R-05-72

Effects of complexing compounds on sorption of metal ions to cement

Lars Lövgren, Inorganic chemistry,
Dept of Chemistry, Umeå University

December 2005

Svensk Kärnbränslehantering AB
Swedish Nuclear Fuel
and Waste Management Co
Box 5864
SE-102 40 Stockholm Sweden
Tel 08-459 84 00
+46 8 459 84 00
Fax 08-661 57 19
+46 8 661 57 19

SKB

ISSN 1402-3091
SKB Rapport R-05-72

Effects of complexing compounds on sorption of metal ions to cement

Lars Lövgren, Inorganic chemistry,
Dept of Chemistry, Umeå University

December 2005

Abstract

This present report is a literature review addressing the effects of complexing ligands on the sorption of radionuclides to solid materials of importance for repositories of radioactive waste. Focus is put on laboratory studies of metal ion adsorption to cement in presence of chelating agents under strongly alkaline conditions. As background information, metal sorption to different mineral and cement phases in ligand free systems is described. Furthermore, surface complexation model (SCM) theories are introduced.

According to surface complexation theories these interactions occur at specific binding sites at the particle/water interface. Adsorption of cationic metals is stronger at high pH, and the adsorption of anions occurs preferentially at low pH. The adsorption of ions to mineral surfaces is a result of both chemical bonding and electrostatic attraction between the ions and charged mineral surfaces. By combining uptake data with spectroscopic information the sorption can be explained on a molecular level by structurally sound surface complexation models.

Most of the metal sorption studies reviewed are dealing with minerals exhibiting oxygen atoms at their surfaces, mainly oxides of Fe(II,III) and Al(III), and aluminosilicates. Investigations of radionuclides are focused on clay minerals, above all montmorillonite and illite. Which mechanism that is governing the metal ion adsorption to a given mineral is to a large extent depending on the metal adsorbed. For instance, sorption of Ni to montmorillonite can occur by formation of inner-sphere mononuclear surface complexes located at the edges of montmorillonite platelets and by formation of a Ni phyllosilicate phase parallel to montmorillonite layers. Also metal uptake to cement materials can occur by different mechanisms. Cationic metals can both be attached to cement (calcium silicate hydrate, C-S-H) and hardened cement paste (HCP) by formation of inner-sphere complexes at specific surface sites and by incorporation of metal ions into the cement phase.

Adsorption of metal ions to particle surfaces can be affected by the presence of complexing ligands. The adsorption can be enhanced due to ternary complexation, i.e. indirect bonding of metal ions to surface functional groups through coordination to adsorbed anions and due to electrostatic effects. Correspondingly, anion adsorption under certain circumstances may be enhanced by adsorption to adsorbed metal ions. On the other hand, formation of metal ligand complexes in the aqueous solution may result in reduced adsorption.

Sammanfattning

Denna rapport ger en översikt över aktuell litteratur med avseende på effekter av närvaron av komplexbildande ligander på sorption av radionuklider till mineralpartiklar och cementmaterial. Tonvikt har lagts på sorption till cement under starkt alkaliska förhållanden. Inledningsvis beskrivs metalsorption i frånvaro av ligander. Rapporten innehåller även en kort beskrivning av teorier för beskrivning av ytkomplexbildningsreaktioner. Adsorption av joner till mineralytor sker på specifika bindningsplatser genom såväl kemisk bindning som elektrostatisk attraktion mellan joner och ladddade mineralytor. Katjonadsorption gynnas av höga pH och anjonadsorption sker framförallt vid låga pH. Genom att kombinera data från sorptionsförsök med spektroskopisk information kan metalljonsorptionen beskrivas på molekylär nivå med jämviktsmodeller som är sunda ur strukturell synvinkel.

De flesta studier som refereras i denna rapport gäller mineral som exponerar syreatomer vid sina ytor, i huvudsak oxider av Fe(II, III) och Al(III), samt aluminiumsilikater. Lermineral, främst montmorillonit och illit, har varit i fokus när det gäller undersökningar av radionuklider. Vilken den styrande mekanismen för sorption är beror av såväl den adsorberade metalljonens som adsorbentens egenskaper. Exempelvis kan nämnas att Ni kan adsorberas till montmorillonit dels genom att bilda enkärniga ytkomplex av innersfärstyp på kanterna av de platta montmorillonitkristallerna och dels genom att bilda ett Ni-innehållande skiktsilikat parallellt med montmotillonitens lagerstruktur. Även metallupptag till cementmaterial kan ske genom olika reaktionsmekanismer. Metallkatjoner kan både adsorbera till kalciumsilikathydrat och härdad cementpasta genom att bilda innersfärskomplex på specifika ytbindningsplatser och genom att inkorporeras i cementfasen.

Graden av adsorption av metalljoner på partikelytor kan påverkas av komplexbildande ligander. En ökad adsorption kan ske genom bildning av s.k. ternära ytkomplex, vilket betyder att metalljoner indirekt binds till ytan genom att koordineras till adsorberade anjoner och genom elektrostatiska effekter. På motsvarande sätt kan anjonadsorption under vissa förhållanden öka genom att anjonen binds till adsorberade metalljoner. Å andra sidan kan bildning av metall-ligand komplex i vattenfasen resultera i minskad adsorption. En sådan löslighetsökning är mest påtaglig vid höga pH-värden. Detta gäller inte minst cementsystem som normalt är starkt alkaliska.

Contents

1 Introduction

1.1 Background

Adsorption to surfaces of solid phases is commonly considered to immobilise contaminants. However, adsorption onto colloidal solids, which are present in surface waters as well as groundwater aquifers and water-permeable engineered barrier systems, may facilitate the migration of radionuclides in soils, barrier systems and other natural and engineered environments. The extent to which different contaminants are adsorbed is strongly dependent on both the character of the contaminant and the geochemical composition of the aqueous phase. Ionic compounds present at high concentrations in the aqueous phase may affect the sorption processes in a rather unspecific way by altering the surface charge. Complexing ligands (inorganic as well as organic) may also affect the association of metal ions to particle surfaces by forming complexes in the aqueous phase or by competing with metal ions for binding sites at the particle surfaces. Besides that the attachment of negatively charged ligands to particle surfaces will influence electrostatic forces, these ligands can enhance the adsorption of cationic compounds by forming complexes involving both the binding sites at the particle/water interface and the metal ion, i.e. forming so called ternary surface complexes. Hence, there are processes by which complexing ligands present in the aqueous phase can increase the solubility of metal ions and other processes that can enhance the uptake of the same metal ions to solid phases.

In the context of disposal of waste from the handling and use of nuclear fuel there are several barrier systems involving geologic materials with an objective to act as substrates for sorption processes. There are also large quantities of waste materials that can attenuate metal ions, e.g. structures constructed of concrete. On the other hand, there are many soluble substances present that may affect the sorption processes as described above, e.g. chemicals used in the handling of the nuclear fuel and also compounds formed by degradation of organic matter /Fanger et al. 2001/. Hence, there is an obvious need for a sound knowledge on all the different geochemical processes that can affect the association of contaminants to geologic materials in the near and far field of nuclear waste disposals.

1.2 Objectives

The main objective of this literature study is to summarise experiences from studies of the effect of complexing ligands on the sorption of radionuclides to solid materials of importance for repositories of radioactive waste. Focus will be put on laboratory studies of metal ion adsorption to cement in presence of chelating agents under strongly alkaline conditions. As background information metal sorption to different mineral and cement phases will also be treated.

2 Method

The present work is a literature study based on article reprints, reports and books already available at our department and partly on literature identified by search using online databases. The literature search has mainly been performed using the databases Science Citation Index Expanded (online search engine: ISI Web of Science) and Chemical Abstracts (online search engine: SciFinder).

3 Sorption processes – an overview

3.1 Sorption processes

Association of ionic substances to solid matter can occur through several different processes /Stumm 1992/. Ions may be removed from the aqueous solution by the incorporation of metal ions in solid matter through precipitation of secondary minerals or weakly crystalline or amorphous precipitates. The solubility and mobility of trace elements are in many natural systems regulated by sorption processes at mineral/water-interfaces. In fact, the precipitation of solid matter involves attachment of substances in solution with the particulate phase. Metal ions may be adsorbed to mineral particles under both oxic and anoxic conditions, although the substrate to which they adsorbed may vary. Under anoxic conditions in natural systems, such as sediments and sulphate rich soils, sulphide minerals are stable and can attract ions of metals commonly referred to as soft and borderline Lewis acids according to the Pearsons Hard Soft Acid Base (HSAB) principle /Pearson 1963/, e.g. Zn(II), Cd(II), Hg(II), Pb(II) and Ag(I), and also As(III).

Under oxic conditions oxides and hydroxides mainly of Fe(III) but also of Al(III) and Mn(III,IV) are present as coatings on parent mineral particles and in some cases also as massive deposits of secondary precipitates. These minerals have a well documented ability to act as adsorbents of ionic compounds. A third group of minerals ubiquitous in natural systems and active sorbents are primary and secondary (alumino)silicates. Furthermore, phosphate and carbonate minerals are well-known adsorbents /e.g. Moore et al. 2005, Rouff et al. 2002/. In surface waters, trace metal solubilities are often regulated by suspended and colloidal matter. In this section, sorption processes at oxidic minerals will be briefly summarised.

By diffusion and structural re-arrangement adsorbed metal ions and anions can be transported into the solid phase and with time these ions will form part of the crystal lattice. In general adsorption processes are considered reversible, but by transformation processes of this type the sorbed contaminants can be associated to the solid matter in a way that is, at least apparently, irreversible /Stipp et al. 2002/. Besides acting as a site for scavenging contaminants, the mineral surfaces often form important playgrounds for transformation processes, for instance, redox processes /Silvester et al. 1995, Liger et al. 1999/.

3.2 Surface complexation

3.2.1 Methods for quantification of sorption processes – empirical methods

Traditionally, sorption processes have been quantified applying empirical representations, such as, distribution coefficients, K_d, or adsorption isotherms when nonlinearities must be accounted for. The distribution coefficient postulates a constant relationship between the amount of substance associated with solid matter (C_s) and amount of the substance in present in the aqueous phase (C_w) according to equation (1) /Stumm and Morgan 1996/.

$$K_d = \frac{C_s(mol \cdot kg^{-1})}{C_w(mol \cdot dm^{-3})} \qquad (1)$$

Distribution coefficients are particularly useful in cases with highly heterogeneous sorbents and when dealing with sorption of hydrophobic substances to organic particles or mineral particles coated with organic matter.

Langmuir and *Freundlich* isotherms are frequently used to describe adsorption equilibria. Adsorption isotherms are visualised by plotting the amount of adsorbate A adsorbed per mass of adsorbent (Γ_A; mol/g or mol/m^2) vs. the equilibrium concentration of A in the solution (mol/dm^3).

$\Gamma_A = f([A])$ (or $\log\Gamma_A = f(\log[A])$) (2)

While the Langmuir isotherm is valid up to the formation of a surface coverage of adsorbed ions/molecules corresponding to a monolayer, the Freundlich isotherm is applied mainly for energetically heterogeneous solid surfaces.

3.2.2 Methods for quantification of sorption processes – surface complexation

From a mechanistic point of view, both these concepts, the K_d coefficients and adsorption isotherms, do not provide much information. Also, their applicability in modelling exercises is limited. By applying concepts of solution coordination chemistry to the description of the interaction of metal ions and inorganic/organic ligands at the particle/solution interface it is possible to include adsorption processes in thermodynamic modelling /Stumm 1992/.

The concept of surface complexation is based on the assumption that adsorption takes place at specific coordination sites and that adsorption processes are reversible. Such sites at metal (hydr)oxide surfaces are often referred to as surface hydroxyl groups, noted as ≡MeOH, where ≡ symbolises the bulk oxide phase, and Me and OH denotes the metal and hydroxide ions at the surface. However, a closer study of the structure of mineral surfaces reveals that (hydr-)oxide surfaces exhibit a range of structurally different functional groups, /Hiemstra et al. 1989ab/.

The surface hydroxyl groups are able to take up and release protons and metal ions from the solution, e.g. reactions (3 and 4). Adsorption of metal ions involves competition with hydrogen ions for binding sites, implying that adsorption is favoured by increasing pH. Commonly there is a rather narrow pH-range within which most metal ions are being transferred from the aqueous solution to the particle surface. This so called adsorption edge is element specific and also depends on the metal to surface site ratio.

$\equiv FeOH \leftrightarrow \equiv FeO^- + H^+$ (3)

$\equiv FeOH + Me^{z+} \leftrightarrow \equiv FeOMe^{(z-1)} + H^+$ (4)

The surface also exhibits metal atoms capable of accepting electrons in chemical bonding (Lewis acid sites), enabling complexation with donor groups (ligands, L) in the solution, reaction (5). Charged species can also be taken up by electrostatic attraction to surface sites of opposite charge. Hence, anions can be adsorbed to positively charged surface sites, reaction (6). Uptake of protons results in increased surface charge ($\equiv MeOH_2^+$). Thus, anion sorption is favoured by low pH. While strongly sorbed anions such as phosphate (PO_4^{3-}) /Persson et al. 1996/ and arsenate (AsO_4^{3-}) are directly coordinated by the metal ion, the more weakly bonded sulphate ions are mainly adsorbed by electrostatic attraction /Persson and Lövgren 1996/.

$\equiv FeOH + L + H^+ \leftrightarrow \equiv FeL^+ + H_2O$ (5)

$\equiv FeOH + H^+ + L^- \leftrightarrow \equiv FeOH_2^+, L^-$ (6)

Adsorption of metal ions from the solution can also be a result of ternary complexation, which means that the metal ion is bound indirectly to the surface by complexation with an adsorbed anion forming a so called Type A ternary surface complex, ($\equiv$FeOMeL). Correspondingly, anion adsorption may under certain circumstances be enhanced by adsorption to adsorbed metal ions under formation of a Type B ternary surface complex ($\equiv$FeLMe).

The mechanisms behind site specific adsorption to iron(hydr-)oxide surfaces can be distinguished between formation of outer-sphere and inner-sphere complexes /Stumm 1992/. An inner-sphere surface complex is formed when there is a direct chemical bond between the adsorbing ion and the metal ion at the surface. In outer-sphere complexes hydroxyl groups or water molecules separate the adsorbed ions and the surface metal ion centre or hydroxyl group. The dominating driving force for the adsorption is the attraction of opposite charges, with the surface waters and hydroxyls possibly acting as proton donors in hydrogen bond arrangements. Outer-sphere complexes are often considered to be weaker than inner-sphere.

3.2.3 Surface complexation – Modelling aspects

According to surface complexation theories coordination reactions at particle surfaces can be described by mass law equations. A complication in this respect is that, due to the density of surface hydroxyl groups, adsorption of charged species from the solution results in the development of an electric double layer at the particle/water interface. The surface charge affects the stability of the surface complexes by electrostatic attraction or repulsion. From a thermodynamic point of view, the total Gibbs free energy for a given reaction consists of both a chemical and a coulombic term /Stumm 1992/.

$\Delta G^0_{tot} = \Delta G^0_{chem} + \Delta G^0_{coul}$ (7)

$\Delta G^0{}_{chem}$ represents the direct chemical interaction between the donor/acceptor atom of the surface and the sorbing ion/molecule, or in other terms, the charge independent (intrinsic) function of the stability constant. ΔG^0_{coul} represents the electrostatic interactions at the charged surface. To correct for the electrostatic effects resulting from the build up of surface charge a handful of electric double layer (EDL) models have been developed. The different EDL's differ with respect to the number of planes of specifically adsorbed ions and to what extent a diffuse layer of counter ions in solution is considered.

In high ionic strength systems in which only inner-shere complexes are formed the Constant Capacitance Model can be applied /Schindler and Gamsjäger 1972/. The Diffuse Layer Model (DLM), also known as the Gouy-Chapman model, involves the surface plane and a diffuse layer of counter ions in solution close to the surface /Stumm et al. 1970, Huang and Stumm 1973/. In the Basic Stern Model two planes (a surface plane and plane of adsorbed electrolyte ions) and a diffuse layer are used /Stern 1924, Westall and Hohl 1980/.

For outer-sphere complexation two planes of adsorption must be considered: a surface plane for the strongly bound ions (inner-sphere complexation) and a plane for the weakly bound ions (outer-sphere complexation). The electrostatic model most commonly used for outer-sphere complexation is the Triple Layer Model (TLM), which besides the above mentioned surface planes also considers a diffuse layer of counter ions in solution /Davis et al. 1978/. The Basic Stern Model has also been modified to give the Three Plane Model /Hiemstra and van-Riemsdijk 1996/.

For speciation modelling of surface complexation equilibria it is critical that the EDL model parameters are consistent because the density of active surface sites, specific capacitances and intrinsic equilibrium constants are interrelated. The following example is intended to demonstrate the additional information required to account for the electrostatic forces at charged surfaces. Surface hydroxyl groups at the surface of goethite (α-FeOOH) can take up and give away protons as described by the two reactions:

$$\equiv FeOH + H^+ \leftrightarrow \equiv FeOH_2^+ ; \quad \beta_{1,1,0} \tag{8}$$

$$\equiv FeOH \leftrightarrow \equiv FeO^- + H^+ ; \quad \beta_{-1,1,0} \tag{9}$$

The intrinsic equilibrium constants for these reactions at an ionic strength of 0.1 mol dm^{-3} was determined by /Lövgren et al. 1990/ applying the Constant Capacitance Model (CCM) to be $\log\beta_{1,1,0\,(intr)} = 7.47$ and $\log\beta_{-1,1,0(intr)} = -9.51$. These values represent the equilibrium constants at an uncharged surface. According to the CCM, the effect of the surface charge on the apparent equilibrium constants are adjusted for by invoking the specific capacitance (1.28 C V^{-1} m^{-2}; fitted parameter), which in turn is coupled to the density of proton active sites at the mineral surface. In this example the maximum proton uptake was determined by addition of protons in access and the surface area of the goethite was determined by the so called BET method. This exercise resulted in an experimentally determined density of surface hydroxyl groups of 1.68 nm^{-2}, corresponding to 2.79 $\mu mol/m^2$. In a series of studies metal ion complexation to goethite, Lövgren and co-workers have determined model parameters based on the above mentioned model. For instance, the uptake of Cu(II) to goethite was interpreted as formation of a series of inner-sphere surface complexes according to equations (10) to (12) /Palmkvist et al. 1997/:

$$\equiv FeOH + Cu^{2+} \leftrightarrow \equiv FeOHCu^{2+} \qquad \log \beta_{0,1,1(intr)} = 8.8\ (\pm 0.21) \tag{10}$$

$$\equiv FeOH + Cu^{2+} \leftrightarrow \equiv FeOCu^{+} + H^+ \qquad \log \beta_{-1,1,1(intr)} = 0.9\ (\pm 0.40) \tag{11}$$

$$\equiv FeOH + Cu^{2+} + H_2O \leftrightarrow \equiv FeOCuOH + 2\ H^+ \qquad \log \beta_{-2,1,1(intr)} = -6.6\ (\pm 0.12) \tag{12}$$

Effects at high pH and at high total copper concentration were explained by formation of a solid phase of the type CuO(s).

The above described surface complexation model postulates that the adsorption properties of goethite can be ascribed to one type of functional group at the mineral surface only. This assumption can be considered as a simplification of the true nature of the mineral/water interface. A more recent development in surface complexation modelling is the Charge-distribution Multisite Surface Complexation Model (CD-MUSIC), which describes the proton affinity of different types of surface hydroxyl groups on a mineral surface and accounts for spatial distribution of charge at the mineral surface /Hiemstra and Van Riemsdijk 1996/.

Phyllosilicates, i.e. aluminosilicates with a layer structure are expected to show surface properties that differ from those of simple oxides and oxyhydroxides of several reasons. Surfaces of aluminium silicates exhibit both oxygen atoms coordinating to Al(III) atoms and oxygens coordinating to Si(IV) atoms. Phyllosilicates, such as kaolinite, consist of tetrahedral silica sheets and octahedral alumina sheets bonded together by the sharing of oxygen atoms between the silicon and aluminium atoms in adjacent sheets. In kaolinite, the O-Al-O-Si-O layers are attached to each other in the crystal lattice by hydrogen bonding. Resulting from isomorphic substitution of Si(IV) by Al(III) atoms the crystals carry negatively charged sites at all pH. For particularly 2:1 minerals (O-Si-O-Al-O-Si-O), e.g. smectites, the net negative charge of each 2:1 layer is neutralised by cations in the interlayer region. Since the charge density of these surfaces is low the interlayer metal ions are rather weakly bonded and may be exchanged with other metal ions. The edges of layer silicates contain both ≡AlOH and ≡SiOH sites, which may be considered as one common type of surface site (≡SOH) which can exhibit amphoteric properties, i.e. they can both take up and give away protons. /Angove et al. 1997/. Consequently, metal ions may be attached to layer silicates in three different ways: ion exchange at layers with a permanently negative surface charge, ion-exchange in the interlayer region and formation of surface complexes at the ≡SOH sites.

In the case of kaolinite, exchange in the interlayer region does not occur. Thus, metal ions may be adsorbed to kaolinite by ion exchange and also form surface complexes with ≡SOH groups. /Angove et al. 1997/ propose that the sorption of Cd(II) by kaolinite involves bidentate ion exchange onto permanent negatively-charged sites on the silanol faces (≡XH), and formation of bidentate inner sphere complexes on pH-dependent surface hydroxyl groups (≡SOH).

With few exceptions, the different surface complexation models available in the literature are not internally consistent. This creates a problem for modellers that is not easily circumvent. The first ambitious attempt to provide a set of consistent thermodynamic data for sorption of inorganic compounds for hydrous oxide minerals was presented 1990 by Dzombak and Morel. Based on a *generalized two-layer model* the authors reinterpreted previousy published experimental data for adsorption of cations and anions to hydrous ferric oxide (HFO), also called amorphous ferric hydroxide /Dzombak and Morel 1990/. HFO is the solid formed by rapid hydrolysis of ferric iron at 20°C to 30°C. Based on a compilation of results from earlier studies, two different types of active surface sites were distinguished: strongly complexing sites (≡Fe^{s}OH) and weakly complexing sites (≡Fe^{w}OH). For further details about the model parameters for the fundamental properties of the material the reader is referred to /Dzombak and Morel 1990/. The database for cation sorption covers 12 metal ions and models for anion sorption is presented for 10 inorganic anions, e.g. sulphate, arsenate, arsenite and vanadate. Since HFO is a material of relevance for many different natural environments, and the database is the largest known set of consistent models for surface complexation it is often included in computer programs for geochemical calculations, such as PHREEQC /Parkhurst and Appelo 1999/ and MINTEQA2 /Allison et al. 1991/.

The lack of consistent surface complexation models is partly due to that the definition of the standard state for surface species is unclear /Kulik 2004/. Another difficulty is to determine the number and nature of the surface sites taking part in metal ion coordination. Furthermore, the variety of surface complexation models available creates an additional complexity. Recently, a couple of interesting initiatives were taken to transform the spread information available in the scientific literature into a format that can be applied in modelling exercises involving multicomponent systems. One of these is RES^{3}T – the Rossendorf Expert System for Surface and Sorption Thermodynamics, which is a digitized thermodynamic sorption database, implemented as a relational database with MS Access /Brendler et al. 2003/. RES^{3}T is mineral-specific and can therefore also be used for additive models of more complex solid phases such as rocks or soils. Another intiatives in the same direction have been announced by e.g. /Jakobsson and Lützenkirchen 2004, Lomenech and van der Lee 2004/.

4 Sorption studies in the laboratory and in the field

This chapter addresses sorption to mineral surfaces and cement materials of metal ions in general and radionuclides in particular. Sections 4.1 to 4.3 deal with metal sorption in ligand free systems and Section 4.4 addresses the effect of complexing ligands.

4.1 Laboratory methods for surface complexation studies

Surface complexation equilibria can be studied in the laboratory involving both microscopic and macroscopic methods. The most accurate models are those evaluated from a combination of quantitative information about the different components involved in complex formation and information on structural features. Quantitative aspects of sorption processes are commonly studied by wet chemistry methods, such as uptake experiments /e.g. Miyazaki et al. 1996/. It has also been shown that potentiometric titrations can be applied in investigations of surface complexation equilibria /Sjöberg and Lövgren 1993/. Especially powerful is the combination of quantitative information provided by wet chemistry experiments and structural information obtained by performing spectroscopic studies.

Among the spectroscopic methods commonly applied in surface chemistry investigations we find Fourier Transform-InfraRed spectroscopy (FT-IR) which, among other things, provides information on the symmetry and coordination mode of adsorbed anions at mineral surfaces. Oxidation states can be determined by X-ray Photoelectron Spectroscopy (XPS). Synchrotron based X-ray Absorption Spectroscopy (XAS) is increasingly frequent used to elucidate the local structure of adsorbed metal ions and inorganic anions. There are different methods applying XAS principle, e.g. Extended X-ray Absorption Fine Structure (EXAFS) and X-rayThe effect of complexing ligands on r Absorption Near Edge Structure (XANES) /Fenter et al. 2002/. By using EXAFS it is possible to obtain information on coordination properties of adsorbed ions, i.e. bond lengths and coordination numbers with respect to atoms in closest vicinity. By using XANES it is possible to determine oxidation states of adsorbed ions.

4.2 Sorption of metal ions to mineral particles

Following the introduction of the surface complexation concept, there has been a strongly increasing interest in studying metal ion sorption in more detail. Since many of these investigations have been initiated from a perspective of environmental geochemistry, most effort has been paid to minerals of relevance for mobility of metals in soils and surface waters. This has resulted in a large number of publications dealing with oxides of Fe(III), Al(III) and Si(IV). Also the surface properties of carbonates and sulphide minerals have attracted the interest of many researchers. These studies have dealt with many different aspects of surface complexation, e.g. effects of ion charge, pH, ionic strength, temperature, metal to solid ratios, presence of complexing ligands, kinetics, etc. Unfortunately, there are few comprehensive reviews of this vast literature.

4.2.1 Sorption of radionuclides

While most of the investigations involving divalent metals of environmental interest have dealt with single metal oxides, less interest has been paid to aluminosilicates, including clay minerals. However, in the case of radionuclides more interest has been paid to clay minerals and cement materials. In Table 4-1 some examples of radionuclide sorption to mineral phases are given and a selection of the results are presented below.

Table 4-1. Examples of sorption studies involving radionuclides and mineral phases.

Studied metal	Solid phase	Reference
Cs(I)	illite	/Comans et al. 1991, Comans and Hockley 1992/
	silica	/Marmier et al. 1999a/
	magnetite	/Marmier et al. 1999b/
Sr(II)	kaolinite, illite and Na- and Ca-montmorillonite	/Chen and Hayes 1999/
	montmorillonite and SiO_2	/Lu and Mason 2001/
Co(II)	quartz and rutile (TiO_2)	/O'Day et al. 1996/
	TiO_2	/Jakobsson and Albinsson 1998/
	kaolinite, illite and Na- and Ca-montmorillonite	/Chen and Hayes 1999/
Ni(II)	montmorillonite	/Dähn et al. 2002b/
	montmorillonite	/Dähn et al. 2003/
	Ca-montmorillonite	/Bradbury and Baeyens 1999/
	magnetite	/Marmier et al. 1999b/
Zn(II)	Ca-montmorillonite	/Bradbury and Baeyens 1999/
La(III)	hematite	/Marmier and Fromage 1999/
Eu(III)	montmorillonite	/Kowal-Fouchard et al. 2004/
	Na- and Ca- montmorillonite	/Bradbury and Baeyens 2002/
	illite	/Wang et al. 1998/
Yb(III)	silica	/Marmier et al. 1999a/
	magnetite	/Marmier et al. 1999b/
Am(III)	SiO_2	/Degueldre et al. 1993/
	montmorillonite	/Degueldre et al. 1994/
Th(IV)	montmorillonite	/Akcay and Kilinc, 1996/
	montmorillonite	/Dähn et al. 2002a/
	TiO_2	/Jakobsson 1999/
	hematite	/Cromieres et al. 1998/
Np(V)	goethite	/Combes et al. 1992/
	montmorillonite	/Turner et al. 1998/
	TiO_2	/Jakobsson and Albinsson1998/
U(VI)	montmorillonite	/Chisholm-Brause et al. 2001/
	α-alumina	/Prikryl et al. 1994/
	silica, alumina and montmorillonite	/Silvester et al. 2000/
	SiO_2	/Gabriel et al. 2001, 2002/
	hematite	/Lenhart and Honeyman 1999/
	ferrihydrite	/Waite et al. 1994/
Pu(VI)	TiO_2	/Olsson et al. 2003/

A surface complexation model is used to describe sorption of ytterbium and caesium on the silica surface. In the case of caesium, the sorption of sodium was found to be competitive /Marmier et al. 1999a/. In another study /Marmier et al. 1999b/ investigated the sorption of ytterbium, nickel and caesium on magnetite. The affinity of the magnetite surface decreased in the order ytterbium > nickel > caesium. Three different surface complexation models, with three different electrostatic descriptions of the interface, are used to fit the experiment data.

/Jakobsson and Albinsson 1998/ studied the uptake of Co(II) and neptunyl ions (Np(V)) onto TiO_2. They found that the adsorption of these two ions was independent of ionic strength. Based on this observation of the authors concluded that both Co(II) and Np(V) were adsorbed via formation of inner-sphere surface complexes.

The sorption and desorption of thorium on a West Anatolian montmorillonite was studied by /Akçay and Kilinç 1996/. The data was fitted to Freundlich and Langmuir isotherms. The quantity of the sorbed thorium was much lower than its theoretical CEC, which was attributed to a blocking of montmorillonite's CEC by thorium islands in the interlayer.

/Olsson et al. 2003/ studied the sorption of Pu(VI) onto TiO_2 as a function of pH (2–10) in a wide range in total Pu concentration (10^{-8}–10^{-4} M) in 0.1 M NaClO4. A batch-wise method was used, in which pH was measured in separate experimental containers after removal of a sample to determine the amount of Pu that had been sorbed. No ionic strength dependence was discerned, which was taken as an indication of inner sphere complex formation. The authors described their data in the range pH 2–7 by invoking the formation of two positively charged surface complexes using a 1-pK Stern model.

In their study of Ni(II) sorption to montmorillonite over an extended time period by polarized extended X-ray absorption fine structure (P-EXAFS) spectroscopy /Dähn et al. 2003/ found evidences for the formation of Ni inner-sphere mononuclear surface complexes located at the edges of montmorillonite platelets. Thus, heavy metal binding to edge sites is a possible sorption mechanism for dioctahedral smectites. On the basis of low Ni-Al coordination numbers, it appeared that over an extended reaction time (1 year) diffusion of Ni atoms in the octahedral layer is not the major uptake mechanism of Ni onto montmorillonite. In a preceding paper on Ni uptake to montmorillonite /Dähn et al. 2002b/ presented spectroscopic evidences for the formation of a Ni phyllosilicate phase parallel to montmorillonite layers.

The sorption of Th, U, Np, Pu and Am on hydrotalcite, tobermorite, ettringite and calcium silicate hydrate gel was investigated in water, saturated NaCl solution and Q-brine at 25, 55 and 85°C. Data were modelled applying Freundlich's and Langmuir isotherms /Altenheinhaese et al. 1994/.

Retention of Eu(III) onto Na-montmorillonite was studied, combining both macroscopic and microscopic methods by /Kowal-Fouchard et al. 2004/. They concluded that Eu was sorbed, on the montmorillonite clay, on exchange sites as an outer-sphere complex and onto both "aluminol" and "silanol" edge sites as inner-sphere surface complexes, depending on the pH value and the ionic strength of the suspension.

The uptake of uranyl to two silicate minerals (clinoptilite and quartz) was studied by /Prikryl et al. 2001/. They found Similar pH-dependent trends in U(VI) sorption behaviour for these two minerals and for a mixture of both. In fact, if normalised to surface area the K_d sorption values were similar for the minerals.

From EXAFS measurements it was suggested that adsorption of the uranyl ion onto montmorillonite at low pH occurs via ion exchange, leaving the inner-sphere uranyl aquo-ion structure intact /Silvester et al. 2000/. At near-neutral pH and in the presence of a competing cation, inner-sphere complexation with the surface predominates. The authors also studied adsorption of the uranyl to silica and γ-alumina surfaces and found that the uranyl appears to form inner-sphere, bidentate complexes at the surface. Polynuclear surface complexes is occurring at near-neutral pH.

4.3 Sorption of radionuclides to cement materials

Cements exhibit a rather complicated composition. The most important component within a hardened cement is the CSH gel (calcium silicate hydrate). Calcium silicate hydrates have a wide range of chemical compositions: $x\mathrm{CaO}\times\mathrm{SiO_2}\times y\mathrm{H_2O}$ ($1.4 < x < 1.8$ for common Portland cements and $y \geq x$. Another interesting cement material is hardened cement paste (HCP). Also sorption processes involving calcite are of interest in this context. Below is a selection of investigations of radionuclide sorption to cement materials reviewed.

The mechanisms behind immobilization of Sn(IV) onto C-S-H and HCP was investigated by /Bonhoure et al. 2003/ by combining wet chemistry experiments with X-ray absorption spectroscopy (XAS). Evidence for the formation of a Sn(IV) inner-sphere surface complex on C-S-H with a $\mathrm{CaO/SiO_2}$ weight ratio of 0.7 was presented. Two possible structural models, implying a corner sharing between the Sn octahedra and Si tetrahedra were developed on the basis of structural parameters determined by EXAFS. In HCP, the formation of a different type of Sn(IV) inner-sphere complex has been observed, indicating that C-S-H may not be the uptake controlling phase for Sn(IV) in the cement matrix. An alternative structural model for Sn(IV) binding in HCP was presented, assuming that ettringite is the solid phase controlling the uptake of Sn(IV). At high Sn(IV) concentrations, Sn(IV) immobilization in HCP occurs due to the formation of $\mathrm{CaSn(OH)_6}$.

/Pointeau et al. 2001/ used site-selective and time-resolved luminescence spectroscopy, XPS, high-resolution SEM coupled with EDX, and XRD to study of sorption mechanisms of $\mathrm{Eu^{3+}}$ on CSH phases of hydrated cement. Their results showed that europium was not precipitated in the solution despite its low solubility limit. It was strongly retained on CSH, resulting in a more than 99.8% sorption rate. Two main sorption sites were characterized by luminescence spectroscopy, One site, with a long lifetime, can be interpreted as Eu included in the framework of CSH. Another site, with a shorter lifetime, was interpreted as a site with a hydrated environment that is high but is less than that of europium hydroxide, corresponding to surface complexation or precipitation.

/Ziegler et al. 2001a/ studied the sorption of Zn(II) to C-S-H in pre-equilibrated aqueous suspensions as a function of time (up to 87 d), pH (11.7, 12.5, and 12.8) and Zn(II) concentration using wet chemistry methods and a microscopic technique (Electron probe microanalysis (EPMA)). They observed at Zn(II) concentrations larger than 1,000 μM the precipitation of β_2-Zn-$\mathrm{(OH)_2}$ (< pH 12) and calcium zincate ($\mathrm{Zn_2Ca(OH)_6\times 2H_2O}$, > pH12). Surface precipitation could not be discerned. At lower concentrations, the sorption process was initially very rapid with > 50% sorbed within 30 min. The sorption continued more slowly to at least 87 d. The data was interpreted using a Freundlich isotherm up to a Si: Zn(II)sorbed atomic ratio of ca 6:1. Zinc was observed to incorporate into the C-S-H(I) particles but without substituting for Ca or Si, which was interpreted as incorporation of Zn(II) in the interlayer of C-S-H or sorption to internal surfaces. Adsorption at the surface appears to be the first rapid step in the sorption process. Whether the incorporation of Zn(II) into the C-S-H particles was due to a diffusion process or a re-dissolution and precipitation process of the C-S-H could not be determined. Several processes are possible. One option is isomorphic substitution of Zn(II) for Ca within the C-S-H. Another alternative is incorporation into the interlayers of the C-S-H structure, where Zn may sorb as ZnO_4 tetrahedra to Si-O sites from the SiO_4 chains oriented toward the interlayer. The XAFS measurements performed by /Ziegler et al. 2001a/ suggest Si-O-Zn bonds. As a third option, it was suggested that binding occurs at internal surfaces between ordered domains in the C-S-H gels. A fourth possibility was the precipitation of Zn silicates. However, formation of such phases would result in a release of Ca either to solution or for uptake by the interlayers of the remaining C-S-H gels. As this was not observed, and on the basis of thermodynamic arguments the authors excluded this alternative. Instead they found that all the indications pointed at that binding at Si-O sites within the interlayer or at domain "surfaces" was the most likely process. In another paper by /Ziegler et al. 2001b/ an XAFS (X-ray Absorption Fine Structure) investigation of Zn sorption to C-S-H was presented. Also in that paper the incorporation of Zn(II) in the interlayer of C-S-H was postulated.

Adsorbed Pb has shown to act as a diffusional barrier to water, which leads to the retardation of hydration of the C_3S /Rose et al. 2000/. However, when C_3S is previously hydrated without Pb, lead is strongly retained by the hydrated C_3S (CSH). By ^{29}Si NMR it was shown that Pb is chemically fixed to the CSH structure through a Pb-O-Si bond /Moulin et al. 1999/. XAS experiments confirmed that Pb is incorporated within the matrix of CSH and directly linked at the end of the silicate chains through Pb-O-Si bonds. /Moulin et al. 1999/ found that lead has a much higher affinity than zinc for both nonhydrated and hydrated calcium silicate.

Solubility experiments and sorption studies were carried out with microcrystalline ThO_2 and alkaline cement pore waters. For fresh pore water, a solubility of thorium of 10^{-9} M was found and for aged (portlandite, equilibrated) pore waters, 10^{-10} M, which is expected in aqueous systems with elevated pH-values /Wierczinski et al. 1998/.

Uptake of selenate and chromate on fresh and leached Portland and high-alumina cements, and in addition with selenate and selenite on synthetic ettringite was studied by /Ochs et al. 2002/. In all experiments with cements, exceptionally high uptake could be observed under conditions where significant amounts of secondary ettringite were formed. Experimental data obtained for pure ettringite corroborated the important role of this mineral phase. However, uptake kinetics show opposite trends in these two systems, which was interpreted as end-members of the same process.

Sorption of Eu(III) and Th(IV) to Merck calcite in an artificial cement pore water at pH 13.3 and in the absence and the presence of α-isosaccharinic acid (ISA) and gluconic acid (GLU) by /Tits et al. 2002/. A strong interaction of Eu(III) and Th(IV) with the calcite was observed in organic free suspensions. The sorption kinetics were fast.

X-ray absorption fine structure (XAFS) spectroscopy and diffuse reflectance spectroscopy(DRS) were applied to assess the solubility-limiting phase of Ni in cement systems. The study provides evidence for the formation of Ni- and Al-containing hydrotalcite-like layered double hydroxides (Ni-Al LDHs) when cement material was treated with Ni in artificial cement pore water under highly alkaline conditions (pH = 13.3). Ni-Al LDHs were formed in cement suspensions oversaturated with respect to beta -$Ni(OH)_2$ and aged at room temperature for 150 days, which indicates that Ni-Al LDHs and not Ni-hydroxides may determine the solubility of Ni in cement materials. /Scheidegger et al. 2000, 2001/.

The interaction of Cm(III) and Eu(III) with CSH at pH 13.3 was investigated in batch-type sorption studies using Eu(III) and complemented with time-resolved laser fluorescence spectroscopy (TRLFS) using Cm(III) /Tits et al. 2003/. Fast sorption kinetics and a strong uptake of Ru(III) by CSH phases were observed. Three different Cm(III) species were identified: A nonfluorescing species, which was identified as a curium hydroxide (surface) precipitate, and two fluorescing Cm(III)/CSH-sorbed species. From the fluorescence lifetimes, it was calculated that the two fluorescing cm(III) species have one or two and no water molecules left in their first coordination sphere, suggesting that these species are incorporated into the CSH structure.

The curium(III) interaction with cement was also investigated by /Stumpf et al. 2004/ using time-resolved laser fluorescence spectroscopy at trace concentrations. Four different Cm(III) species were identified: a nonfluorescing species which corresponds to curium hydroxide real colloids, a fluorescing Cm(III)/portlandite sorption species, and two fluorescing Cm(III)/calcium silicate hydrate (CSH) species. From the fluorescence emission lifetimes it is predicted that the two fluorescing Cm(III)/CSH species have one to two and no water molecules, respectively, left in their first coordination sphere, suggesting that these species are incorporated into the CSH structure

Immobilization of Sn(IV) onto calcium silicate hydrates (C-S-H) and hardened cement paste (HCP) was investigated by combining wet chemistry experiments with X-ray absorption spectroscopy (XAS) Bonhoure et al. 2003. The study demonstrated evidences for formation of a Sn(IV) inner-sphere surface complex on C-S-H with a CaO/SiO2 weight ratio of 0.7. In HCP, the formation of a different type of Sn(IV) inner-sphere complex was observed, indicating that C-S-H may not be the uptake-controlling phase for Sn(IV) in the cement matrix. /Bonhoure et al. 2003/ also developed an alternative structural model for Sn(IV) binding in HCP, assuming that ettringite is the uptake-controlling phase. At high Sn(IV) concentrations, Sn(IV) immobilization in HCP occurs due to the formation of $CaSn(OH)_6$.

To study processes occurring in connection to solidification/stabilization by cement of metal-bearing hazardous waste, zinc oxide was added during hydration of alite (C_3S) by /Tommaseo and Kersten 2002/. The reaction products were sampled at various intervals and analyzed by X-ray diffraction and EXAFS. Calcium zincate hydrate ($CaZn_2(OH)_6 \times 2H_2O$) initially formed together with CSH disappeared from X-ray diffractograms after 14 d, and no other crystalline Zn-bearing phase could be detected thereafter. Based on EXAFS data analysis a structural model for the site occupation of Zn in CSH was proposed in which $Zn(O,OH)_4$ tetrahedra are bound in layer rather than interlayer positions substituting for the silicate bridging tetrahedra and/or at terminal silicate chain sites.

Chemical change of trace zinc in ordinary Portland cement was investigated in a hydration process using XANES and EXAFS /Tsuyumoto and Uchikawa 2004/. The interatomic distances and the coordination numbers of the first and the second shells calculated from EXAFS spectra indicated that ZnO hydrolyzed to zincate ion $[Zn(OH)_4]^{2-}$ with cement hydration keeping their fundamental structure of ZnO_4 tetrahedra.

/Schlegel et al. 2004/ studied the uptake of Eu by C-S-H phases as a function of Eu/sorbent ratio, and initial supersaturating conditions was probed by solution kinetics experiments and EXAFS. The rates of Eu uptake in C-S-H suspensions and in solutions at equilibrium with C-S-H were rapid;. more than 90% of dissolved Eu was generally sorbed within 15 min. Europium EXAFS spectra collected on samples of Eu sorbed on, or co-precipitated in, C-S-H differed from that of Eu(OH)(3)(s) expected to precipitate under the pH conditions of C-S-H waters, ruling out compelling precipitation of pure hydroxide phases. The results indicated that sorbed or coprecipitated Eu is located at Ca structural sites in a C-S-H-like environment. Kinetics and spectroscopic results are consistent with either Eu diffusion within C-S-H particles or precipitation of Eu with Ca and Si creating a C-S-H-like solid phase.

/Wieland et al. 2004/ performed batch experiments to study the possible reduction in sorption to HCP caused by colloidal material. In their experiments they used a colloidal matter corresponding to that of calcium silicate hydrates (CSH). Uptake studies were carried out with Cs(I), Sr(II) and Th(IV). The influence of uptake by colloids on radionuclide mobilisation was expressed in terms of sorption reduction on the immobile phase (HCP). At colloid concentration levels typically encountered in highly alkaline cement pore waters, colloid-induced sorption reduction is predicted to be negligibly small even for strongly sorbing radionuclides, such as Th(IV).

4.4 The effect of complexing ligands on metal ion sorption

This section reviews the effect of complexing ligands on the sorption of metal ions to mineral particles. While the first part covers a broader range of metal ions, those of special interest in nuclear waste management, such as Cs(I), Ni(II) and lanthanides and actinides, are addressed later on. Most of the investigations reviewed are performed in the laboratory with well-defined solid phases. The section ends with a discussion of a number of papers reporting field studies or column experiments involving field materials.

4.4.1 Laboratory studies of metal ion sorption in presence of ligands

The presence of organic and inorganic ligands in the aqueous solution may affect the adsorption behaviour of metal ions significantly. Adsorption of ions to the particles affects the surface charge. Hence, the sorption processes is affected in a rather unspecific manner induced by a changed electrostatic environment. Furthermore, ions may also form complexes with surface sites at the particle surfaces as well as with metal ions in the aqueous solution. For instance, that the adsorption of Pb(II) /Gunneriusson et al. 1994/ and Hg(II) /Gunneriusson et al. 1995/ to goethite (α-FeOOH) is affected by chloride ions, although the effect was different for the two metal ions. While the chloride ions shifted the adsorption edge of Pb(II) to slightly lower pH, the adsorption of Hg(II) was strongly decreased in the presence of chloride ions. The stronger adsorption of Pb(II) was interpreted in terms of formation of ternary surface complexes of the type ≡FeOPbCl. In the case of Hg(II), formation of very strong aqueous complexes, above all $HgCl_2(aq)$, reduced the amount of adsorbed mercury.

What concerns organic ligands, the class of substance that plays the most significant role in sorption processes is carboxylic acids. Structural features determine which types of interactions that are possible. Although other structural units, such as hydroxyl and amine groups, can take part in coordination reactions, the carboxylate groups play a particularly important role. As in homogeneous solution the number of functional groups available for coordination of metal ions largely determines their properties. Monodentate ligands, such as acetate ions and bensoate are weak ligands and do not affect metal adsorption to any substantial extent. On the other hand, multidentate ligands, e.g. citrate, lactate, nitrilotriacteic acid (NTA) and ethylenediaminetetraacacetic acid (EDTA) can strongly alter the metal adsorption pattern. As indicated earlier, the ligands can both increase and decrease the metal ion adsorption.

Which effect a certain ligand may impose is also coupled to solution pH. Metal adsorption is often increased at low pH due to reduced surface charge and/or formation of ternary surface complexes of Type B, i.e. complexes in which the metal ions is adsorbed to the surface by coordinating a molecule that is adsorbed to surface functional groups. At higher pH, formation of aqueous complexes can result in decreased adsorption. An alternative fate at higher pH is formation of ternary surface complexes of Type A, which are complexes formed by adsorption of ligands to metal ions coordinating surface atoms of the solid matter. All different types of complexes may be formed simultaneously in the same system. It has turned out to be difficult to predict which type of interaction that is the governing.

In the case of polydentate ligands, such as EDTA, the effect of the ligand upon the adsorption of metal ions can be very strong. Actually, there can be a completely reversed pH-dependence for the metal ion adsorption. /Nowack et al. 1996/ have shown that EDTA induced removal of Ni and Pd from the solution by ternary complex formation on goethite at low pH. At high pH desorption of EDTA, to which the metal ions are coordinating, results in desorption of these metals. A similar observation for Co(II) adsorbed to δ-Al_2O_3 was made by /Girvin et al. 1993/. In the same paper, Girvin and co-workers studied Co(III) adsorption. The effect of EDTA at low pH was in this case less pronounced, but still significant. At high pH all Co(III) was found in the aqueous solution.

/Bargar et al. 1999/ performed Fourier transform infrared (FTIR) and extended X-ray absorption fine structure (EXAFS) spectroscopic measurements on Pb(II)ethylenediamine-tetraacetic (EDTA) adsorbed on goethite in the range pH 4 to 6 and at different ionic strength. The FTIR measurements showed no evidence for carboxylate-Fe(III) bonding or protonation of EDTA at Pb:EDTA = 1:1. Both FTIR and EXAFS spectroscopic measurements suggested that EDTA acts as a hexadentate ligand, with all four of its carboxylate and both of its amine groups bonded to Pb(II). No evidence was observed for inner-sphere Pb(II)-goethite bonding at Pb:EDTA = 1:1. The substantial uptake of $PbEDTA(II)^{2-}$ was interpreted by that $Pb(II)EDTA^{2-}$ was adsorbed as outer-sphere complexes and/or as complexes that have lost part of their solvation shells and was hydrogen bonded directly to goethite surface sites. The authors proposed the term "hydration-sphere" for the latter type of complexes because they should occupy space in the primary hydration spheres of goethite surface functional groups and to distinguish this mode of sorption from common structural definitions of inner- and outer-sphere complexes.

Another example of spectroscopic evidences for ternary surface complexation was presented by /Lenhart et al. 2001/. By using EXAFS and ATR-FTIR measurements they observed that a major fraction of surface-bound malonate was bonded to adsorbed Pb(II). In the absence of Pb(II), ATR-FTIR measurements of sorbed malonate suggest the formation of more than one malonate surface complex. The dissimilarity of the IR spectrum of malonate sorbed on hematite to those for aqueous malonate indicated that at least one of the sorbed malonate species was directly coordinated to surface Fe atoms in an inner-sphere mode, Little change was seen in the IR spectrum for sorbed malonate in the presence of Pb, indicating that geometry of malonate as it coordinates to sorbed Pb(II) adions is similar to the geometry of malonate as it coordinates to Fe in the hematite surface, which was interpreted as that malonate was bonded to sorbed Pb(II), i.e. forming ternary metal-bridging surface complexes.

Humic substances are of particular importance for metal speciation and mobility in natural water systems. Besides being omnipresent in natural waters and in soils the humic substances offers a wide range of structural units capable of complexing metal ions. A pioneering work is the study by /Tipping 1983/ of Cu adsorption onto goethite (α-FeOOH) in the absence and the presence of humic substances. Tipping found that the copper adsorption was enhanced under weakly acidic conditions and decreased at higher pH.

Similar results were obtained by /Zachara et al. 1994/ in his study of Co(II) adsorption to subsurface mineral materials. Zachara observed a shift in adsorption edge of Co towards lower pH in the range of 0.5 to 1 pH unit in the presence of leonardite humic acids (LHA). At higher pH the solubility enhancing aqueous complexation of Cu by LHA was not found in more than one case. However, it should be noted, that the net effect of the simultaneously occurring complexation reactions is not only depending on the affinity between the different components of the system but also on ratios in total concentration of metal ions and ligands as well as the reactive surface area, i.e. the total concentration of surface functional groups available for adsorption. In his book on cation binding to humic substances /Tipping 1998/ has reviewed the vast literature on this subject.

4.4.2 Radionuclide sorption in presence of ligands relevant to nuclear waste repositories

Complexation in solution

Organic additives that may be used in the preparation of cementitious materials in the construction and backfilling of a radioactive waste repository vault can change the solubility and sorption behaviour of radionuclides in the repository. /Greenfield et al. 1998/ studied the effects of two cement additives on the solubilities of Tc, U, Pu and Am at pH 12. They found, radionuclide solubility enhancements up to more than two orders of magnitude, which was interpreted in terms of the formation of aqueous complexes involving metal ions, the organic additives and hydroxide ions.

The complexation of Th(IV) and Eu(III) by α-isosaccharinic acid (ISA) was studied in the pH range from 10.7 to 13.3 by batch sorption experiments, and the influence of Ca on the complexation was investigated /Vercammen et al. 2001/. Based on best-fit analysis of the sorption data, it was postulated that 1:1 Th:ISA complexes were formed in the absence of Ca according to the complexation reaction:

$$\mathrm{Th} + \mathrm{ISA} \leftrightarrow (\mathrm{ThISA})(-4\mathrm{H}) + 4\mathrm{H}^+ \qquad (13)$$

with log K = –10.1 (I = 0.3 M). In the presence of Ca, the sorption data was interpreted best by a mixed-metal complex, according to the complexation reaction:

$$\mathrm{Th} + 2\mathrm{ISA} + \mathrm{Ca} \leftrightarrow (\mathrm{Th(ISA)_2Ca})(-4\mathrm{H}) + 4\mathrm{H}^+ \qquad (14)$$

with log K = –3.6 (I = 0.3 M). There were no indications that Ca participated in complexes of ISA with Eu. The sorption data suggested that 1:I Eu:ISA complexes are dominant in the pH range from 10.7 to 13.3 according to the complexation reaction:

$$\mathrm{Eu} + \mathrm{ISA} \leftrightarrow (\mathrm{EuISA})(-4\mathrm{H}) + 4\mathrm{H}^+ \qquad (15)$$

with log K = –30.6 (I = 0.3 M). It should be noted that the stoichiometric numbers and stability constants proposed are dependent of the hydrolysis reactions of the two metal cations.

The effect of humic substances on radionuclide sorption has been studied by /Glaus et al. 2000/ who determined conditional stability constants for the formation of complexes of Aldrich humic acid with Ca^{2+}, NpO_2^+, Co^{2+}, Ni^{2+}, UO_2^{2+} and Eu^{3+}, and complexes of two fulvic acid samples with Co^{2+},UO_2^{2+} and Eu^{3+}. The authors used the equilibrium dialysis-ligand exchange method in a pH-range 5 to 10 at different ionic strengths (0.02 to 0.2 M). The equilibrium coefficients increased in the order $Ca^{2+} < NpO_2^+ < Co^{2+} < Ni^{2+} < UO_2^{2+} < Eu^{3+}$. The influence of ionic strength was of less importance for all metals tested, and the conditional stability constants did not significant depend on the type of humic substance.

The effect of ligands on sorption of radionuclides to minerals and cement materials

There is a rather limited number of studies published concerning the effects of organic matter on radionuclide sorption to minerals and other materials relevant for repositories of radioactive waste, including cement materials. In many cases, these studies have been focused on authentic and simulated products of degradation of cellulose, often simulated by isosaccharinic acid and gluconic acid. Initially in this section, sorption studies dealing with pure mineral particles, including calcite, and clays are described followed by results from investigations of sorption studies dealing with cement materials.

The net effect of organic matter with metal complexing properties on radionuclide sorption is the sum of a number of simultaneously occurring processes which can enhance or suppress adsorption of metal ions to the solid phase: i) formation of ternary complexes at the water/solid interface involving both surface sites, metal ions and ligands, ii) metal-ligand complex formation in aqueous solution, iii) adsorption of anions to particles resulting in changes in surface charge favourable for sorption of cationic metals, iv) competition between different compounds for the same surface sites, v) formation of surface precipitates at the water/solid interface.

Baston and co-workers studied the effects of both authentic degradation products and model substances on the sorption to volcanic materials and clays of Pu and Th /Baston et al. 1994/ and of U, Th and Pu /Baston et al. 1992/ at pH 7–8 and pH 11–12. Gluconic acid resulted in significantly larger reduction in Th and Pu sorption to volcanic tuff (Borrowdale) than the authentic degradation products, especially at higher organic concentrations ($> 10^{-4}$ M). At lower concentrations of organic ligands, the reduction in sorption was small and in some cases the sorption was slightly enhanced. In the case of gluconate, the highest concentration tested (2×10^{-3} M) resulted in a significantly larger reduction at pH $\approx$ 8 than at pH $\approx$ 12. For iso-saccharinate the sorption reducing effect appeared to be slightly larger pH $\approx$ 12 than at pH $\approx$ 8. Finally, the sorption seemed to be unaffected by authentic degradation products at both pH.

/Baston et al. 1992/ did also study Pu, Th and U sorption to London clay, St. Bees sandstones and Caithness flagstones in absence and presence of gluconate and authentic degradation products (ADP). The reducing effect of gluconate on Th sorption was significantly stronger than that of ADP at pH $\approx$ 11 to all three geologic materials. However, when it came to pH $\approx$ 8, the picture became less clear. For London clay the sorption was strongly enhanced by the presence of gluconate at pH $\approx$ 9 and at a higher water to rock ratio. At pH $\approx$ 11 gluconate was an effective sorption reducer, even in the case of London clay. For the other two materials, the gluconate caused a strong decrease in sorption of Th at both pH. Uranium sorption was strongly reduced at both pH by all three geologic materials. Plutonium sorption appeared to be very sensitive to the presence of especially gluconate. The effects of ADP was much less and in several cases the sorption was increased when authentic degradation products was present, especially at higher pH. Similar results were obtained by /Berry et al. 1991/ in their study of U and Pu sorption onto London clay and Caithness flagstones.

/Tits et al. 2002/ found that ISA and GLU present in the solution at high concentrations affected the sorption of both Eu(III) and Th(IV) to calcite significantly. This effect was interpreted as complex formation in solution. In the case of Eu(III) the metal-ligand complexes were found to have a 1:1 stoichiometry. In the thorium systems it was assumed that a Th(IV) – ISA – Ca complex and a Th(IV) – GLU – Ca complex were formed at a 1:2:1 stoichiometry and with the complexation constants $\log\beta^0_{\mathrm{ThISA}} = -5.0$ and $\log\beta^0_{\mathrm{ThGLU}} = -2.14$. Assuming that the concentrations of ISA and GLU in the pore water of the disturbed zone are similar to the maximum concentrations estimated for the cement pore water in the near-field of the repository, i.e. 10^{-5} M ISA and 10^{-7} M GLU, then the formation of aqueous complexes with ISA or GLU would not significantly affect Eu(III) and Th(IV) sorption on calcite.

The adsorption of uranyl ions is significantly enhanced at low pH ($\leq$ pH 5) by the presence of citrate ions /Redden et al. 2001/. From EXAFS measurements in the range $3.5 < \text{pH} < 5.5$ two surface species were found: One species was identified as an inner-sphere, uranyl-goethite complex, which existed at pH 5.5 in the absence of citrate. A second species was interpreted to be an adsorbed uranyl + citrate complex displacing the binary uranyl-goethite complex as the concentration of adsorbed citrate increased. The uranyl + citrate surface complex appeared to dominate adsorbed uranyl speciation at ligand to metal ratios of 10 to 1, or when the total surface-bound citrate approached saturation. Although the exact structural configuration of the uranyl + citrate surface complex could not be identified, coordination between uranyl and one or more citrate molecules appeared to involve both a bidentate bond (four-membered ring structure) and a putative eight-membered ring structure.

Ternary uranyl-carbonate surface complexes have been identified in several studies, e.g. by /Bargar et al. 1999, 2000/ and /Waite et al. 1994/.

/Lenhart and Honeyman 1999/ reported results of a study of the effect of Suwannee river humic acid (HA) on U(VI) sorption to hematite over a range of other system conditions (e.g. pH and ionic strength). By postulating two ternary surface (Type A) complexes composed of the uranyl ion, hematite surface sites, and the model ligands comprising the HA it was found possible to simulate the HA effects on U(VI) sorption over a range of solution conditions using a general speciation model.

/Artinger et al. 1998/ studied the influence of aquatic humic substances on the transport behaviour of Am III. Quartz sand from the Gorleben site was equilibrated with groundwaters with different humic substance concentrations (DOC: 1 to 80 mg/l) under inert gas atmosphere with 1% CO for at least 3 months. Increasing humic substance concentration was found to reduce the Am sorption onto sand and enhance the transport as colloid-borne Am species. Results from column experiments indicated a reversible binding of Am onto mobile humic colloids. The observation that humic colloids were not significantly sorbed onto sand during the equilibration period of several months was seen as support to that the Am fraction retained on sand (94 to 66%) was not sorbed as humic colloid-complex.

The influence of humic acids (HA) on the retention of thorium (IV) onto the surface of silica colloids was investigated by /Reiller et al. 2002/ at 0.1 M $NaClO_4$. A strong reduction of the amount of Th(IV) sorbed onto silica in the presence of HA compared to silica colloids without HA was found. This was explained by a predominant part of thorium present in solution as humic complexes. In a pH range where no organic coating onto silica occurs there was a competition observed between Th sorption to silica and complexation by HA reactive functional groups. Large interaction constant values indicate a strong affinity of HA for Th(IV).

The influence of soil-derived fulvic acid (SFA) on Ni(II) sorption in boehmite (γ-AlOOH) suspensions was studied by /Strathmann and Myneni 2004/ using a combination of sorption experiments and EXAFS spectroscopy measurements. In SFA-free suspensions, Ni(II) is adsorbed by forming inner-sphere bidentate mononuclear complexes with surface aluminol groups. Addition of SFA resulted in increased Ni(II) sorption at pH conditions below the sorption edge observed in SFA-free suspensions and reduced Ni(II) sorption at pH above the SFA-free sorption edge. In presence of SFA, Ni(II) was found to adsorb by forming both ligand-bridging ternary surface complexes (Ni(II)-SFA-boehmite) as well as surface complexes in which Ni(II) ions remains directly bonded to aluminol groups (binary Ni(II)-boehmite or metal-bridging ternary surface complexes (SFA-Ni(II)-boehmite). The distribution of Ni(III) between different surface species depends heavily on geochemical conditions; the concentration of ligand-bridging complexes was found to increase with increasing SFA sorption and decreasing pH.

/Fairhurst et al. 1995/ studied the effect of pH (2–10) and humic acid (HA) concentration on the adsorption of HA onto several pure-phase inorganic colloids (δ-Al_2O_3, Fe_2O_3 (hematite), MnO_2, am-SiO_2 and TiO_2). The presence of HA was found to strongly influence the adsorption of Eu over the pH range investigated, except in the manganese dioxide system. In the absence of HA, Eu adsorption was shown to be highly pH dependent, adsorption increasing with pH. In the presence of HA, Eu adsorption generally showed an increase at low pH, which was interpreted as being due to adsorption of EuHA complexes onto the colloids. At high and intermediate pH, adsorption was generally reduced owing to desorption of EuHA complexes from the colloid surface, and because inorganic Eu species were being prevented from adsorbing onto the colloid surface, a possible cause being a blocking mechanism by the HA.

/Glaus et al. 2001, 2005/ studied sorption of Ni(II), Eu(III) and Th(IV) to 6 Opalinus Clay (OPA) samples from Mont Terri and Benken (Switzerland)in presence of water-extractable organic matter using an ion exchange technique. No significant differences in sorption were observed in most cases as compared with experiments without organic C. A minor reduction in sorption was observed for Eu(III) and Ni(II). By laser fluorescence spectroscopy it was shown that the extracts did not affect Cm(III) speciation. The authors suggested that the reduction of sorption occasionally observed in the ion exchange experiments was probably not caused by the formation of complexes between the radionuclides and the organic matter in the extracts, but was rather due to an underestimation of systematic uncertainties. The small effect of the dissolved organic substances and results of UV–VIS spectroscopic characterisation of the organic matter in the extracts indicated that only a negligible fraction of the organic matter present was in the form of humic or fulvic acids.

Sorption of ISA (isosaccharinic acid) to CSH was studied by /Van Loon et al. 1997/ at solid to liquid ratios ranging from 1:2 (10 g of cement:20 mL of APW) to 1:40. CSH was equilibrated in N_2 atmosphere with artificial cement pore water, containing ISA between 10^{-5} and 3×10^{-1} M, for 1 day, 1 week, 1 month, 3 months, and 9 months. The sorption of ISA on cement was fast, almost reaching equilibrium after one day. The affinity of ISA to binding sites at the cement surface was found to be strong since the negatively charged ISA molecules could overcome the electrostatic repulsion at the negatively charged cement surface.

The effect of alpha-isosaccharinic acid (ISA) on Th(IV) uptake by hardened cement paste (HCP) at pH 13.3 was studied by /Wieland et al. 2002/. It was observed that the formation of Ca-ISA complexes in solution enhances portlandite solubility. The fraction of portlandite dissolved from the HCP matrix depends on the solid to liquid (S/L) ratio of the system and the ISA concentration in solution. Th(IV) uptake by HCP was found to be reduced above an aqueous ISA concentration of about 10^{-4} M. Reduction of Th(IV) uptake was modelled invoking a Th : ISA : Ca = 1 : 2 : 1 complex in solution. The authors concluded that the formation of ternary Th(IV)-ISA complexes may be important in cement systems.

/Holgersson et al. 1998/ studied the effects of gluco-isosaccharinate on Cs(I), Ni(II), Pm(III) and Th(IV) onto and diffusion into crushed cement. While the sorption of Cs and Ni remained unaffected by the organic acid, a significant but transient reduction in sorption of Pm and Th was observed.

4.4.3 Field and column studies

The effect of complexing ligands on radionuclide mobility in geological materials has also been studied in several field and column studies. Below, a few examples are discussed.

/Kent et al. 1991/ performed a field scale tracer test in which the transport was studied of Zn complexed by EDTA in a shallow sand and gravel aquifer. The experiment covered a pristine recharge zone (oxic conditions) and a sewage-contaminated zone (slightly reducing conditions). In the polluted part of the aquifer the Zn was conservatively transported as Zn-EDTA complexes which were only weakly adsorbed to the soil minerals. In the unpolluted zone the Zn was strongly retarded. This was interpreted as being the result of Fe(III) replacing Zn(II) in the EDTA complexes. Hence, the Zn(II) was made available for adsorption to mineral particles. Similar results were obtained in a later experiment at the same site involving Ni-EDTA and Zn-EDTA complexes /Kent et al. 2002/.

Cobalt migration through glacial sand was studied in a fulvic rich groundwater by /Warwick et al. 1991/. As long as the cobalt was associated with fulvic acid present in the groundwater the metal appeared to be mobile. A column test indicated that dissociation of the complexes resulted in increased adsorption of Co to the sand.

In a field experiment $Co(II)EDTA^{2-}$, $CdEDTA^{2-}$, and Cr(VI) were injected into a fracture zone of a contaminated fractured shale bedrock and monitored for 500 days by /Jardine et al. 2002/. A significant retardation of the chelated radionuclides and metals by the solid phase was observed. The retardation was explained largely by redox reactions and sorption related to dissociation of the radionuclide-EDTA complexes coupled to formation of Fe(III)-EDTA complexes. This was believed to be the result of surface interactions with biotite which was the only Fe(III)-bearing mineral phase present in these Fe-reducing environments.

Migration experiments were performed to study the influence of aquatic humic substances on the transport behaviour of Am-241(III). Four groundwaters with different humic substance concentrations (DOC: 1 to 80 mg/l) were sampled together with Pleistocene aeolian quartz sand from the Gorleben site. Sand, groundwaters and humic substances were characterized by different analytical methods (e.g. ICP-MS, X-ray diffraction, X-ray fluorescence analysis, ultrafiltration). The sand was equilibrated with each groundwater under inert gas atmosphere with 1% CO2 for a period of at least 3 months. As confirmed by ultrafiltration, the size distribution of humic colloids remained unchanged during equilibration. The hydraulic properties of sand columns were characterized with tritiated water as an inert tracer. Column and batch experiments were carried out with each groundwater as a function of the reaction period and flow velocity. In addition, the influence of the equilibration period of Am with groundwater was investigated prior to the injection into a column. The results revealed that increasing humic substance concentration reduced the Am sorption onto sand and enhanced the transport as colloid-borne Am species. The migration of colloid-borne Am was slightly faster than the groundwater flow velocity. Furthermore, the migration behaviour of Am was found to depend on kinetically controlled interaction of humic colloid-bound Am with the sand surface. Artinger et al. 1998.

A mobility enhancing effect of the humic substances was also observed by /Liu et al. 2001/ in a column experiment involving neptunium, plutonium and americium. The mobility of Np and Pu was increased by addition of humic substances. On the other hand, no influence was observed on Am.

5 Discussion

The present review of research performed in the field of radionuclide sorption to inorganic materials, including mineral particles and cement, reveals that the solubility and hence the mobility of radionuclides in soils, bedrock and in engineered barriers can be significantly affected by the presence of complexing ligands. However, the net effect of all the different simultaneously occurring geochemical reactions is dependent on both the stability of every species and the ratios in total concentration of each of the individual components involved. Therefore, *a priori* predictions of the effect of complexing agents on metal ion sorption cannot be made without thermodynamic information for all interactions in the different subsystems and in the multicomponent system. Unfortunately, model parameters for multi-component equilibrium systems are greatly lacking. Some simplifications may be allowed, but still there is no universal tool available for predictions in systems previously not studied. Despite the great research efforts made in the field of metal coordination at mineral surfaces during the last two decades, not many systems have been addressed by both structural and equilibrium studies resulting in information applicable in equilibrium modelling. With regard to the complicated coordination environment of cement, providing opportunities for both adsorption reactions at surface sites and centres for formation of surface precipitates, it can be anticipated that the number of equilibrium models for metal sorption to cement will be limited also in the future.

A common result in many of the studies reported here is that complexing ligands enhances the adsorption of metal cations at low pH, i.e. shifting the so called adsorption edge to lower pH. On the other hand, formation of aqueous metal-ligand complexes at higher pH can result in reduced adsorption. Once again it must be pointed out that the net effect of the presence of ligands is depending on both the stability of each individual species, in solution as well as at mineral surfaces, and of the total concentrations of the individual ligands and metals. An important difference between studying sorption processes on mineral particles and on cement is that studies in "non-cement" systems commonly cover wide pH-regions, from acidic to weakly alkaline to alkaline conditions. Experiments with cement is commonly restricted to the highly alkaline regions buffered by interactions between cement and water under a limited access to CO_2. This implies that the effect of ligands in cement systems commonly is limited to be solubility enhancing rather than increasing the adsorption. Another factor that should not be forgotten is that the high pH buffered by cementitious materials is a result of weathering/dissolution processes coupled to release of metal cations at high concentrations, above all K^+ and Na^+, but also Ca^{2+}, which have a potential of interacting with the organic chelators. Once again, the net effect is a result of the thermodynamics and ratios in total concentrations of the individual metals/ligands.

During the last decade it has become increasingly evident that the evaluation of data from uptake experiments, potentiometric titrations and other types of quantitative experiments is strongly facilitated by additional information from structural characterisation of surface species using various spectroscopic techniques, such as EXAFS and FT-InfraRed spectroscopy. Such combinations of information provide a powerful basis for the evaluation of equilibrium models which are sound from a structural point of view.

6 References

Akcay H, Kilinc S, 1996. Sorption and desorption of thorium from aqueous solutions by montmorillonite. J Radioanal Nucl Chem-Lett 212(3):173–185.

Allison J D, Brown D S, Novo-Gradac K J, 1991. MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems. EPA/600/3-91/021. USEPA Natl. Exposure Res. Lab, Athens, GA.

Altenheinhaese C, Bischoff H, Fu L, Mao J, Marx G, 1994. Adsorption of actinides on cement compounds. Journal of Alloy Compounds 213:554–556.

Angove M J, Johnson B B, Wells J D, 1997. Adsorption of cadmium(II) on kaolinite. Colloids and Surfaces A 126, 137–147.

Artinger R, Kienzler B, Schussler W, Kim J I, 1998. Effects of humic substances on the Am-241 migration in a sandy aquifer: column experiments with Gorleben groundwater/sediment systems. Journal of Contaminant Hydrology 35(1–3):261–275.

Bargar J R, Persson P, Brown G E, 1999. Outer-sphere adsorption of Pb(II)EDTA on goethite. Geochimica et Cosmochimica Acta 63 (19–20): 2957–2969.

Bargar J R, Reitmeyer R, Davis J A, 1999. Spectroscopic confirmation of uranium(VI)-carbonato adsorption complexes on hematite Environmental Science & Technology 33 (14): 2481–2484.

Bargar J R, Reitmeyer R, Lenhart J J, et al. 2000. Characterization of U(VI)-carbonato ternary complexes on hematite: EXAFS and electrophoretic mobility measurements. Geochimica et Cosmochimica Acta 64 (16): 2737–2749.

Baston G M N, Berry J A, Bond K A, Brownsword M, Linklater C M, 1992. Effects of organic degradation products on the sorption of actinides. Radiochimica Acta 58–9:349–356.

Baston G M N, Berry J A, Bond K A, Boult K A, Linklater C M, 1994. Effects of cellulosic degradation product concentration on actinide sorption on tuffs from the borrowdale volcanic group, sellafield, cumbria. Radiochimica Acta 66–7:437–442.

Berry J A, Bond K A, Ferguson D R, Pilkington N J, 1991. Experimental studies of the effects of organic materials on the sorption of uranium and plutonium. Radiochimica Acta 52–3:201–209.

Bonhoure I, Wieland E, Scheidegger A M, Ochs M, Kunz D, 2003. EXAFS study of Sn(IV) immobilization by hardened cement paste and calcium silicate hydrates. Environmental Science and Technology 37:2184–2191.

Bradbury M H, Baeyens B, 1999. Modelling the sorption of Zn and Ni on Ca-montmorillonite. Geochimica et Cosmochimica Acta 63(3–4):325–336.

Bradbury M H, Baeyens B, 2002. Sorption of Eu on Na- and Ca-montmorillonites: Experimental investigation and modelling with cation exchange and surface complexation. Geochimica et Cosmochimica Acta 66:2325–2334.

Brendler V, Vahle A, Arnold T, Bernhard G, Fanghanel T, 2003. RES^{3}T-Rossendorf expert system for surface and sorption thermodynamics. Contam Hydrol. 61(1–4):281–91.

Chen C C, Hayes K F, 1999. X-ray absorption spectroscopy investigation of aqueous Co(II) and Sr(II) sorption at clay-water interfaces. Geochimica et Cosmochimica Acta 63(19–20):3205–3215.

Chisholm-Brause C J, Berg J M, Matzner R A, Morris D E, 2001. Uranium(VI) sorption complexes on montmorillonite as a function of solution chemistry. Journal of Colloid and Interface Science 233(1):38–49.

Comans R N J, Haller M, De Preter P, 1991. Sorption of Cesium on illite: Non-equilibrium behaviour and reversibility. Geochimica et Cosmichimica Acta 55:433–440.

Comans R N J, Hockley D E, 1992. Kinetics of cesium sorption on illite. Geochimica et Cosmochimica Acta 56:1157–1164.

Combes J M, Chisholm-Brause C J, Brown G E Jr, Parks G A, Conradson S D, Eller P G, Triay I R, Hobart D E, Meijer A, 1992. EXAFS spectroscopic study of neptunium(V) sorption at the a-FeOOH/water interfaces. Environmental Science and Technology 26:376–382.

Cromieres L, Moulin V, Fourest B, Guillaumont R, Giffaut E, 1998. Sorption of thorium onto hematite colloids. Radiochimica Acta 82:249–255.

Davis J A, James R O, Leckie J O, 1978. Surface ionization and complexation at oxide/water interface. I: Computation of electrical double layer properties in simple electrolytes Journal of Colloid and Interface Science 63, 480–499.

Dähn R, Scheidegger A M, Manceau A, Curti E, Baeyens B, Bradbury M H, Chateigner D, 2002a. Th uptake on montmorillonite: A powder and polarized extended X-ray absorption fine structure (EXAFS) study. Journal of Colloid and Interface Science 249(1):8–21.

Dähn R, Scheidegger A M, Manceau A, Schlegel M L, Baeyens B, Bradbury M H, Morales M, 2002b. Neoformation of Ni phyllosilicate upon Ni uptake on montmorillonite: A kinetic study by powder and polarized extended X-ray absorption fine structure spectroscopy. Geochimica et Cosmochimica Acta 66:2335–2347.

Dähn R, Scheidegger A M, Manceau A, Schlegel M L, Baeyens B, Bradbury M H, Chateigner D, 2003. Structural evidence for the sorption of Ni(II) atoms on the edges of montmorillonite clay minerals: A polarized X-ray absorption fine structure study. Geochimica et Cosmochimica Acta 67(1):1–15.

Degueldre C, Wernli B, 1993. Association behavior of am-241(iii) on sio2(amorphous) and sio2(quartz) colloids. Journal of Environmental Radioactivity 20(3):151–167.

Degueldre C, Ulrich H J, Silby H, 1994. Sorption of 241Am onto montmorillonite, illite and hematite colloids. Radiochimica Acta 65:173–179.

Dzombak D A, Morel F M M, 1990. Surface Complexation Modeling: Hydrous Ferric Oxide, Wiley-Interscience, New York.

Fanger G, Skagius K, Wiborgh M, 2001. Project SAFE Complexing agents in SFR. SKB R-01-04, Svensk Kärnbränslehantering AB.

Fairhurst A J, Warwick P, Richardson S, 1995. The influence of humic acid on the adsorption of europium onto inorganic colloids as afunction of pH. Colloids and surfaces A: Physicochemical and engineering aspects 99:187–199.

Fenter P, Rivers M, Sturchio N, Sutton S (eds), 2002. Applications of Synchrotron Radiation in Low-Temperature Geochemistry and Environmental Science. Reviews in Mineralogy 49, Mineral. Soc. America.

Gabriel U, Charlet L, Schlapfer C W, Vial J C, Brachmann A, Geipel G, 2001. Uranyl surface speciation on silica particles studied by time-resolved laser-induced fluorescence spectroscopy. Journal of Colloid and Interface Science 239(2):358–368.

Gabriel U, Charlet L, Schläpfer C W, 2002. In situ speciation of uranium(VI) at the silica-water interface: A combined TRLIFS and surface complexation study. Pages 423–440 in Hellman RA, Wood SA (eds.) Water-rock inteactions, ore deposits and environmental geochemistry – A tribute to David A Crear. The Geochemical Society, St. Louis.

Girvin D C, Gassman P L, Bolton H, 1993. Adsorption of aqueous cobaltthylenediamine-tetraacetate by δ-Al_2O_3. Soil Science Societ of America Journal 57 (1): 47–57.

Glaus M A, Baeyens B, Lauber M, Rabung T, Van Loon L R, 2001. Water-extractable organic matter from Opalinus clay: Effect on sorption and speciation of Ni(II), Eu(III) and Th(IV). Nagra Technical Report 01-07.

Glaus M A, Hummel W, Van Loon L R, 2000. Trace metal-humate interactions. I. Experimental determination of conditional stability constants. Applied Geochemistry 15:953–973.

Glaus M A, Baeyens B, Lauber M, Rabung T, Van Loon L R, 2005. Influence of water-extractable organic matter from Opalinus Clay on the sorption and speciation of Ni(II), Eu(III) and Th(IV). Applied Geochemistry 20, 443–451.

Greenfield B F, Ilett D J, Ito M, McCrohon R, Heath T G, Tweed C J, Williams S J, Yui M, 1998. The effect of cement additives on radionuclide solubilities. Radiochimica Acta 82:27–32.

Gunneriusson L, Lövgren L, Sjöberg S, 1994. Complexation of Pb(II) at the goethite (α-FeOOH) water interface – The influence of chloride. Geochimica et Cosmochimica Acta 58 (22): 4973–4983.

Gunneriusson L, Baxter D, Emteborg H, 1995. Complexation at low concentrations of methyl and inorganic mercury(II) to a hydrous goethite (α-FeOOH) surface. Journal of Colloid and Interface Science 169 (2): 262–266.

Hiemstra T, Van Riemsdijk W H, Bolt G H, 1989a. Multisite proton adsorption modeling at the solid-solution interface of (hydr)oxides – a new approach.1. Model description and evaluation of intrinsic reaction constants. Journal of Colloid and Interface Science 133 (1): 91–104.

Hiemstra T, De Wit J C M, Van Riemsdijk W H, 1989b. Multisite proton adsorption modeling at the solid-solution interface of (hydr)oxides – a new approach.2. Application to various important (hydr)oxides. Journal of Colloid and Interface Science 133 (1): 105–117.

Hiemstra T, VanRiemsdijk W H, 1996. A surface structural approach to ion adsorption: The charge distribution (CD) model Journal of Colloid and Interface Science 179 (2): 488–508.

Holgersson S, Albinsson Y, Allard B, Boren H, Pavasars I, Engkvist I, 1998. Effects of gluco-isosaccharinate on Cs, Ni, Pm and Th sorption onto, and diffusion into cement. Radiochimica Acta 82:393–398.

Huang C P, Stumm W, 1973. Specific adsorption of cations on hydrous α-Al_2O_3 Journal of Colloid and Interface Science 22, 231.

Jakobsson A M, Albinsson Y, 1998. Sorption of NpO2+ and Co2+ onto TiO2. Radiochimica Acta 82:257–262.

Jakobsson A M, 1999. Measurement and modeling of Th sorption onto TiO2. Journal of Colloid and Interface Science 220(2):367–373.

Jakobsson A M, Lützenkirchen J, 2004. Towards a surface complexation model. Proceedings from International Workshop on Sorptopn processes at oxide and carbonate mineral surfaces – SOPRO 2004, 25–26 March 2004, Karlsruhe, Germany.

Jardine P M, Mehlhorn T L, Larsen I L, Bailey W B, Brooks S C, Roh Y, Gwo J P, 2002. Influence of hydrological and geochemical processes on the transport of chelated metals and chromate in fractured shale bedrock. Journal of Contaminant Hydrology 55(1–2):137–159.

Kent D B, Davis J A, Anderson L D, Rea B A, 1991. Transport of zinc in the presence of a strong complexing agent in a shallow aquifer on Cape Cod, Massachusetts. Pages 78–83 in Mallard GE, Aronson DA (eds.) U.S Geological Survey Toxic Substances Hydrology Program – Proceedings of the technical meeting, Monterey, California, March 11–15, 1991. US Geological Survey, Reston, Virginia.

Kent D B, Davis J A, Anderson L C D, Rea B A, Coston J A, 2002. Effect of adsorbed metal ions on the transport of Zn- and Ni-EDTA complexes in a sand and gravel aquifer Geochimica et Cosmochimica Acta 66 (17): 3017–3036.

Kowal-Fouchard A, Drot R, Simoni E, Marmier N, Fromage F, Ehrhardt J J, 2004. Structural identification of europium(III) adsorption complexes on montmorillonite. New Journal of Chemistry 28, 864–869.

Kulik D A, 2004. On standard-state chemical potentials and activity coefficients of surface species on mineral-water interfaces. Proceedings from International Workshop on Sorptopn processes at oxide and carbonate mineral surfaces – SOPRO 2004, 25–26 March 2004, Karlsruhe, Germany.

Lenhart J J, Honeyman B D, 1999. Uranium(VI) sorption to hematite in the presence of humic acid. Geochimica et Cosmochimica Acta 63(19–20):2891–2901.

Lenhart J J, Bargar J R, Davis J A, 2001. Spectroscopic evidence for ternary surface complexes in the lead(II)-malonic acid-hematite system. Journal of Colloid and Interface Science 234 (2): 448–452.

Liger E, Charlet L, Van Cappellen P, 1999. Surface catalysis of uranium(VI) reduction by iron(II). Geochimica et Cosmochimica Acta 63(19–20):2939–2955.

Liu C L, Yang Y E, Wang Z M, Li S S, Guo Z D, Li B, Jiang L, Jiang H, Wang L, Li D, Du Z D, 2001. Influence of humic substances on the migration of Np-237, Pu-238 and Am-241 in a weak loess aquifer. Radiochimica Acta 89(6):387–391.

Lomenech C, van der Lee J, 2004. Integrating sorption reactions in a thermodynamic database for use in speciation models. Proceedings from International Workshop on Sorptopn processes at oxide and carbonate mineral surfaces – SOPRO 2004, 25–26 March 2004, Karlsruhe, Germany.

Lu N P, Mason C F V, 2001. Sorption-desorption behavior of strontium-85 onto montmorillonite and silica colloids. Applied Geochemistry 16(14):1653–1662.

Lövgren L, Sjöberg S, Schindler P W, 1990. Acid/base reactions and Al(III) complexation at the surface of goethite. Geochimica et Cosmochimica Acta, 54: 1301–1306.

Marmier N, Delisee A, Fromage F, 1999a. Surface complexation modeling of Yb(III) and Cs(I) sorption on silica. Journal of Colloid and Interface Science 212(2):228–233.

Marmier N, Delisee A, Fromage F, 1999b. Surface complexation modeling of Yb(III), Ni(II), and Cs(I) sorption on magnetite. Journal of Colloid and Interface Science 211(1):54–60.

Marmier N, Fromage F, 1999. Comparing electrostatic and nonelectrostatic surface complexation modeling of the sorption of lanthanum on hematite. Journal of Colloid and Interface Science 212(2):252–263.

Miyazaki A, Matsuo M, Tsurumi M, 1996. Surface-complex formation between Zn ions and amorphous aluminosilicate in aquatic systems Journal of Colloid and Interface Science 177 (2): 335–338.

Moore R C, Gasser M, Awwad N, Holt K C, Salas F M, Hasan A, Hasan M A, Zhao H, Sanchez C A, 2005. Sorption of plutonium(VI) by hydroxyapatite.J. Radioanal. Nucl. Chem. 263 (1): 97–101.

Moulin I, Stone W E E, Sanz J, Bottero J Y, Mosnier F, Haehnel C, 1999. Lead and zinc retention during hydration of tri-calcium silicate: A study by sorption isotherms and Si-29 nuclear magnetic resonance spectroscopy. Langmuir 15(8):2829–2835.

Nowack B, Lutzenkirchen J, Behra P, Sigg L, 1996. Modeling the adsorption of metal-EDTA complexes onto oxides. Environmental Science and Technology 30 (7): 2397–2405.

O'Day P A, Chisholm-Brause C J, Towle S N, Parks G A, Brown G E Jr, 1996. X-ray absorption spectroscopy of Co(II) sorption complexes on quartz (a-SiO2) and rutile (TiO2). Geochimica et Cosmochimica Acta 60:2515–2532.

Ochs M, Lothenbach B, Giffaut E, 2002. Uptake of oxo-anions by cements through solid-solution formation: experimental evidence and modelling. Radiochimica Acta 90(9–11):639–646.

Olsson M, Jakobsson A M, Albinsson Y, 2003. Sorption of Pu(VI) onto TiO_2. J. Coll. Int. Sci. 266, 269–275.

Palmqvist U, Ahlberg E, Lövgren L, Sjöberg S, 1997. In situ voltammetric determinations of metal ions in goethite suspensions: Single metal ion systems. J. Colloid Interface Sci. 196: 254–266.

Parkhurst D L, Appelo C A J, 1999. Users guide to PHREEQC (version 2): A computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water Resources Investigations 99-4259.

Pearson R G, 1963. Hard and soft acids and bases Journal of the America.Chemical Society, 85 (22), 3533–3543.

Persson P, Lövgren L, 1996. Potentiometric and spectroscopic studies of sulfate complexation at the goethite-water interface Geochimica et Cosmochimica Acta 60 (15): 2789–2799.

Persson P, Nilsson N, Sjöberg S, 1996. Structure and bonding of orthophosphate ions at the iron oxide aqueous interface Journal of Colloid and Interface Science 177 (1): 263–275.

Pointeau I, Piriou B, Fedoroff M, Barthes M G, Marmier N, Fromage F, 2001. Sorption mechanisms of Eu^{3+} on CSH phases of hydrated cements. Journal of Colloid and Interface Science 236(2):252–259.

Prikryl J D, Pabalan R T, Turner D R, Leslie B W, 1994. Uranium sorption on α-alumina – effects of pH and surface-area solution-volume ratio. Radiochimica Acta 66–7:291–296.

Prikryl J D, Jain A, Turner D R, Pabalan R T, 2001. Uranium(VI) sorption behavior on silicate mineral mixtures. Journal of Contaminant Hydrology 47(2–4):241–253.

Redden G, Bargar J, Bencheikh-Latmar R, 2001. Citrate enhanced uranyl adsorption on goethite: An EXAFS analysis Journal of Colloid and Interface Science 244 (1): 211–219.

Reiller P, Moulin V, Casanova F, Dautel C, 2002. Retention behaviour of humic substances onto mineral surfaces and consequences upon thorium(IV) mobility: case of iron oxides. Applied Geochemistry 17:1551–1562.

Rose J, Moulin I, Hazemann J L, Masion A, Bertsch P M, Bottero J Y, Mosnier F, Haehnel C, 2000. X-ray absorption spectroscopy study of immobilization processes for heavy metals in calcium silicate hydrates: 1. Case of lead. Langmuir 16(25):9900–9906.

Rouff A A, Reeder R J, Fisher N S, 2002. Pb (II) Sorption with Calcite: A Radiotracer Study. Aquatic Geochemistry, 8(4): 203–228.

Scheidegger A M, Wieland E, Scheinost A C, Dahn R, Spieler P, 2000. Spectroscopic evidence for the formation of layered Ni-Al double hydroxides in dement. Environmental Science and Technology 34(21):4545–4548.

Scheidegger A M, Wieland E, Scheinost A C, Dahn R, Tits J, Spieler P, 2001. Ni phases formed in cement and cement systems under highly alkaline conditions: an XAFS study. J Synchrot Radiat 8:916–918.

Schindler P W, Gamsjäger H, 1972. Acid-base reactions of the TiO_2 (anastase) – water interface and the point of zero charge of TiO_2 suspensions. Kolloid Z. u. Z. Polymere, 250, 759–765.

Schlegel M L, Pointeau I, Coreau N, Reiller P, 2004. Mechanism of europium retention by calcium silicate hydrates: An EXAFS study. Environmental Science and Technology38 (16): 4423–4431.

Silvester E J, Charlet L, Manceau A, 1995. The mechanism of Cr(III) oxidation by Na-buserite. Journal of Physical Chemistry, 99, 16662–16669.

Silvester E R, Hudson E A, Allen P G, 2000. The structure of uranium (VI) sorption complexes on silica, alumina, and montmorillonite. Geochimica et Cosmochimica Acta 64(14):2431–2438.

Sjöberg S, Lövgren L, 1993. The application of potentiometric techniques to study complexation reactions at the mineral/water interface. Aquatic Science 55: 324–335.

Stern O, 1924. Zur theory der electrolytischen doppelschicht, Z. Electrochem, 30, 508.

Stipp S L S, Hansen M, Kristensen R, Hochella M F, Bennedsen L, Dideriksen K, Balic-Zunic T, Leonard D, Mathieu H J, 2002. Behaviour of Fe-oxides relevant to contaminant uptake in the environment Chemical Geology 190 (1–4): 321–337.

Strathmann T, Myneni S B, 2004. Effect of Soil Fulvic Acid on Nickel(II) Sorption and Bonding at the Aqueous-Boehmite (γ-AlOOH) Interface. Environmental Science and Technology 39,4027–4034.

Stumm W, Huang C P, Jenkins S R, 1970. Specific chemical interactions affecting the stability of dispersed systems, Croatica Chimica Acta 42, 223.

Stumm W, 1992. Chemistry of the Solid-Water Interface, Wiley Interscience.

Stumm W, Morgan J J, 1996. Aquatic chemistry. 3nd edition, John Wiley & sons, New York, 1996.

Stumpf T, Tits J, Walther C, Wieland E, Fanghanel T, 2004. Uptake of trivalent actinides (curium(III)) by hardened cement paste: a time-resolved laser fluorescence spectroscopy study. Journal of Colloid Interface Science 276 (1): 118–124.

Tipping E, 1983. The effect of adsorbed humic substances on the uptake of copper(II) by goethite. Chroatica Chimica Acta 56: 613–621.

Tipping E, 1998. Cation Binding by Humic Substances. Cambridge University Press

Tits J, Wieland E, Bradbury M H, Eckert P, Schaible A, 2002. The uptake of Eu(III) and Th(IV) by calcite under hyperalkaline conditions. PSI Bericht 02–03.

Tits J, Stumpf T, Rabung T, Wieland E, Fanghanel T, 2003. Uptake of Cm(III) and Eu(III) by calcium silicate hydrates: A solution chemistry and time-resolved laser fluorescence spectroscopy study Environmental Science and Technology 37,: 3568–3573.

Tommaseo C E, Kersten M, 2002. Aqueous solubility diagrams for cementitious waste stabilization systems. 3. Mechanism of zinc immobilization by calcium silicate hydrate. Environmental Science and Technology 36(13):2919–2925u.

Tsuyumoto I, Uchikawa H, 2004. Chemical speciation of trace zinc in ordinary Portland cement using X-ray absorption fine structure analysis. J. Amer. Ceram. Soc. 87 (12): 2294–2296.

Turner D R, Pabalan R T, Bertetti F P, 1998. Neptunium(V) sorption on montmorillonite: An experimental and surface complexation modeling study. Clays and Clay Minerals 46(3):256–269.

VanLoon L R, Glaus M A, Stallone S, Laube A, 1997. Sorption of isosaccharinic acid, a cellulose degradation product on cement. Environmental Science and Technology 31, 1243–1245.

Vercammen K, Glaus M A, Van Loon L R, 2001. Complexation of Th(IV) and Eu(III) by α-isosaccharinic acid under alkaline conditions. Radiochimica Acta 89 (6): 393–401.

Waite T D, Davis J A, Payne T E, Waychunas G A, Xu N, 1994. Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. Geochimica et Cosmochimica Acta 58,5465–5478.

Wang L, Maes A, De Canniere P, van der Lee J, 1998. Sorption of europium on illite (Silver Hill Montana). Radiochimica Acta 82, 233–237.

Warwick P, Hall A, Shaw P, Higgo J J W, Williams G M, Smith B, Haigh D, Noy D, 1991. The influence of organics in field migration experiments. 2. Radionuclide speciation and mobility studies. Radiochim. Acta 52: 465–471.

Westall J, Hohl H, 1980. A comparison of electrostatic models for the oxide/solution interface, Adv. Colloid Interface Sci, 12, 265.

Wieland E, Tits J, Dobler J P, Spieler P, 2002. The effect of alpha-isosaccharinic acid on the stability of and Th(IV) uptake by hardened cement paste. Radiochimica Acta 90:683–688.

Wieland E, Tits J, Bradbury M H, 2004. The potential effect of cementitious colloids on radionuclide mobilisation in a repository for radioactive waste Applied Geochemistry 19, 119–135.

Wierczinski B, Helfer S, Ochs M, Skarnemark G, 1998. Solubility measurements and sorption studies of thorium in cement pore water. Journal of Alloys and Compounds 271–273: 272–276.

Zachara J M, Resch C T, Smith S C, 1994. Influence of humic substances on Co^{2+} sorption by a subsurface mineral separate and its mineralogic components. Geochimica Cosmochimica Acta 58 (2): 553–566.

Ziegler F, Giere R, Johnson C A, 2001a. Sorption mechanisms of zinc to calcium silicate hydrate: Sorption and microscopic investigations. Environmental Science and Technology 35(22):4556–4561.

Ziegler F, Scheidegger A M, Johnson C A, Dahn R, Wieland E, 2001b. Sorption mechanisms of zinc to calcium silicate hydrate: X-ray absorption fine structure (XAFS) investigation. Environmental Science and Technology 35(7):1550–1555.