve calculated with $K$ and $K^0$ (equation 5.3)

$$\log K_d = \log K_0^0 - \log \left(1 + \frac{K}{(\text{H})^4 \cdot A} (\text{ISA}_{\text{tot}})^2 + \frac{K^0 \cdot (\text{Ca})}{(\text{H})^4 \cdot A} (\text{ISA})^2\right) \quad (5.3)$$

are compared in Figure 5.5. The experimental data follow the curve based on $K^0$ rather than the curve based on $K$ and $K^0$. The experimental data confirm the assumption that $\text{Th(ISA)}_2\text{Ca}$ complexes dominate in the presence of Ca. The model combining $\text{ThISA}$ and $\text{Th(ISA)}_2\text{Ca}$ complexes as given in Figure 5.3 or by the curve based on $K$ and $K^0$ in Figure 5.5, apparently overestimate the effect of $\text{ThISA}$ complexes in the presence of Ca. Consequently, the critical ISA concentration in Figure 5.3 at which the concentration of $\text{ThISA}$ complexes equals the concentration of $\text{Th(OH)}_4$, might be overestimated. However, in the absence of Ca, the complexation constant $K$ describes well the experimental results at pH 13.3. This discrepancy is an indication that the model postulating the existence of $\text{ThISA}$ and $\text{Th(ISA)}_2\text{Ca}$ complexes does not perfectly reflect
the Th species actually present in the systems under consideration. However, this simple model is able to describe the experiments in the pH range from 10.7 to 13.3 well and, therefore, considered as a good first attempt in describing the data.

As a comparison, the distribution of the ThISA and ThISA, Ca complexes as a function of the total ISA concentration was calculated for the other two pH's in the batch sorption study, i.e. pH 10.7 and 12.0. In the ISA range from $2.5 \times 10^{-7}$ M to $1.6 \times 10^{-5}$ M, the concentration of ThISA complexes is larger than the concentration of (ThISA),Ca complexes at both pH's (results not shown). Figure 5.6 shows the experimental data at pH 12.0 in the presence of 0.7 mM Ca fitted by the determined values of $K$ and/or $K_{Co}$. It demonstrates that the assumption made earlier for the determination of $\beta_2/A$ (see section 3.3.3.1), i.e. that the ThISA,Ca complexes are dominant, was valid.

---

**Figure 5.5** Influence of ISA on the sorption of Th on an ion exchange resin at pH 13.3 in the presence of 0.35 mM Ca. The three lines represent the fitting curves based on equation 5.1 ($K$), equation 5.2 ($K_{Ca}$) and equation 5.3 ($K + K_{Ca}$).
Finally, the solubility data for Th in the presence of Ca and ISA (see Table C4 in Appendix C) are compared with the calculations based on K and K\textsuperscript{Ca}. The results are given in Table 5.2.

The values for K and K\textsuperscript{Ca} are determined from systems with small Th concentrations (\(\approx 10^{-13} \text{ M}\)), whereas in the systems given in Table C4 the presence of polynuclear Th-ISA complexes cannot be precluded, in view of the high Th concentrations. This may explain the differences between measured and calculated concentrations. Moreover, a closer look at the data shows that if the initial total Ca concentration is higher than the initial total Th concentration, the calculated Th concentrations are always overestimated. Moreover, in these samples a precipitate was detected. This might be explained by the formation of a new solid phase containing Th and Ca.
Table 5.2 Comparison between the measured solubility data of Th in the presence of ISA (and Ca) and the calculated concentration of total Th in solution, based on the values determined for K and Kc.

<table>
<thead>
<tr>
<th>sample preparation</th>
<th>pH</th>
<th>measured</th>
<th>calculated</th>
<th>measured</th>
<th>calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISA (mM) Ca(NO₃)₂ (mM) Th(NO₃)₄ (mM)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 0 10</td>
<td>13.3</td>
<td>6.6</td>
<td>3.5</td>
<td>3.9 x 10⁻³</td>
<td>0</td>
</tr>
<tr>
<td>100 5 2.5</td>
<td>13.3</td>
<td>0.8</td>
<td>2.5</td>
<td>0.9</td>
<td>2.5</td>
</tr>
<tr>
<td>100 0 10</td>
<td>12.8</td>
<td>10.1</td>
<td>6.9</td>
<td>0.02</td>
<td>0</td>
</tr>
<tr>
<td>100 5 2.5</td>
<td>12.8</td>
<td>1.2</td>
<td>2.5</td>
<td>1.4</td>
<td>2.5</td>
</tr>
<tr>
<td>100 5 10</td>
<td>12.8</td>
<td>10.1</td>
<td>10.0</td>
<td>5.0</td>
<td>5</td>
</tr>
<tr>
<td>100 0 5</td>
<td>10.7</td>
<td>5.2</td>
<td>5.0</td>
<td>0.04</td>
<td>0</td>
</tr>
<tr>
<td>100 20 10</td>
<td>10.7</td>
<td>4.3</td>
<td>10.0</td>
<td>8.9</td>
<td>10</td>
</tr>
</tbody>
</table>

5.3.2 Speciation of Eu(III)

Figure 5.7 shows the distribution of the species as a function of pH at (ISA) = 10⁻¹ M. Under the given chemical conditions, the concentration of Eu(OH)⁷ is much smaller than the concentration of EuISA complexes.

Figure 5.8 shows the distribution of the Eu-ISA species as a function of pH in the presence of the expected concentration of ISA (based on Van Loon and Glaus (1998)): (ISA) = 10⁻⁴ M. The total concentration of Eu-ISA species is slightly higher than the Eu(OH)⁷ concentration.

As shown in Figure 5.9, at 1 x 10⁻⁴ M ISA the concentration of Eu-ISA species equals the concentration of Eu(OH)⁷ at pH 13.3. This means that if the total ISA concentration in the cement pore water is well below 1 x 10⁻⁴ M, there is no effect of ISA on the distribution of the Eu species. However, if the ISA concentration is close to or beyond this limit, more Eu goes into solution than in the absence of ISA.
Figure 5.7  Distribution of the Eu species in solution as a function of pH in the presence of $10^3$ M ISA. (A discussion on the high total Eu concentrations is given in the Introduction.)

Figure 5.8  Distribution of the Eu species in solution as a function of pH in the presence of $10^{-5}$ M ISA.
The effect of the uncertainty of the complexation constants on the speciation was studied. The upper limits of the complexation constants ($\log K = -30.1$) were compared with the lower limits ($\log K = -31.1$). At the upper and lower limits, the ratio Eu(OH)$_4^-$ over EuISA complexes equals one at (ISA) = 3.4 $\times$ 10$^{-6}$ M and 3.4 $\times$ 10$^{-5}$ M, respectively.
6

General conclusions

This work is the first detailed study on the complexation of radionuclides with ISA under alkaline conditions (pH 10.7 - 13.3) and in well defined systems. Based on the measured complexation constants for Eu and Th by ISA, it is concluded that ISA forms stable complexes with these tri- and tetravalent radionuclides. Its complexation behaviour has to be taken into account in safety assessment studies.

An important aspect of the present work is the formation of ternary Th(IV)-ISA-Ca complexes in the presence of Ca, whereas for the complexation of the trivalent Eu by ISA such complexes are absent. Further research is necessary to determine whether other tetravalent actinides such as U(IV), Np(IV) or Pu(IV) also form ternary complexes with ISA and Ca, and whether trivalent radionuclides generally do not form such complexes.

The comparison of the Th batch sorption experiments with the theoretical calculations based on the measured values of $K_1$ and $K_3$ shows a small difference for the systems with Ca. This is an indication that the postulated model of ThISA and Th(ISA)$_2$Ca complexes might be too simple. Other complexes might be present in solution. Because the batch sorption method produced in the present work data sets with large uncertainties, only simple models could be postulated. Techniques with smaller uncertainties must be applied to extend the model with more species. However, this simple model, as well as the model for Eu complexation are able to describe the experimental data at alkaline pH (pH 10.7 - 13.3).
A Chi-square minimisation method

The aim of the fitting procedure is to find those values of the parameters which best describe the data. The standard way of defining the best fit is to choose the parameters so that the sum of the squares of the deviations of the theoretical curve from the experimental data points

$$\chi^2 = \frac{1}{n^{\text{eff}} - p} \sum w_i [Y_i^{\text{meas}} - Y_i^{\text{model}}]^2$$  \hspace{1cm} (A.1)

is at its minimum. $Y_i^{\text{meas}}$ are the measured values of the dependent (output) variable, $Y_i^{\text{model}}$ are the values calculated according to the theoretical model. $i = 1, 2, ..., n^{\text{eff}}$ with $n^{\text{eff}}$ the total number of experimental data points used in the fitting, and $p$ is the total number of adjustable parameters used in the fitting (the difference between $n^{\text{eff}}$ and $p$ is usually referred to as the number of degrees of freedom). The quantity $w_i$ represent the weight of each experimental data point. Two different weighting methods were used in the present work:

- no weight: $w_i = 1$,
- instrumental weight: $w_i = 1/u_i^2$, where $u_i$ is the standard uncertainty of the experimental data point, calculated according to equation B.1 in Appendix B.
B Calculating the uncertainty of \( K_d \)

B.1 Uncertainty estimation process

Unfortunately, there is no simple and widely applicable method for determining the reliability of data with absolute certainty. It often requires as much effort to estimate the quality of experimental results as it requires to collect them.

The estimation of the uncertainty of \( K_d \) is calculated by following the general rules for evaluation and expression of uncertainty as described by the Eurachem Working Group (1995). The concept for the estimation of this uncertainty is described in the following and valid for the batch sorption experiments with Th(IV) as well as with Eu(III), unless mentioned differently. First, the uncertainty sources involved in the determination of \( K_d \) are identified. For a batch sorption experiment these sources are pipetting, weighting, radiochemical measurement. Then, these sources are quantified and expressed as standard deviations (standard uncertainties, notation “u”). According to the error propagation rules, these standard deviations are combined to determine the uncertainty of \( K_d \). Finally, the sensitivity of the uncertainty of \( K_d \) for changes in the uncertainty of its components is evaluated.

In this estimation process, the rectangular probability distribution is used as an important tool in the assessment of systematic uncertainties. Moreover, the combination of statistical and systematical uncertainties by combining the normal and the rectangular distributions (Dietrich 1991) is an important characteristic.

The definition of \( K_d \) is given by equation 3.31 (section 3.3.2.1.). To calculate the uncertainty of \( K_d \), first all the uncertainty sources need to be identified. For this purpose, each parameter of equation 3.31 is resolved into measurable components. \( K_d \) is then defined as:

\[
K_d = \frac{V_1 \cdot V_3 \cdot N_{\text{sol}}}{m \cdot V_2 \cdot N_1} - \frac{V_4 \cdot V_3 \cdot N_{\text{sol}}}{m \cdot V_4 \cdot N_2}\]  

(B.1)

with \( V_1 \): volume (ml) of the solution in equilibrium with the solid phase,
\[ V_2: \text{ weighted aliquot (mg) of the stock solution used for radiochemical isotope analysis to determine the activity of the radionuclide added to the system,} \]

\[ V_3, V_4: \text{ aliquot (ml) of the equilibrium solution used for radiochemical isotope analysis to determine the activity of the radionuclide in the equilibrium solution and sorbed on the tube wall, respectively,} \]

\[ V_5: \text{ volume (ml) of a 2 M HNO}_3\text{ solution added to the emptied tubes,} \]

\[ m: \text{ mass of the solid phase (g),} \]

\[ N_i^1: \text{ net count rate (cpm) of isotope in } V_i, V_3 \text{ and } V_4 \text{ with } i = \text{init, sol or wall,} \]

In a following step, the standard uncertainty of each component of equation B.1 is quantified.

- In Table B.1, the standard uncertainties of \( V_1, V_2, \ldots, V_5 \) and \( m \) are given.

**Table B.1 Estimation of the standard uncertainties of \( V_1, V_2, V_3, V_4, V_5 \) and \( m \).**

<table>
<thead>
<tr>
<th>parameter</th>
<th>standard uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_1 )</td>
<td>0.024 ml</td>
</tr>
<tr>
<td>( V_2, m )</td>
<td>0.152 mg</td>
</tr>
<tr>
<td>( V_3, V_4, V_5 )</td>
<td>0.021 ml</td>
</tr>
</tbody>
</table>

The uncertainty associated with pipetting \( (V_1, V_3, V_4 \text{ and } V_5) \) arises from three components (Eurachem 1995):

1. The uncertainty in the internal volume of the pipette.
2. Variation in filling the pipette to the mark.
3. The pipette and solution temperatures differing from the calibrated temperature.
The uncertainty associated with weighting \((V_2\) and \(m\)) arises from the reproducibility of weightings and the calibration accuracy of the balance.

- The net count rate \(N_i\) (with \(i = \text{init}, \text{sol}, \text{wall}\)) is defined as the difference of the total count rate \(N_i\) and the background count rate \(N_0\):

\[
N_i = N_i - N_0 \quad \text{(B.2)}
\]

In general, the statistic nature of radioactive decay follows the Poisson distribution (Brandt, 1976). Therefore, the uncertainty of \(N_i\) can be written as:

\[
u(N_i) = \sqrt{\frac{N_i}{T_i} + \frac{N_0}{T_0}} \quad \text{(B.3)}
\]

with \(T_i\) and \(T_0\) the counting times of the total count rate and the background count rate in minutes, respectively.

It was observed that the count rate of the background varied during the measurement of series of samples and that this variation was insufficiently described by the Poisson distribution. For the batch sorption experiments with Th, knowledge on the variation of the background was nearly absent. Therefore, a correction factor \(f_0\) for the parameter \(N_0\) was inserted in equation B.2:

\[
N_i = N_i \cdot N_0 \cdot f_0 \quad \text{(B.4)}
\]

Then, the uncertainty of \(N_i\) becomes:

\[
u(N_i) = \sqrt{\frac{N_i}{T_i} + \left(\frac{N_0}{T_0}\right)^2 \cdot u(f_0)^2} \quad \text{(B.5)}
\]

The correction factor was set equal to one, because the systematical error could not be exactly quantified. For its uncertainty, a reasonable, but conservative value based on lower and upper limits of the variation of \(N_0\) was chosen: \(u(f_0) = 0.23\).
In the batch sorption experiments with Eu, the background was controlled during the measurement of series of samples. For \( n \) repeated measurements of the background \((x_i)\), the standard uncertainty of \( N_0 \) is defined as:

\[
s(N_0) = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \tag{B.6}
\]

with \( \bar{x} \) the average of \( x_i \) and \( n \geq 2 \).

The uncertainty of \( N_s \), then, equaled:

\[
u(N_s) = \sqrt{\frac{N_s}{T_s} + s(N_0)^2} \tag{B.7}
\]

Finally, after having quantified all uncertainty sources, the combined uncertainty of \( K_d \) is determined. For this purpose, the partial differentials of \( K_d(V_1, V_2, V_3, V_4, V_5, m, N_1^{\text{init}}, N_2^{\text{sol}}, N_2^{\text{wall}}) \) are calculated with respect to \( V_1, V_2, V_3, V_4, V_5, m, N_1^{\text{init}}, N_2^{\text{sol}} \) and \( N_2^{\text{wall}} \). The combined uncertainty of \( K_d \), \( u_c(K_d) \), is then given by:

\[
u_c(K_d) = \sqrt{\left(\frac{\delta K_d}{\delta V_1}\right)^2 \cdot (u(V_1))^2 + \left(\frac{\delta K_d}{\delta V_2}\right)^2 \cdot (u(V_2))^2 + \ldots} \tag{B.8}
\]

As an example, this uncertainty estimation process is applied to two batch sorption experiments with Th, performed at pH 13.3 and pH 10.7 in the absence of Ca.

In the Figures B.1 and B.2, the combined uncertainty of \( K_d \) is represented by the error bars. The experimental data are given by the open points.

In Figure B.1, \( u_c(K_d) \) is small over the whole ISA concentration range, whereas in Figure B.2, at lower ISA concentrations, the combined uncertainty of \( K_d \) becomes larger. Because \( K_d \) is plotted on a logarithmic scale, the error bars are asymmetrical and the lower part of \( u_c(K_d) \) crosses the X-axis if \( u_c(K_d) > K_d \). Therefore, only the upper part of \( u_c(K_d) \) is given in Figure B.2. This phenomenon is discussed further on.
Figure B.1 Effect of ISA on the sorption of Th on a cation exchange resin at pH 13.3. The experimental data points (open points) are given together with their calculated standard uncertainty.

Figure B.2 Effect of ISA on the sorption of Th on feldspar at pH 10.7. The experimental data points (open points) are given together with their calculated standard uncertainty. Only the upper part of the error bars is shown.
The sensitivity of \( u_i(K_d) \) for changes in the estimated standard uncertainty \( u(f_0) \) was tested for the experiments with Th. The extreme case with a 100% fluctuation of \( N_0 \), i.e. \( N_0 \pm 100\% \cdot N_0 \) or \( u(f_0) = 0.58 \) had no significant influence on the combined standard uncertainty of \( K_d \). The reason is that the most dominant source of uncertainty in the determination of \( u_i(K_d) \) is \( N_{\text{vol}} \).

### B.2 The assignment of an uncertainty to the mean value of \( K_d \)

After having calculated for each data point a combined standard uncertainty of \( K_d \), the next step is to provide for each ligand concentration one mean value for \( K_d \) and to assign an uncertainty to it.

The uncertainty of \( K_d \) of each individual data point was calculated according to the uncertainty estimation process described in the former paragraph. Comparing this uncertainty with the scatter of the experimental data points, gives rise to two scenarios:

1. the spread of the experimental \( K_d \) values at a given ligand concentration, is larger than the calculated uncertainty of each \( K_d \) value, i.e. the uncertainty ranges do not overlap (Figure B.1), and
2. the calculated uncertainty of each \( K_d \) value at a given ligand concentration is larger than the spread of the experimental \( K_d \) values (Figure B.2 at lower ligand concentrations).

In the first scenario, it seems that the calculated uncertainty \( u_i(K_d) \) is too optimistic and does not sufficiently take into account the scatter of the data points. This can mean that one or more sources of uncertainty of \( K_d \) were not taken into account.

In the second scenario, the calculated uncertainty \( u_i(K_d) \) seems to overestimate the "true" uncertainty. Probably one or more sources of uncertainty are overestimated in the uncertainty estimation process. However, applying the same calculation procedure at the higher ligand concentration of the same experiment, gives a totally different result (Figure B.2).

It is not possible to have exact knowledge on how much each scenario over- and underestimates the "true" uncertainty of \( K_d \). Therefore, at each concentration the
Uncertainty for the average of the experimental data points is calculated by taking into account the spread of the data points around the mean as well as the calculated uncertainties of the data points. For this purpose, the formula used in the compilation of the NEA Thermochemical Data Base (Grenthe et al. 1992) for two independent and discrepant data was slightly modified for the situation with more than two data. The uncertainty \( u_X \) assigned to the mean \( \bar{X} \) covers the range of expectation of all the data \( X_1, X_2, \ldots \) as shown in equation B.1:

\[
    u_X = |X_i^{\text{max}} - \bar{X}| + u_i^{\text{max}}
\]  

(B.1)

where \( i = 1, 2, \ldots, n \) with \( n \) the number of data points, \( X_i^{\text{max}} \) the maximum difference between a data point and the mean \( \bar{X} \), and \( u_i^{\text{max}} \) the largest calculated uncertainty \( u(K_d) \) of the data set.

Applying equation B.1 to the data points belonging to each ligand concentration, the data given in the Figures B.1 and B.2 are replotted. The results are shown in the Figures B.3 and B.4.

![Graph](image)

**Figure B.3** The uncertainty of the averaged \( K_d \) (\( u_X \)) calculated by combining the spread of the data points around the mean and the calculated individual standard uncertainties of Figure B.1.
Figure B.4 The uncertainty of the averaged $K_d$ ($u_K$) calculated by combining the spread of the data points around the mean and the calculated individual standard uncertainties of Figure B.2. Only the upper part of the error bars is shown.

As already mentioned, the error bars become asymmetrical on the logarithmic scale. Because the error bars of the data points in Figure B.4 at [ISA] > $10^4$ M cross the X axis if $u_K(K_d) > K_d$, the lower part of the error bar is omitted. This asymmetrical error bar means that the distribution of $K_d$ is symmetrical, e.g. $K_d = 1000 \pm 500$. However, negative values of $K_d$ as suggested by the (omitted) error bars in Figure 7, are from a physical point of view impossible. Experimental experience shows that $K_d$ is rather asymmetrically distributed or the error bars on a logarithmic scale are rather symmetrical, e.g. \( \log K_d = 3 \pm 0.2 \). From this point of view, a more “realistic” picture of the figures B.3 and B.4 is presented in the Figures B.5 and B.6, respectively. In these figures an asymmetrical distribution of $K_d$ is assumed (or a symmetrical distribution of $\log K_d$ !) with the lower part of the error bar equal to the upper part of the error bar as calculated in the Figures B.3 and B.4. These error bars still cover all the experimental data points.
Figure B.5 The uncertainty of $K_d$ ($u_x$) as it is expected from an experimental point of view (based on Figure B.3).

Figure B.6 The uncertainty of $K_d$ ($u_x$) as it is expected from an experimental point of view (based on Figure B.4).
Although the uncertainties as pictured in the Figures B.5 and B.6 correspond more with the experimental reality, there is no mathematical model to describe this asymmetrical distribution of $K_a$. Moreover, it is unknown how asymmetrically distributed $K_a$ exactly is. Therefore, the average values of $K_a$ and their uncertainties as shown in the Figures B.3 and B.4 were used for the determination of $\beta$ and $\beta^{(c)}$ (section 3.3.3.2).
Classical solution chemical studies performed in the present work, such as the batch sorption study and chromatographic studies only gave information about the stoichiometry of the complexes formed. Information about the detailed bonding of the ligand and the coordination geometry of the complexes formed require additional information. In the present work, the spectroscopic techniques Nuclear Magnetic Resonance (NMR) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy were used to provide experimental information on the structure of the complexes. If the metal ion of interest (Ca, Eu, Th) coordinates with a (deprotonated) hydroxyl group of the ISA ligand, it is expected to influence the magnetic field of the neighbouring protons. As a result, with the $^1$H-NMR technique a shift of the proton signals may be observed, compared with the proton signals of ISA solutions containing no metal ion. EXAFS was used as a technique to provide information on the coordination environment of Th. By comparing the EXAFS spectra of Th/ISA solutions and Th/ISA/Ca solutions, it was studied whether the presence of Ca in the coordination environment of Th could be shown.

C.1 $^1$H- and $^{13}$C-NMR of the Ca/ISA system

At alkaline pH, both CaISA$^+$ and CaISA$^0$ species are present in a Ca-ISA system (see section 2). Depending on pH, the ratio of both species changes. Speciation calculations were performed using the stability constants given in Tables 2.1 and 2.6. Based on these calculations, three solutions were prepared with different ratios of ISA$^-$, CaISA$^+$ and CaISA$^0$ (Table C1). It was tested whether differences between the $^1$H-spectra of the three solutions were present. Also $^{13}$C-NMR measurements were performed.
**Table C1**  
*Samples with ISA and Ca in NaOD/D$_2$O used for $^1$H-NMR (500 MHz) and $^{13}$C-NMR (126 MHz) measurements.*

<table>
<thead>
<tr>
<th>Sample preparation$^a$</th>
<th>pD$^b$</th>
<th>Precipitation$^c$</th>
<th>ISA$^d$</th>
<th>CaISA$^e$</th>
<th>CaISA$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mM ISA lactone/</td>
<td>10.8</td>
<td>no</td>
<td>4.1 mM</td>
<td>5.7 mM</td>
<td>0.2 mM</td>
</tr>
<tr>
<td>100 mM Ca(NO$_3$)$_2$</td>
<td></td>
<td></td>
<td>(41%)</td>
<td>(57%)</td>
<td>(2%)</td>
</tr>
<tr>
<td>10 mM ISA lactone/</td>
<td>13.3</td>
<td>yes</td>
<td>1.5 mM</td>
<td>1.1 mM</td>
<td>7.4 mM</td>
</tr>
<tr>
<td>120 mM Ca(NO$_3$)$_2$</td>
<td></td>
<td></td>
<td>(15%)</td>
<td>(11%)</td>
<td>(74%)</td>
</tr>
<tr>
<td>Ca(ISA)$_2$</td>
<td>11.4</td>
<td>yes</td>
<td>18 mM</td>
<td>2 mM</td>
<td>10$^{-3}$ mM</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(89%)</td>
<td>(10%)</td>
<td>(1%)</td>
</tr>
</tbody>
</table>

$^a$ under N$_2$ atmosphere (O$_2$, CO$_2$ < 1 ppm), $^b$ pD = pH meter reading + 0.40 (Bates 1973), $^c$ samples with precipitation were filtered (0.45 μm Nylon, Semadeni) before NMR analysis, $^d$ expected concentration of free species in solution, speciation calculation based on the Tables 2.1 and 2.6, the percentage of the total ISA concentration is given between parentheses.

Based on the water exchange rates of Ca, the ligand exchange is expected to be very fast with respect to the NMR time scale. Therefore, it is expected that only averaged signals of species being in equilibrium with each other are observed.

The comparison of the $^1$H-NMR spectra showed that the differences between the samples were rather small and not significant. Obviously, the effect of the coordination of Ca$^{2+}$ to the ligand is not strong enough to significantly change the spectral properties. The $^1$H-NMR spectra of the samples containing ISA and Ca were found to be identical with the $^1$H-NMR spectra of solutions containing only ISA, independent on pH. The $^1$H-NMR data of these spectra were identical with the data of Glaus et al. (1999) for ISA in open chain form.

No conclusions could be drawn from the $^{13}$C-NMR measurements due to the low signal to noise ratio.
C.2 $^1$H-NMR of the Eu/ISA/Ca system

The NMR spectra of a pure ISA solution and of an Eu/ISA mixture were compared. For this purpose, solutions with different Eu/ISA ratios were prepared. Also the additional effect of Ca on the magnetic environment of the protons was studied, by adding Ca to a solution of ISA and Eu. The different samples used are described in Table C2.

**Table C2** Samples with ISA, Eu (and Ca) in NaOD/D$_2$O used for $^1$H-NMR (500 MHz) measurements.

<table>
<thead>
<tr>
<th>sample preparation$^a$</th>
<th>sample analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISA (mM)</td>
<td>Eu(NO$_3$)$_3$ (mM)</td>
</tr>
<tr>
<td>100</td>
<td>/</td>
</tr>
<tr>
<td>100</td>
<td>49.9</td>
</tr>
<tr>
<td>100</td>
<td>12.2</td>
</tr>
<tr>
<td>100</td>
<td>4.0</td>
</tr>
<tr>
<td>100</td>
<td>50.6</td>
</tr>
</tbody>
</table>

$^a$ under N$_2$ atmosphere (O$_2$, CO$_2$ < 1 ppm), $^b$ samples with precipitation were centrifuged (1800g, 15 min.) before NMR analysis, $^c$ pD = pH meter reading + 0.40 (Bates 1973).

It was observed that the differences of the chemical shifts were very small, almost absent, and not sufficient to use this method for an identification of the different complexes and the free ligand. Also the system with Ca showed only a very small difference (0.04 - 0.05 ppm for all the aliphatic protons) compared to the solutions without Ca. Such very small shifts are negligible compared to the literature data (Angyal 1974, Angyal et al. 1974, Kieboom et al. 1975, Kieboom et al. 1977, Escandar et al. 1995, Frutos et al. 1999). To a certain extent this is probably due to the large excess of ligand. However, the 1/4 ratio of Eu/ISA is the maximum possible amount of Eu in solution at pH 13.3, because of the precipitation of Eu-hydroxide. At the moment, the reason for the absence of clear shifts is not understood.
C.3 $^1$H-NMR of the Th/ISA system

Different amounts of Th(NO$_3$)$_4$ were mixed with an ISA solution. The solutions studied are described in Table C3. No significant changes of the $^1$H-NMR spectra were observed, except for the sample with the highest initial Th concentration. In this sample, a new peak was observed. However, the pH of this solution had also dropped from pH 13.3 to 7.4. This pH is beyond the scope of the present work.

**Table C3** Samples with ISA and Th in NaOD/D$_2$O used for $^1$H-NMR (300 MHz) measurements.

<table>
<thead>
<tr>
<th>sample preparation$^{(a)}$</th>
<th>sample analysis$^{(b)}$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ISA (mM)</td>
<td>Th(NO$_3$)$_4$ (mM)</td>
<td>precipitation$^{(a)}$</td>
</tr>
<tr>
<td>100</td>
<td>/</td>
<td>no</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>yes</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>yes$^{(a)}$</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>no</td>
</tr>
<tr>
<td>100</td>
<td>17</td>
<td>no</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>no</td>
</tr>
</tbody>
</table>

$^{(a)}$ under N$_2$ atmosphere (O$_2$, CO$_2$ < 1 ppm), $^{(b)}$ the total ISA concentration was not determined, $^{(c)}$ samples with precipitation were centrifuged (1800g, 15 min.) before NMR analysis, $^{(d)}$ after centrifugation, the sample was filtered (0.45 μm, Nylon, Semadeni) but was still slightly turbid, $^{(e)}$ pD = pH meter reading + 0.40 (Bates 1973), $^{(f)}$ new peak at 2.4 ppm appeared in the $^1$H-NMR spectrum.

It was concluded that these preliminary studies are not very encouraging to use NMR for the determination of the coordination geometry of the complexes or of the stability constants.
C.4 EXAFS of the Th/ISA/Ca system

In the present study it was demonstrated that in solutions of Th and ISA different complexes exist, depending on whether Ca is present in the system or not. When Ca is present, Th-ISA-Ca complexes are formed, whereas in the absence of Ca, Th-ISA complexes are dominant.

Solutions with different ratios of Ca and Th in the presence of ISA were measured at pH 10.7, 12.8 and 13.3. A description of the samples is given in Table C4.

<table>
<thead>
<tr>
<th>sample preparation$^a$</th>
<th>sample analysis$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISA (mM)</td>
<td>Ca(NO$_3$)$_2$ (mM)</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>20</td>
</tr>
</tbody>
</table>

$^a$ under N$_2$ atmosphere (O$_2$, CO$_2$ < 1 ppm). $^b$ the total ISA concentration was not determined; samples were filtered (0.22 µm Acrodisc filter, Millipore). $^c$ initial calculated pH

Irrespective of the pH, the background subtracted EXAFS spectra are almost matching each other. The first coordination sphere consists of ± 10 oxygen atoms at a distance of approximately 2.45 Å. Furthermore, the spectra reveal structure beyond the first coordination shell. Preliminary data analysis suggests the presence of carbon atoms at various distances (between approximately 3 and 4 Å). These similar EXAFS spectra indicate that in the pH range from 10.7 to 13.3 the same complexes are present, which is a confirmation of the model postulated in section 3.3.
The spectra of samples with and without Ca were compared. No significant difference could be detected. However, the absence of a Ca effect does not preclude the existence of Th-ISA-Ca complexes. Probably the distance between the Ca and the Th ions is too large to detect a Ca signal or, less likely, the Ca atoms are strongly disordered and do not contribute to the EXAFS spectra.
References


References


References


Seite Leer / Blank leaf
Curriculum Vitae

1973 Born on June 1 in Leuven (Belgium).
1979 - 1985 Primary school in Vossem (Belgium).
1991 - 1996 University of Leuven (Belgium),
Master in Engineering in Environmental Technology.
1997 - 1999 PhD work at the Laboratory for Waste Management (Paul Scherrer Institute in Villigen, Switzerland) under the supervision of Prof. Dr. H. Sticher (Institute of Terrestrial Ecology, Swiss Federal Institute of Technology in Zürich, Switzerland).

Publications
• Vercammen, K., Glaus, M.A. and Van Loon, L.R. (2000): Complexation of Th(IV) and Eu(III) by α-isosaccharinic acid under alkaline conditions. (in preparation)