

**Effect of organic ligands on the sorption of europium on  $\text{TiO}_2$  and cement at high pH**

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

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# Abstract

Cement and cement-based materials are used as matrices and as containers for various categories of low-level and medium-level waste. The cement generally contains additives of various kinds, usually organic polymers that will act as plasticisers (up to a few percent). The degradation of these agents will, with time, generate low molecular organics and, eventually, carbon dioxide. The fraction of organic matter (ion exchange resins, filter materials, cellulose, cleaning agents etc) in the cement matrix will be therefore substantial. It can not be ruled out that these agents may act as metal complexing agents with ability to enhance the solubility and mobility of radionuclides from the radioactive waste within or in contact with the cement.

Laboratory studies were performed to assess the potential effects of cement additives, spent organic adsorbent resins and some organic cleaning agents in a cement/concrete system on the mobility and distribution of radionuclides using Eu(III) as a model element (for lanthanides as well as actinides in the trivalent state). Batch distribution studies were conducted in the following systems:

Solid adsorbents:	Standard Portland cement, TiO <sub>2</sub> .
Water phase:	0.3 M NaCl equilibrated with cement or TiO <sub>2</sub> ; 0 or 2 mM Ca (for the TiO <sub>2</sub> -systems); pH 12.5.
Organic ligands:	EDTA, DTPA, NTA, citric acid, D-gluconic acid, oxalic acid, fulvic acid, isosaccharinic acid, acetyl acetone, TTA.
Cement additives:	Sikament 10, Sikament 210, Peramin Conpac 30, Peramin F, Glenium 51, Cementa Melcrete, Mighty 150.
Cleaning agents:	Clax Delta Balans, Industrikombi, Prefect Citron.
Organics:	Dissolved organic matter from the degradation of two solid organic components: an ion exchange resin and a filter aid (Acrisorb LSR 33 and Ricem UP2).
Element:	Eu (10 <sup>-8</sup> M).

The distribution of Eu was measured radiometrically (constant solid/liquid ratio, 1g/L) as a function of time (up to 420 d) and additive concentration (0.001–10% of water phase) or as TOC concentration (0.3–8 mM). Distribution measurements were also performed using additives that had been stored at pH 12.5, 60°C, up to 107 d prior to the addition of solid adsorbent and Eu.

Generally, there is a significant reduction of the sorption (expressed as the distribution coefficient) of Eu on cement as well as on TiO<sub>2</sub> due to the presence of cement additives at concentration levels expected in fresh cement and concrete of technical quality.

Most of the liquid agents had some effect on the adsorption. The effects of the presence of these organic agents are compared and the presence of additives at various concentrations on the distribution of Eu is assessed. Possible consequences for the safety and performance of a cement-based waste deposition concept are analysed and discussed.

## Foreword

This report summarises the results from experimental work performed by M. Dario as part of his Ph.D. studies supervised by Prof. B. Allard. The evaluation of the data, reporting, and discussion of the data has been performed by the three authors.

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# 1 Introduction

Cement-based materials are used as the main near-field barriers in repositories for low- and intermediate level radioactive waste (L/ILW). Operational waste from nuclear power plants and similar waste from the industrial, health care and research sectors, has a low or intermediate level of radioactivity and a short half-life (after 500 years, the radioactivity of the waste will have declined to the level naturally present in the surrounding bedrock). It comprises dry waste, such as packaging, clothes and other protective equipment (*e.g.* concrete structures), scrap metal and wet waste, such as ion-exchange resins from nuclear power plant filter systems. The total level of radioactivity in the operational waste is a mere fraction of that found in the spent fuel. Operating waste contains thus, only traces of long-lived radioactive substances and, when stored normally, consists of concrete containing several organic substances, the composition and amounts of which vary considerably between repositories designed for different purposes /Albinsson et al, 1999/. Many of the organic substances are able to form complexes with radionuclides. At high pH values formation of complexes often reduces the sorption of metal ions /Holgersson et al, 1998; Ledin et al, 1993/ and increases the possibility of migration.

Complexing agents in or close to the waste have different origin:

1. Cement additives.
2. Chemicals used for decontamination and cleaning.
3. Soluble substances formed when ion exchange resins and similar products degrade.
4. Products from degrading cellulose, which is often present in L/ILW /Wiborgh, 1995/. At the high pH and calcium concentration of cement pore water the main degradation product of cellulose is isosaccharinic acid (ISA) /Bleas et al, 1957; Whistler and BeMiller, 1958/.
5. Humic substances, of which fulvic acid (FA) is a part, are present almost everywhere, even in deep groundwaters. Concentration of humic substances in these groundwaters is often very low (<1 mg/L) /Paxéus et al, 1985; Thurman, 1985/.

In addition to the above-mentioned substances some organic acids, which can be part of the other chemicals, are tested.

Two sorbent materials are used: Portland cement and titanium dioxide, TiO<sub>2</sub>.

L/ILW is often mixed with cement or placed in steel containers surrounded by cement. When cement degrades, pH is raised to 13.4, when NaOH and KOH dissolve. In a second step, pH drops to 12.5 when Ca(OH)<sub>2</sub> dissolves and in a third step silicate hydrate phases give a pH of approximately 10.5. The degradation is described in *e.g.* /Lagerblad and Trägårdh, 1995/. Calculations made by /Neall, 1994/ predict the pH in cement pore water to remain above 12.5 for 100000 years in a nuclear waste repository.

The other solid phase used as a sorbent, TiO<sub>2</sub>, is not present in a repository. The sorbents are compared in order to investigate if it is possible to use TiO<sub>2</sub> as an analogue to cement in the experiments. Titanium dioxide was chosen because it has very low solubility, and surface complexation can thus be studied at a wide pH interval without the interference of dissolution, and it has a p*H*<sub>pzc</sub> between the high values of alumina and iron oxides and the

lows of silica oxides /Jakobsson and Albinsson, 1998/. The sorption was studied at a constant pH, constant ionic strength and the use of a glove box precluded the presence of carbonate.  $\text{TiO}_2$  is stable at high pH /Neumueller, 1983/ and purchased as a powder, which needs almost no preparation before use compared to cement, that needs to be cast, crushed and sieved. The experiments are designed to resemble the conditions near cement, but some simplifications are made. The ionic strength of the background electrolyte is constant for all the experiments (0.3 M) and pH 12.5. Eu is not one of the most important elements in low- and intermediate level radioactive waste /Albinsson et al, 1999/, but it can be used as a model for other trivalent ions, e.g.  $\text{Am}^{3+}$  or  $\text{Pu}^{3+}$ . Eu is easier to handle than many other elements, which emit  $\alpha$ -radiation.

## 1.1 Objectives

The aim of this study was to find a method, as simple and fast as possible, to compare the influence of different complexing agents on the sorption of Eu.



## 2 Materials

### 2.1 Materials

#### 2.1.1 Eu

Radioactive  $^{152}\text{Eu}$  (Amersham) and inactive Eu was mixed to get appropriate concentrations and activities. The initial concentration of Eu(III) was  $1 \cdot 10^{-8}$  M. Eu(III) solutions contained at least 0.01 M HCl to avoid sorption to the vessel walls and precipitation. All Eu concentrations were determined by counting the  $\gamma$ -activity (LKB Wallac 1282 Compugamma).

#### 2.1.2 NaOH

To reduce the content of carbonate in the NaOH solution a 50% NaOH (by weight) solution was filtered through a fibre-glass filter to separate carbonate as  $\text{Na}_2\text{CO}_3$ . The filtrate was diluted and concentration determined by titration of potassium hydrogen phthalate.

#### 2.1.3 Background electrolyte solutions

$\text{NaCl}_{(\text{aq})}$  and  $\text{CaCl}_2_{(\text{aq})}$  were used as background electrolyte solutions to give a total ionic strength of 0.3M.

#### 2.1.4 Titanium dioxide

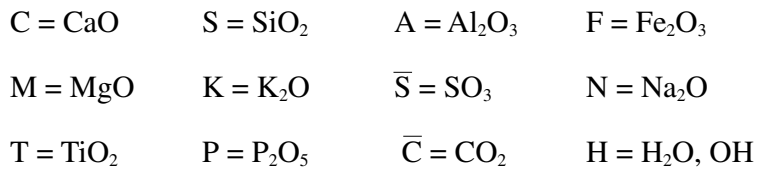
$\text{TiO}_2$  (Feinchemikalien und Forschungsbedarf GmbH, Karlsruhe) used in the sorption experiments was a powder with a particle size less than  $1 \mu\text{m}$  (estimated from SEM pictures) and a purity of 99.5%. The  $\text{TiO}_2$  was washed with a solution of 0.1 M HCl and 0.2 M NaCl and rinsed with 0.3 M NaCl at a pH of 9. The solid phase was separated from the solution by centrifugation (353 g, 10 min). The rinsing was completed, when the pH of the supernatant was 7–8. Then the  $\text{TiO}_2$  was rinsed with water once and dried for 6 days in  $80^\circ\text{C}$  and 1 day in  $130^\circ\text{C}$ .

The  $\text{TiO}_2$  was analysed with powder X-ray diffraction (XRD) to examine the phase composition (anatase/rutile/brookite). Surface area was determined by the BET method with  $\text{N}_2$ . The XRD measurement indicated that the  $\text{TiO}_2$  consisted of anatase and no other phases could be detected. The surface area was  $8.40 \text{ m}^2/\text{g}$ . With an assumed site density of  $12.5 \text{ sites}/\text{nm}^2$  /Sahai and Sverjensky, 1997/, the site concentration in the  $\text{TiO}_2$  suspension was  $1.7 \cdot 10^{-4}$  M, *i.e.* approximately 17000 times the Eu concentration.

Other authors /Jakobsson, 1999/ have proposed that the site density of  $\text{TiO}_2$  can be as low as  $1 \text{ site}/\text{nm}^2$ , being the site concentration in the  $\text{TiO}_2$  solution then  $1.4 \cdot 10^{-5}$  M, *i.e.* approximately 1400 times the Eu concentration.

## 2.1.5 Cement

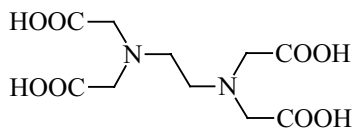
Standard Portland cement was cast in 40 mm acrylonitrilebutadienestyrene copolymer tubes. The ratio of cement to water was 2:1 by weight. After 1 day, the tubes were placed under water (to protect the cement from CO<sub>2</sub>) during 4 months. Then the cement was crushed and sieved. The fraction less than 0.125 mm was used in the experiments. Surface area was determined by the BET method with N<sub>2</sub>. The surface area was 9.34 m<sup>2</sup>/g. The mineralogical and chemical characterisation of Swedish standard Portland cement is shown in Table 2-1. Cement typical nomenclature is:



## 2.2 Complexing agents

### 2.2.1 Ethylenediaminetetraacetic acid (EDTA)

EDTA is an aminopolycarboxylate chelating agent (C<sub>10</sub> H<sub>16</sub> N<sub>2</sub> O<sub>8</sub>) which has the potential to perturb the natural speciation of metals and to influence metal bioavailability, through metal-exchange reactions in solution, adsorption to mineral surfaces, dissolution of minerals, and remobilisation of adsorbed metals.

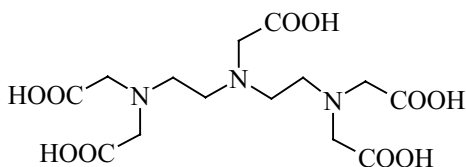


**Table 2-1. Mineralogical and chemical characterisation of a Standard Portland cement (weight %) /Lagerblad and Trägårdh, 1995/.**

Oxide	Notation	weight %	Mineral Components	Weight %
CaO	C	64.5	C <sub>3</sub> S	51
SiO <sub>2</sub>	S	22.2	C <sub>2</sub> S	25
Al <sub>2</sub> O <sub>3</sub>	A	3.5	C <sub>3</sub> A	1.2
Fe <sub>2</sub> O <sub>3</sub>	F	4.7	C <sub>4</sub> AF	14
MgO	M	1.0	Specific surface: 300 m <sup>2</sup> /kg	
SO <sub>3</sub>	$\bar{S}$	2.0	Density: 3200 kg/m <sup>3</sup>	
K <sub>2</sub> O	K	0.6		
Na <sub>2</sub> O	N	0.1		
Cl		< 0.01		
Free lime		0.8		

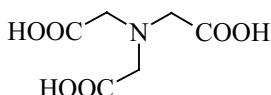
### 2.2.2 Diethylenetriaminepentaacetic acid (DTPA)

DTPA is also an aminopolycarboxylate chelating agent ( $C_{14}H_{23}N_3O_{10}$ ). DTPA belongs to the group of synthetic polyamino polycarboxylic acids which form stable complexes (metal chelates) with a large number of metal ions, such as plutonium, americium, californium, and curium. It is known that DTPA complexes are much more stable than those of EDTA /Anderegg et al, 1959/.



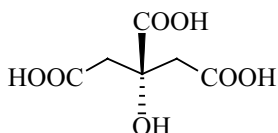
### 2.2.3 Nitrilotriacetic acid (NTA)

NTA is also an aminopolycarboxylate chelating agent ( $C_6H_9NO_6$ ). It is found in cleaning agents such as Industriekombi (See 2.4). NTA is a tetradentate ligand known to bind to a variety of transition metals with stability constants of  $10^9$  to  $10^{14}$  /Anderegg, 1982/.



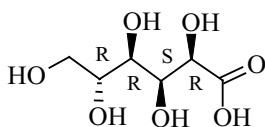
### 2.2.4 Citric acid

Citric acid or 2-Hydroxy-1,2,3-propanetricarboxylic acid with empirical formula:  $C_6H_8O_7$  is an organic carboxylic acid containing three carboxylic groups; it is a solid at room temperature, melts at  $153^\circ C$ , and decomposes at higher temperatures. It is obtained from citric salts or by fermentation of glucose with the aid of the mold *Aspergillus niger* and can be obtained synthetically from acetone or glycerol.



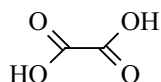
### 2.2.5 D-gluconic acid

This carbohydrate results from the oxidation of D-glucose. The biological (fermentation) method is at present the method of preference for industrial production of gluconic acid ( $C_6H_{12}O_7$ ). It can be used as an analogue to ISA (See 2.2.9). The values of the  $pK_{a,1}$  and  $pK_{a,2}$ , corresponding to deprotonation of two different alcohol groups are 13.66 and 14.02, respectively (1M  $NaClO_4$ ,  $25^\circ C$ ) /Coccioli and Vicedomini, 1978/.



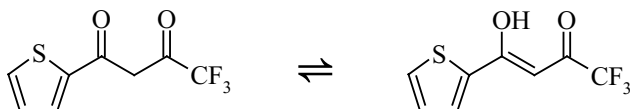
## 2.2.6 Oxalic acid

Oxalic acid or ethanedioic acid ( $C_2H_2O_4$ ) a colorless, crystalline organic carboxylic acid that melts at  $189^\circ C$  with sublimation. Oxalic acid and oxalate salts are poisonous. Oxalic acid is found in many plants usually as its calcium or potassium salts. Oxalic acid is the only possible compound in which two carboxyl groups are joined directly; for this reason oxalic acid is one of the strongest organic acids. Unlike other carboxylic acids (except formic acid), it is readily oxidised.

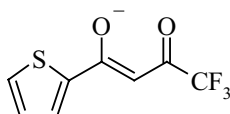


## 2.2.7 Thenoyltrifluoroacetone (TTA)

TTA or thenoyltrifluoroacetone is a complexing agent ( $C_8H_5F_3O_2S$ ) related to Acetyl Acetone (2.2.10). It is interesting to this study to see how the presence of the fluorocarbon group and thienyl ring affect the chemistry of the dione group.



At pH 12.5, TTA is deprotonated ( $pK_a = 6.42$ ) /Schweitzer and Andersson, 1968/ and the species that can complex with  $Eu^{3+}$  will be:



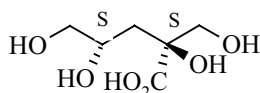
Ethanol was used to dissolve TTA, since this complexing agent is not soluble in water for concentrations higher than 0.9 mM TTA.

## 2.2.8 Fulvic acid (FA)

The FA used in these experiments was previously isolated from a surface water system and purified and characterised according to the procedure by /Pettersson and Allard, 1989; Pettersson et al, 1994/. Its acid capacity (carboxylic groups) was 4.60 meq/g, and molecular weights were 1580 (number average) and 2520 (weight average). The elemental composition (excluding the ash fraction) was 51.8% C, 3.7% H, 43.1% O, 0.8% N and 0.6% S. The concentration of FA is more important than the origin, with respect to metal complexing properties /Pettersson, 1992/. Consequently, FA from surface water can be used when simulating conditions in deep groundwaters.

## 2.2.9 Isosaccharinic acid (ISA)

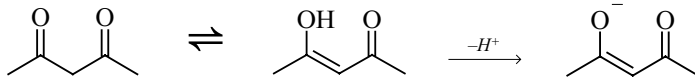
The most important cellulose degradation products with respect to their complexing properties are  $\alpha$ - and  $\beta$ -isosaccharinic acid /Van Loon and Glaus, 1998/. Calciumisosaccharinate was synthesised according to /Whistler and BeMiller, 1963/ and isosaccharinic acid ( $C_6H_{12}O_6$ ) was prepared from calciumisosaccharinate using a cation exchanger (DOWEX 5x50).



$\alpha$ -Isosaccharinic acid

### 2.2.10 Acetyl acetone (AcAc)

Acetyl acetone or pentane-2,4-dione is an organic synthetic intermediate and for instance is an additive of benzine. It is an analytical reagent and extractant with empirical formula  $C_5 H_8 O_2$ .



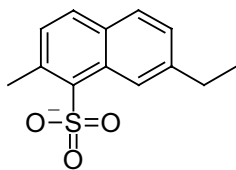
### 2.3 Cement additives

Seven superplasticisers were investigated. **Sikament 10**, **Sikament 210**, **Peramin Conpac 30**, **Peramin F**, **Glenium 51**, **Cementa Melcrete** and **Mighty 150**. Their content is described in Table 2-2. A superplasticizer is one of a class of admixtures called water-reducers that are used to lower the mix water requirement of concrete.

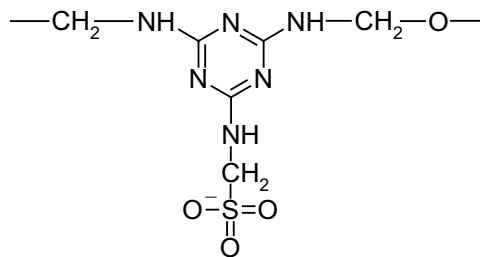
The **Sikament 10** cement additives are copolymers formed by radical polymerisation of N-vinylamides and derivatives of maleic anhydride.



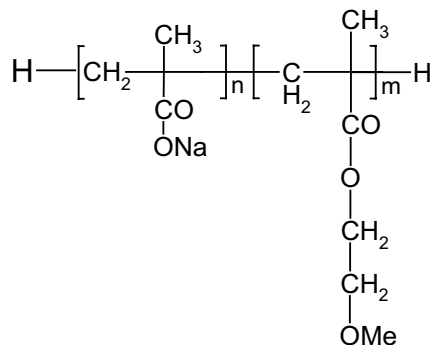
**Sikament 210** contains naphthalenesulfonic acid polymers with formaldehyde groups; **Peramin Conpac 30** is a polyether polycarboxylate; **Peramin F** is a melamine sulfonate polymer with formaldehyde, **Glenium 51** a modified polycarboxylic ether, **Cementa Melcrete** and **Mighty 150** are naphthalenesulfonic acid polymers with formaldehyde.



*Naphtalene formaldehyde condensate*



*Melamine formaldehyde condensate*



*Polycarboxylic acid-base admixture*

**Table 2-2. Complexing agents**

Complexing agents	Description	Empirical Formula / Contents	Conc.(%)	Manufacturer
Ethylenediaminetetra-acetic acid, EDTA	Organic ligand	C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>8</sub>		Merck
Diethylenetriaminepenta-acetic acid, DTPA	Organic ligand	C <sub>14</sub> H <sub>23</sub> N <sub>3</sub> O <sub>10</sub>		Merck
Nitrilotriacetic acid, NTA	Organic ligand	C <sub>6</sub> H <sub>9</sub> N O <sub>6</sub>		Merck
Citric acid	Organic ligand	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>		Merck
D-Gluconic acid	Organic ligand	C <sub>6</sub> H <sub>12</sub> O <sub>7</sub>		Merck
Oxalic acid	Organic ligand	C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>		Merck
Fulvic acid, FA	Organic ligand	51.8% C, 3.7% H, 43.1% O, 0.8% N 0.6% S		
Isosaccharinic acid, ISA	Organic ligand	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>		
Acetylacetone, AcAc	Organic ligand	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>		
4,4,4-Trifluoro-1-(2-thienyl) butane-1,3-dione, TTA	Organic ligand	C <sub>8</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> S		Merck
Sikament 10	Cement additive	Vinyl maleinic acid copolymer	20	Sika AG, Switzerland
Sikament 210	Cement additive	Naphthalenesulfonic acid, Polymer with formaldehyde	40	Sika AG, Switzerland
Peramin Conpac 30 Sweden	Cement additive	Polyether polycarboxylate	27–33	Perstorp AB,
Peramin F	Cement additive	Melamine sulfonate, polymer with formaldehyde	35 <sup>a</sup>	Perstorp AB, Sweden
Glenium 51	Cement additive	Modified polycarboxylic ether	35	Master Builders Inc. USA
Cementa Melcrete	Cement additive	Naphthalenesulfonic acid, Polymer with formaldehyde	30–60	Cementa AB, Sweden
Mighty 150	Cement additive	Naphthalenesulfonic acid, Polymer with formaldehyde	30–60	Cementa AB, Sweden
Clax Delta Balans	Cleaning agent	Sodium triphosphate	5–15 (200–600 mM)	Diversey Lever AB, Sweden
		Potassium silicate/metasilicate	15–30	
		Potassium hydroxide	1–5 (0.3–1.3 mM)	
Industrikombi	Cleaning agent	Sodium metasilicate	3–5	Nordex AB, Sweden
		Alcohols, C9–11, ethoxylated	5–7	
		Dipropylene glycol monomethyl ether	2–3	
		Sodium capryliminodipropionate	1–2	
		NTA	0.2–0.5 (10–30 mM)	
Prefect Citron	Cleaning agent	2-(2-Butoxyethoxy)ethanol	1–5	Rekal AB, Sweden
		Diethanolamine	0.1–1	
		Sodium polyethoxyethyl dodecyl-sulfate	0.1–1	
		Alcohols, C12–18, ethoxylated	1–5	
		Perfume, lemon		
Acrisorb LSR33	Ion exchanger	Metaacrylic polymer Polyvinylbenzyl trimethyl ammonium hydroxide		Aqua Chem SRL, Italy
Ricem UP2	Filter aid	Acrylonitrile polymer		Aqua Chem SRL, Italy

<sup>a</sup>dry content

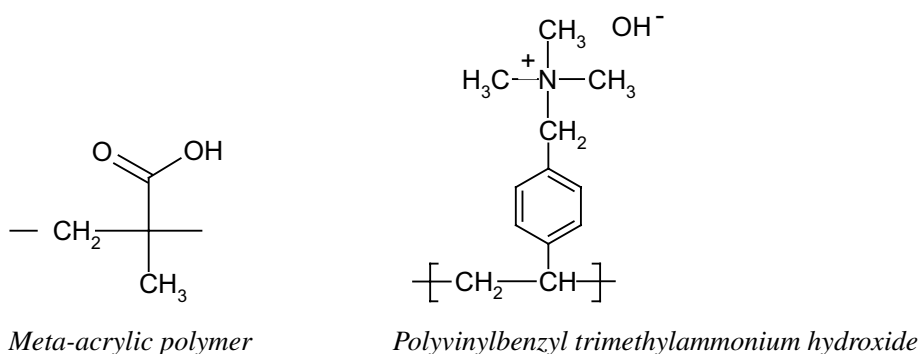
## 2.4 Cleaning agents

Three cleaning agents were investigated: **Clax Delta Balans**, which contains sodium triphosphate, **Industrikombi** which contains 11–27 mM NTA among others, and **Prefect Citron**, which contains non- and anionic surfactants. Their content is also described more in detail in Table 2-2.

## 2.5 Ion exchange resin

Ion exchange resins are used in the condensate clean up system in boiling water reactors in Swedish nuclear power plants (NPP). Used ion exchange resins are conditioned in bitumen or cement matrices and deposited off in SFR, the Swedish final repository for operational low and intermediate level waste.

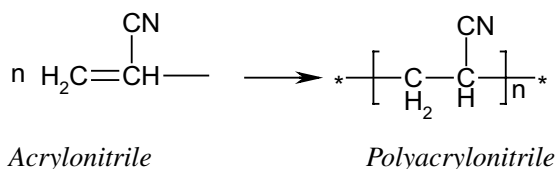
The ion exchange resin **Acrisorb LSR33** from *Aqua Chem* contains a weak cation exchange resin (meta-acrylic polymer) and a strong anion exchange resin (polyvinylbenzyl trimethylammonium hydroxide).



The resin was mixed with water (ratio 1:20 by weight) and the pH was adjusted to 12.5 with 5.5 M NaOH and the suspension was kept at 60°C. After 9–97 days, the suspension was centrifuged (24500 g, 1 h), the aqueous phase analysed with respect to total organic carbon and used in the above mentioned sorption experiments.

## 2.6 Filter Aid

**Ricem UP2** consists of fibers of polyacrylonitrile and was treated as the ion exchange resin, that is to say it was mixed with water, pH adjusted to 12.5 and the suspension kept at 60°C.



## 3 Experimental Setup

### 3.1 Sorption experiments

The batch sorption experiments with  $\text{Eu}^{3+}$  on  $\text{TiO}_2$  were carried out at pH 12.5: about 0.02 g of the solid phase ( $\text{TiO}_2$  or cement) was weighed directly into the centrifuge tubes, which were then transferred to the glove box. Milli-Q water, NaOH to adjust pH (at 12.3–12.7), NaCl to adjust ionic strength and, in most samples, a complexing agent and/or Ca was added (0 or 2 mM  $\text{Ca}^{2+}$ ). The total volume was about 20 mL, whereas the solid-to-volume ratio was kept constant at 1 g/L. The experiments were carried out in 50-mL screw-capped polyallomer centrifuge tubes. The tubes were shaken and left overnight for equilibration. The next day, Eu was added, the tubes transferred out of the glove-box and placed in a rotary tumbler for 24 h. Eu was analysed in 1 mL of the suspension. The difference between the total added Eu concentration and Eu concentration in the suspension is Eu adsorbed on the tube walls. The solid phase was separated from the solution by centrifugation (3920 g, 30 min to separate  $\text{TiO}_2$  and 24500 g, 1 h to separate cement). The efficiency of the separation was checked by measurements of particle concentration with photon correlation spectroscopy (Brookhaven BI90) according to /Ledin et al, 1993/ and of FA and ISA by measuring the total organic carbon (TOC) (Shimadzu 5000 TOC analyser). The latter proved that centrifugation did not remove the FA or ISA from the solution phase. 8 mL of the supernatant were transferred to another tube and the amount of Eu in solution was determined. Then pH was measured in the remaining part of the aqueous phase using a combination electrode (Radiometer Copenhagen, PHC 2412). The electrode was calibrated, using solutions of NaOH and NaCl. The total  $\text{Na}^+$  concentration in the pH-calibration solution was 0.3 M as in the sorption experiments in order to compensate for sodium error. The centrifuge tubes were washed with water and leached with 0.1 M HCl overnight on a rotary tumbler to desorb Eu from the tube walls. Eu was determined and sorption of Eu to the vessel walls was calculated.

Some samples were left for 36 or 60 weeks to monitor the variation of sorption with time. The samples were handled as the 24 h samples, except for the following. The total volume was about 30 mL in this experiment, but the initial solid-to-liquid ratio was also kept constant at 1g/L. After 1, 14, 28, 56, 112, 168, 252 and 420 days, 2 mL of the supernatant was analysed, the tubes shaken and placed in a rotary tumbler over night. Then the tubes were shaken in a rotary tumbler for 15 min three times a week.

To minimise the carbonate concentration, sample preparation was performed in a glove-box with nitrogen atmosphere. Exposure to light was avoided to prevent degradation of the complexing agents /Bahnmann et al, 1994/.  $\text{TiO}_2$  can act as a photocatalyst and increase the rate of degradation of the organic complexing agents /Bangun and Adesina, 1998; Kosanic, 1998/. The experiments were not carried out under sterile conditions and fungi and bacteria can grow at pH 11 /Griffin, 1985/. /Nordén, 1994/ performed similar experiments at pH 11–13 and found no microorganisms after 186 days. Chemicals used in the experiments were of analytical grade. Water was purified by a Milli-Q apparatus (Millipore Corp.), slightly acidified and heated to reduce the carbonate concentration. All containers were leached with acid (3 M  $\text{HNO}_3$ , 0.1 M HCl) for at least 15 h and rinsed with Milli-Q water.

The ionic strength was 0.3 M ( $[\text{NaOH}] + [\text{NaCl}] + 3 \cdot [\text{CaCl}_2] = 0.3 \text{ M}$ ) and the solid to liquid ratio was 1 g/L in all experiments. The temperature was kept at  $20 \pm 1$  °C. The distribution coefficients were calculated using the relation  $K_d = ((C_i - C_e) / C_e) V/m$  where  $C_i$  and  $C_e$



denote initial and equilibrium concentrations in solution ( $\text{Bq m}^{-3}$ ) respectively, and  $V/m$  solution-to-mass ratio ( $\text{m}^3/\text{kg}$ ).

In this work the concentration of the complexing agents (oxalate, citrate, EDTA, etc) is expressed in mol/L; the concentration of fulvic acid (FA) is given in g/L; the concentration of degradation products of ion-exchange resins and filter aid are given as total organic carbon, TOC, in mol/L; while the concentration of cement additives and cleaning agents (Sikament 10, Prefect Citron, etc) is expressed as *flp*: fraction of liquid phase (an *flp* value of  $10^{-6}$  corresponds to 1mL of additive in 1000 L of solution equilibrated with cement or  $\text{TiO}_2$ ).

### **Adsorption of Eu to the vessel walls**

Adsorption of Eu to the centrifuge tubes was measured in two ways:

1. The adsorption was calculated as the difference between total added amount of Eu and Eu left in the aqueous solution. In some experiments, part of  $\text{TiO}_2$ , and Eu sorbed on it, was sorbed on the tube walls. This leads to an overestimation of the adsorption on the tube walls.
2. The tube was washed with water and leached with acid and the amount of Eu in the acid was analysed. If some Eu was lost during the washing, this method leads to an underestimation. This was made on the first 100 samples with  $\text{TiO}_2$  as the solid phase, and on all samples with cement as the solid phase. Log  $K_d$  decreased at most 0.013 and this correction was not necessary, when  $\text{TiO}_2$  was the solid phase. When cement was used as the solid phase, the difference between the corrected and not corrected log  $K_d$  values was larger: 12 of 121 samples showed a difference of more than 0.10 and the highest value was 0.40.

## **3.1 Degradation of organics**

Additional experiments were performed to study the effect on the sorption of Eu onto  $\text{TiO}_2$  and cement with partially degraded organics, both cement additives and an ion exchange resin (Acrisorb LSR33) and a filter aid (Ricem UP2).

Cement additives were diluted 10 times with distilled water, pH adjusted (12.5) with NaOH and stored in solution at 20, 40 or 60°C for different periods of time. Batch sorption experiments as described before were performed with these solutions containing organic degradation products at pH 12.5, the conditions are listed in Table 3-1. The samples were handled as the 24h samples.

The ion exchange resin and the filter aid were mixed with water, the pH adjusted (12.5) with NaOH and stored in solution at 60°C for different periods of time. In some solutions the Ca(II) concentration was adjusted to 0.01 M. The solutions were centrifuged (24500g, 1h) before use. Batch sorption experiments as described before were performed with these solutions containing organic degradation products at pH 12.5. The samples were handled as the 24h samples.

**Table 3-1. Bath sorption experiments performed with degradation products of cement additives.**

Organic complex	Temperature (°C)	Log Fraction liquid phase ( <i>flp</i> ) <sup>a</sup>	Sorbent material
Sikament 10	20	-3	TiO <sub>2</sub>
	40	-3	TiO <sub>2</sub>
Sikament 210	20	-3.5	TiO <sub>2</sub>
	60	-3.5	TiO <sub>2</sub>
Peramin Conpac 30	20	-3.5	TiO <sub>2</sub>
	40	-3.5	TiO <sub>2</sub>
Peramin F	60	-2	TiO <sub>2</sub>
	60	-2	Cement
	60	-4	Cement
Cementa Melcrete	60	-3.5	TiO <sub>2</sub>
	60	-3.5	Cement
Mighty 150	60	-4	TiO <sub>2</sub>
	60	-4	Cement
Glenium 51	20	-2,5	TiO <sub>2</sub>
	60	-2,5	Cement

<sup>a</sup> *flp*: fraction of liquid phase

### 3.2 Ligand sorption experiments

The sorption of water-soluble organic acids with known composition (EDTA, DTPA, NTA, citric acid, gluconic acid, oxalic acid, FA, ISA and AcAc) to TiO<sub>2</sub> and cement was investigated according to the same procedure as the sorption of Eu. The quantity of organic acid adsorbed was calculated as the difference between the total amount acid added and the amount remaining in solution after phase separation. Quantification of the acids was accomplished by TOC measurements (Shimadzu 5000 TOC analyzer). In some experiments, the concentrations of acid and solid phase were increased to get more accurate TOC measurements. Sorption times were 1 and 28 d.

## 4 Results and modelling

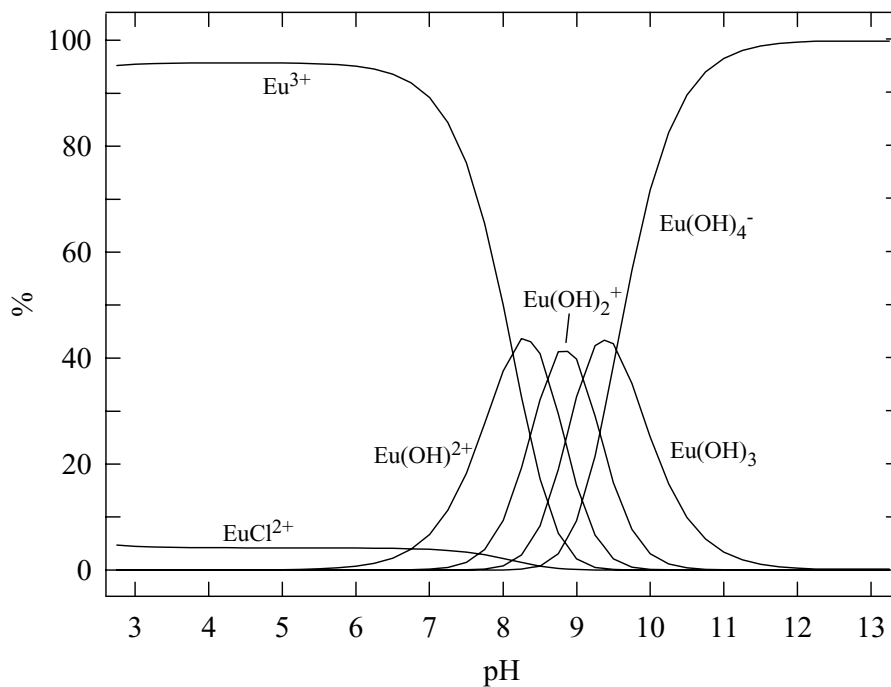
### 4.1 Introduction

A generic term devoid of mechanism and used to describe the partitioning of aqueous phase constituents to a solid phase is **sorption**. It is frequently quantified by the partition coefficient,  $K_d$ , and is defined as the ratio of the quantity of the solute adsorbed per unit mass of solid to the amount of the solute remaining in solution at equilibrium.

$$K_d = \frac{\text{amount of sorbed species per mass unit}}{\text{amount of species in solution per volume unit}} = \left[ \frac{\text{m}^3}{\text{kg}} \right]$$

#### 4.1.1 Solution chemistry of Eu(III) and of the ligands studied

The speciation of europium in aqueous solutions can be seen in Figure 4-1 and the equilibrium constants used given in Table 4-1. The speciation constants of the different organic ligands with  $\text{Eu}^{3+}$  and  $\text{Ca}^{2+}$  are given at ionic strength  $I=0$  in Table 4-2.



**Figure 4-1.** Speciation of europium ( $[\text{Eu}^{3+}] = 10^{-8} \text{ M}$ ) in aqueous solution ( $[\text{NaCl}] = 0.3 \text{ M}$ ).

**Table 4-1. Equilibrium constants for Europium complexes in aqueous solution.**

Equilibrium reaction	log K	Reference
$\text{Eu}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Eu}(\text{OH})^{2+} + \text{H}^+$	-7.9	/Lee and Byrne, 1992/
$\text{Eu}^{3+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Eu}(\text{OH})_2^+ + 2\text{H}^+$	-16.37	/Lee and Byrne, 1992/
$\text{Eu}^{3+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Eu}(\text{OH})_3(\text{aq}) + 3\text{H}^+$	-25.41	/Lee and Byrne, 1992/
$\text{Eu}^{3+} + 4 \text{H}_2\text{O} \rightleftharpoons \text{Eu}(\text{OH})_4^- + 4\text{H}^+$	-35.0	/Glaus et al, 1997/
$\text{Eu}^{3+} + \text{Cl}^- \rightleftharpoons \text{EuCl}^{2+}$	0.908	/Choppin and Unrein, 1963/
$\text{Eu}^{3+} + 2\text{Cl}^- \rightleftharpoons \text{EuCl}_2^+$	1.11	/Choppin and Unrein, 1963/
$2\text{Eu}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Eu}_2(\text{OH})_2^{4+} + 2\text{H}^+$	-14.0	/Allard, 1983/
$3\text{Eu}^{3+} + 5\text{H}_2\text{O} \rightleftharpoons \text{Eu}_3(\text{OH})_5^{4+} + 5\text{H}^+$	-33.0	/Allard, 1983/
$\text{Eu}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Eu}(\text{OH})_3(\text{s}) + 3\text{H}^+$	-16.4	/Martell et al, 1997/
$\text{Eu}^{3+} + \text{CO}_3^{2-} \rightleftharpoons \text{EuCO}_3^+$	8.00	/Lee and Byrne, 1992/
$\text{Eu}^{3+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Eu}(\text{CO}_3)_2^-$	13.52	/Lee and Byrne, 1992/
$\text{Eu}^{3+} + \text{HCO}_3^- \rightleftharpoons \text{EuHCO}_3^{2+}$	11.93	/Haas et al, 1995/
$\text{Eu}^{3+} + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{EuCO}_3(\text{OH})(\text{cr}) + \text{H}^+$	7.8	/Spahiu and Bruno, 1995/

**Table 4-2. Equilibrium constants for Europium and Calcium complexes in aqueous solution.**

Equilibrium reaction	log K	Reference
$\text{EDTA}^{4-} + \text{Eu}^{3+} \rightleftharpoons \text{EuEDTA}^-$	19.2	/Wheelwright et al, 1953/
$\text{EDTA}^{4-} + \text{Ca}^{2+} \rightleftharpoons \text{Ca-EDTA}^{2-}$	12.4	/Anderegg et al, 1975/
$\text{DTPA}^{5-} + \text{Eu}^{3+} \rightleftharpoons \text{Eu-DTPA}^{2-}$	25.5	/Moeller and Ferrus, 1962/
$\text{DTPA}^{5-} + \text{Ca}^{2+} \rightleftharpoons \text{Ca-DTPA}^{3-}$	12.8	/Holloway and Reilley, 1960/
$\text{NTA}^{3-} + \text{Eu}^{3+} \rightleftharpoons \text{Eu(NTA)}$	13.4	/Moeller and Ferrus, 1962/
$2\text{NTA}^{3-} + \text{Eu}^{3+} \rightleftharpoons \text{Eu(NTA)}_2^{3-}$	22.6	/Moeller and Ferrus, 1962/
$\text{NTA}^{3-} + \text{Ca}^{2+} \rightleftharpoons \text{Ca-NTA}^-$	7.7	/Ramamoorthy and Manning, 1975/
$(\text{Citric acid})^{3-} + \text{Eu}^{3+} \rightleftharpoons \text{Eu(Citric acid)}$	10.3	/Skorik and Serebrennikov, 1966/
$(\text{Citric acid})^{3-} + \text{Eu}^{3+} \rightleftharpoons \text{Eu(Citric acid)}_{(\text{s})}$	13.9	/Skorik and Serebrennikov, 1966/
$(\text{Citric acid})^{3-} + \text{Ca}^{2+} \rightleftharpoons \text{Ca(Citric acid)}^-$	4.8	/Ramamoorthy and Manning, 1975/
$(\text{Gluconic acid})^- + \text{Eu}^{3+} \rightleftharpoons \text{Eu (Gluconic acid)}^{2+}$	3.4	/Kostromina, 1963/
$2(\text{Gluconic acid})^- + \text{Eu}^{3+} \rightleftharpoons \text{Eu (Gluconic acid)}_2^+$	6.2	/Kostromina, 1963/
$(\text{Gluconic acid})^- + \text{Ca}^{2+} \rightleftharpoons \text{Ca (Gluconic acid)}^+$	1.7	/Cannon and Kibrick, 1938/
$\text{C}_2\text{O}_4^{2-} + \text{Eu}^{3+} \rightleftharpoons \text{EuC}_2\text{O}_4^+$	6.7	/Lyle and Naqvi, 1966/
$2\text{C}_2\text{O}_4^{2-} + \text{Eu}^{3+} \rightleftharpoons \text{Eu}(\text{C}_2\text{O}_4)_2^-$	11.2	/Lyle and Naqvi, 1966/
$\text{C}_2\text{O}_4^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{CaC}_2\text{O}_4$	3.4	/Craggs et al, 1979/
$\text{C}_2\text{O}_4^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{CaC}_2\text{O}_4(\text{s})$	8.7	/Stary, 1963/
$\text{TTA}^- + \text{Eu}^{3+} \rightleftharpoons \text{Eu-TTA}^{2+}$	7.1	/Meshkova et al, 1995/
$2\text{TTA}^- + \text{Eu}^{3+} \rightleftharpoons \text{Eu-(TTA)}_2^+$	14.7	/Meshkova et al, 1995/
$3\text{TTA}^- + \text{Eu}^{3+} \rightleftharpoons \text{Eu-(TTA)}_3$	17.6	/Meshkova et al, 1995/
$\text{TTA}^- + \text{Ca}^{2+} \rightleftharpoons \text{Ca-TTA}^+$	7.1	/Jablonski et al, 1976/
$2\text{TTA}^- + \text{Ca}^{2+} \rightleftharpoons \text{Ca-(TTA)}_2$	12.6	/Jablonski et al, 1976/
$\text{H}_4\text{ISA}^- + \text{Eu}^{3+} \rightleftharpoons \text{EuHISA}^- + 3\text{H}^+$	-18.3	/Van Loon and Glaus, 1998/
$\text{H}_4\text{ISA}^- + \text{Ca}^{2+} \rightleftharpoons \text{CaH}_3\text{ISA} + \text{H}^+$	-10.4	/Vercammen et al, 1999a/
$\text{H}_4\text{ISA}^- + \text{Ca}^{2+} \rightleftharpoons \text{CaH}_4\text{ISA}^+$	1.7	/Vercammen et al, 1999a/
$2\text{H}_4\text{ISA}^- + \text{Ca}^{2+} \rightleftharpoons \text{Ca}(\text{H}_4\text{ISA})_2(\text{s})$	6.4	/Vercammen et al, 1999a/
$\text{AcAc}^- + \text{Eu}^{3+} \rightleftharpoons \text{Eu-AcAc}^{2+}$	6.4	/Panyushkin and Akhremenko, 1995/
$2\text{AcAc}^- + \text{Eu}^{3+} \rightleftharpoons \text{Eu-(AcAc)}_2^+$	13.1	/Panyushkin and Akhremenko, 1995/
$3\text{AcAc}^- + \text{Eu}^{3+} \rightleftharpoons \text{Eu-(AcAc)}_3$	15.1	/Panyushkin and Akhremenko, 1995/
$\text{AcAc}^- + \text{Ca}^{2+} \rightleftharpoons \text{Ca-AcAc}^+$	2.7	/Hancock and Nakani, 1982/

## 4.2 Data treatment

The experimental results of the interaction between europium, the different sorbing materials and complexing agent solutions at different concentration have been modelled by two different methods: Linear regression and Surface-Complex competition model.

### 4.2.1 Linear regressions

A way of modeling the obtained data is by taking the linear regression of the data giving  $K_d < K_d^0$  ( $[L]=0$ ), which can be represented by:

$$\log K_d = a + b \log [L] \quad (1)$$

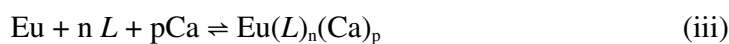
The results from the linear regressions are shown in Figures 4-2–4-23, with dashed lines.

### 4.2.2 Surface-Complex competition model (SCCM)

The experimental results are interpreted with the following assumptions:

- the sorption fits a linear isotherm and is reversible;
- the solid phase is stable at the experiment conditions;
- the ligand does not sorb onto the solid phase;
- no polynuclear complexes are formed;
- sufficient equilibration time.

Based on these assumptions a general complexation reaction, relevant for Eu(III) speciation in solution, can be postulated (where  $L$  stands for ligand, complexing agent or additive):



There are reasons for including the formation of protons in the reactions, in view of the hydrolysis of Eu and the observation that the coordination of polyhydroxy ligands with higher charged ions at alkaline pH is accompanied by deprotonation of the corresponding hydroxo groups /Vercammen et al, 1999a; Vercammen et al, 1999b/. However, this is a very complicated system and we have studied a large number of ligands. The number of species and complexes that can form would be large and difficult to evaluate in each particular case (*e.g.*  $\text{Ca}(L)_n$ ,  $\text{Eu}(L)_n(\text{Ca})_p$ ,  $\text{Eu}(L)_n(\text{Ca})_p(\text{OH})_m$ ) among others, because all data has been obtained at one pH value. Therefore, we have chosen to use a very simple model with one complexation reaction (reaction (i)), in order to find the slopes of the experimental data curves and the concentration range of ligand decreasing the sorption of europium onto the sorbent material and be able to compare them.

The sorption distribution coefficients,  $K_d$  ( $\text{m}^3/\text{kg}$ ) measured as the function of the ligand concentrations can be modeled /Van Loon and Glaus, 1998/ by

$$\log K_d = \log K_d^0 - \log \left( 1 + \frac{\beta}{A} \cdot [L]^n \right) \quad (2)$$

where  $K_d^0$  is the sorption distribution coefficient measured in the absence of ligand,  $\beta$  is the complexation constant for the system,  $[L]$  is the concentration of ligand, and  $n$  is the complexation number. Brackets denote molar concentration of the species.  $\beta$  is the stability constant associated with reaction (i)

$$\beta = \frac{[Eu(L)_n]}{[Eu^{3+}] \cdot [L]^n} \quad (3)$$

A is a side reaction term for the hydrolysis of Eu given by

$$\beta_{Eu(OH)_4^-}^* = \frac{[Eu(OH)_4^-][H^+]^4}{[Eu^{3+}]} \quad (4)$$

$$A = 1 + \frac{\beta_{Eu(OH)_4^-}^*}{[H^+]^4} \quad (5)$$

since  $Eu(OH)_4^-$  is the dominating inorganic species at high pH. Because the total concentration of Eu is much smaller than the total concentration of ligand ( $[L]_{total}$ ), the concentration of free uncomplexed ligand can be approximated by  $[L]_{total}$  and equation (2) can be simplified to:

$$\log K_d = \log K_d^0 - \log \left( 1 + \frac{\beta}{A} \cdot [L]_{total}^n \right) \quad (6)$$

All conditions assumed in the surface-complex competition model are not always fulfilled (*e.g.* some ligands can sorb to some extent onto the solid phase (Section 4.3.8)), and therefore there is no physical meaning to the  $\beta$  constants and parameter  $n$  obtained; and it is generally difficult to compare with the values found in the literature, although it is a good approximation for most cases.

A more useful parameter used to compare the data obtained in this report has been defined as follows:

$$D = \frac{\beta}{A} \quad (7)$$

$$\frac{\log D}{n} = \frac{\log \left( \frac{\beta}{A} \right)}{n} \quad (8)$$

### 4.3 Overview of the sorption data

The results from batch experiments are plotted in Figure 4-2–4-23, where the X-axis corresponds to  $\log [L]_{total}$ , where  $L$  is expressed in molar concentration (M) (except for fulvic acid in g/L) or volume fraction of liquid phase ( $flp$ ), and the Y-axis corresponds to  $\log K_d$  ( $m^3/kg$ ). These data can be found in Appendix I. Solid lines correspond to the regression analysis of the surface-complex competition model whereas dashed lines correspond to the results from the linear regressions.

The main difference between the three systems is expressed by

- the slope of the curves ( $n$ ) and  $\beta$  obtained by fitting the experimental data to equation (6) with the regression analysis and the statistical SPSS program. In this fitting procedure (solid lines)  $D$ ,  $K_d^0$  and  $n$ , are treated as adjustable parameters, whereas  $A$  is calculated using equation (5), at an ionic strength of 0.3 M,  $\log A_{(0.3\text{ M})} = 14.87$ ,
- the slope of the linear regression ( $b$ ) and parameter  $a$  in equation (1).

Eu sorption on  $\text{TiO}_2$  was not affected by the presence of Ca when no ligand was added. Therefore the same  $K_d^0$  values are used for both systems with  $\text{TiO}_2$  as sorbent material.

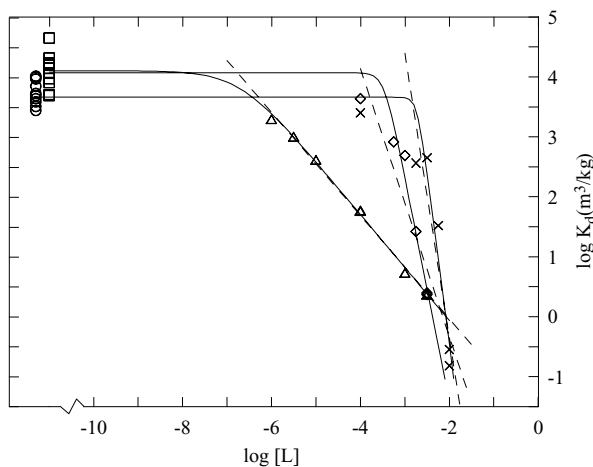
### 4.3.1 Complexing agents effect on Eu sorption

The sorption of europium on  $\text{TiO}_2$  in the presence of EDTA (Figure 4-2) is lower with respect to the sorption onto cement, and the sorption onto  $\text{TiO}_2$  in the presence of both  $\text{Ca}^{2+}$  and EDTA resembles the sorption onto cement. This means that the presence of  $\text{Ca}^{2+}$  in the solution affects the complexation between  $\text{Eu}^{3+}$  and EDTA as expected.  $\text{Ca}^{2+}$  does not complex as strongly to EDTA as  $\text{Eu}^{3+}$ , but can effectively compete with  $\text{Eu}^{3+}$  ( $1 \cdot 10^{-8}$  M Eu) for the ligand, because Ca is found in great excess ( $2 \cdot 10^{-3}$  M Ca). When the concentration of EDTA, equals the concentration of Ca (from  $\log [L] = -2.7$ ) then Eu sorption starts being affected by EDTA in the  $\text{TiO}_2/\text{Ca}$  system, resembling very much the sorption behaviour in cement.

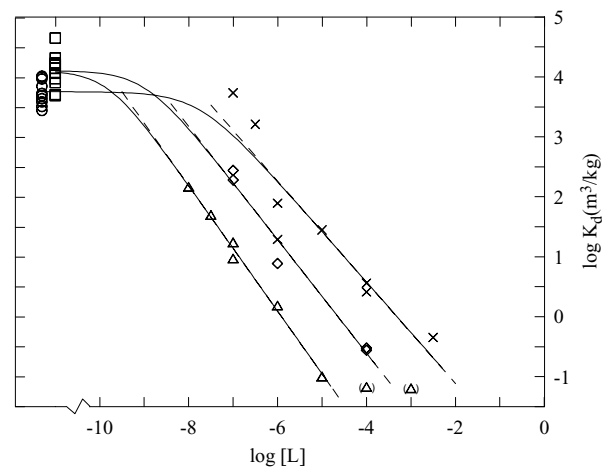
The sorption of europium decreases strongly in the presence of DTPA (Figure 4-3). For very low concentrations of DTPA, we observe much lower sorption:  $\text{Eu-TiO}_2 < \text{Eu-TiO}_2/\text{Ca} < \text{Eu-cement}$ . The presence of  $\text{Ca}^{2+}$  in the solution affects the complexation between  $\text{Eu}^{3+}$  and DTPA.

The sorption of europium with NTA (Figure 4-4) is very similar to the sorption with EDTA. When  $\text{Ca}^{2+}$  is present in the system, higher amounts of ligand are required to remove europium from the surface of  $\text{TiO}_2$  and cement.

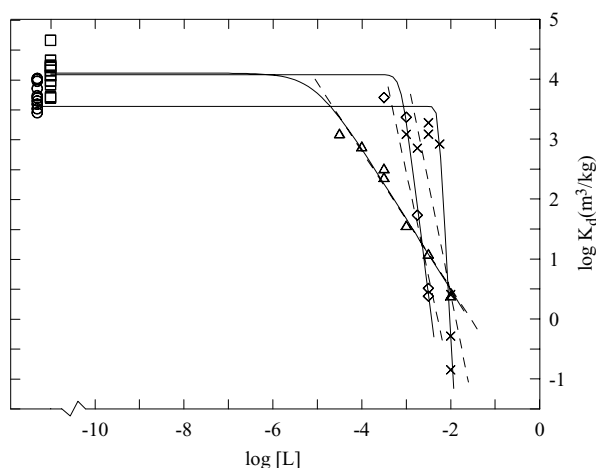
Citric acid complexes with europium are not affected by the presence of calcium (Figure 4-5). Citric acid or citrate can sorb on the surface of cement and higher amounts of ligand are needed to start complexing Eu.



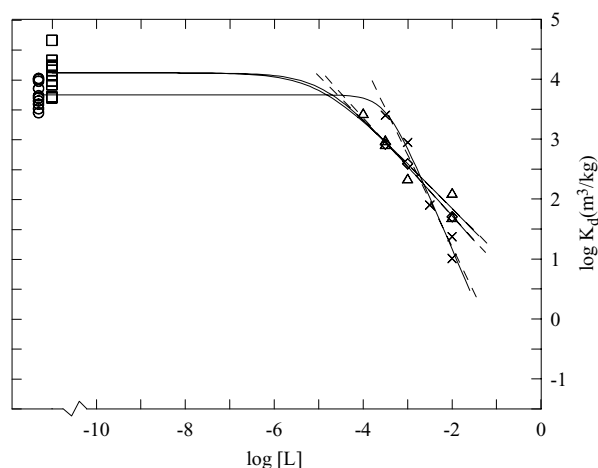
**Figure 4-2.** Eu sorption with  $L=\text{EDTA}$ , ( $\square$ )  $\text{TiO}_2$ ,  $[L]=0\text{ M}$ , ( $\circ$ ) Cement,  $[L]=0\text{ M}$ , ( $\Delta$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002\text{ M}$ , ( $\times$ ) Cement.



**Figure 4-3.** Eu sorption with  $L=\text{DTPA}$ , ( $\square$ )  $\text{TiO}_2$ ,  $[L]=0\text{ M}$ , ( $\circ$ ) Cement,  $[L]=0\text{ M}$ , ( $\Delta$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002\text{ M}$ , ( $\times$ ) Cement.



**Figure 4-4.** Eu sorption with  $L=NTA$ , ( $\square$ )  $TiO_2$ ,  $[L]=0 M$ , ( $\circ$ ) Cement,  $[L]=0 M$ , ( $\Delta$ )  $TiO_2$ , ( $\diamond$ )  $TiO_2$ ,  $[Ca]=0.002 M$ , ( $\times$ ) Cement.



**Figure 4-5.** Eu sorption with  $L=citric\ acid$ , ( $\square$ )  $TiO_2$ ,  $[L]=0 M$ , ( $\circ$ ) Cement,  $[L]=0 M$ , ( $\Delta$ )  $TiO_2$ , ( $\diamond$ )  $TiO_2$ ,  $[Ca]=0.002 M$ , ( $\times$ ) Cement.

The Eu complexation with D-Gluconic acid (Figure 4-6) effectively decreases the sorption on the sorbent materials for rather low concentrations of complexing agent and it is very slightly affected by the presence of  $Ca^{2+}$ . The sorption of Eu is not affected with the presence of oxalic acid as seen in Figure 4-7 in the studied interval ( $< 10^{-2} M$ ) when  $TiO_2$  is the adsorbent material. In the other two systems the sorption is not affected either but most probably because calcium oxalate will precipitate in the systems  $TiO_2/Ca$  and cement. In the latter systems a higher concentration of oxalic acid ( $> 2\text{ mM}$ ) is needed in order to complex  $Eu^{3+}$ . As will be seen in the ligand sorption section (Section 4.3.8), oxalic acid seems to be sorbed but a most likely explanation is that it has precipitated.

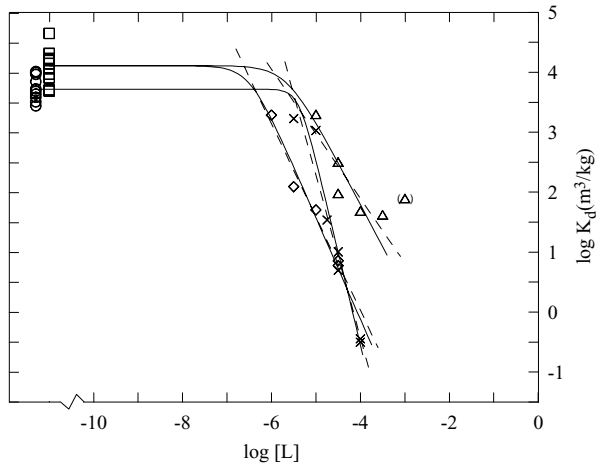
Fulvic acid is shown to decrease the sorption of Eu onto  $TiO_2$ . The sorption of Eu on  $TiO_2$  in the presence of  $Ca^{2+}$  resembles the sorption onto cement (Figure 4-8): the presence of  $Ca^{2+}$  shifts the sorption decrease and therefore Eu is affected at higher concentrations of ligand in the latter systems.

The influence of  $\alpha$ -isosaccharinic acid (ISA) on the sorption of Eu onto  $TiO_2$ ,  $TiO_2/Ca$  and cement is very similar for all three systems. In addition  $TiO_2/Ca$  and cement systems have very similar  $\log(D)/n$  parameter (Figure 4-9).

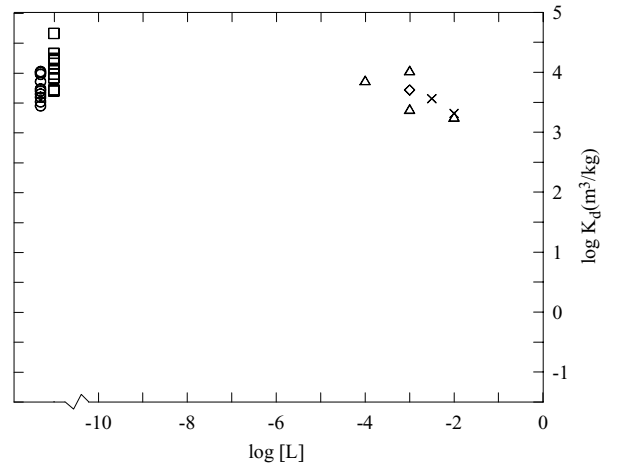
The sorption of Eu is not very much affected with the presence of Acetyl acetone (Figure 4-10) in the studied interval ( $[L] < 10^{-2} M$ ) but for AcAc concentrations higher than  $10^{-2} M$  the sorption of Eu seems to decrease in the system  $TiO_2/Ca$ .

TTA does not seem to affect the sorption of europium on cement or  $TiO_2$  (Figure 4-11). However, the complexation constants found in the literature between TTA and Ca and Eu indicate that sorption should decrease /Jablonski et al, 1976; Meshkova et al, 1995/. In the systems with TTA ethanol was used to facilitate the dissolution of this ligand.

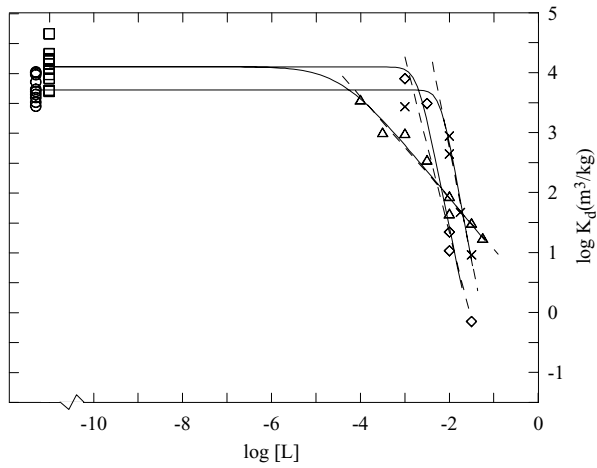




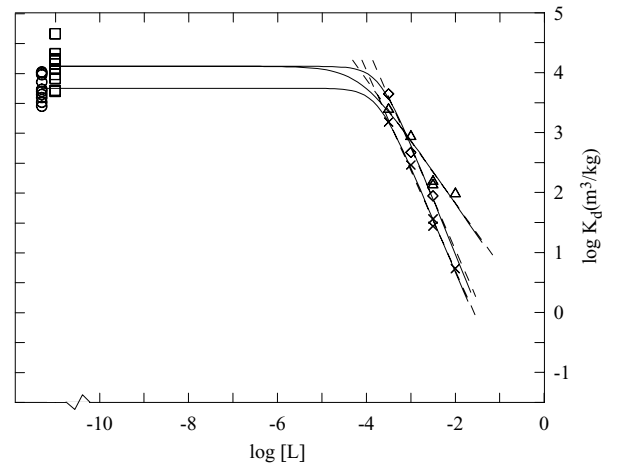
**Figure 4-6.** *Eu sorption with L=D-Gluconic acid, ( $\square$ )  $\text{TiO}_2$ ,  $[\text{L}]=0 \text{ M}$ , ( $\circ$ ) Cement,  $[\text{L}]=0 \text{ M}$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*



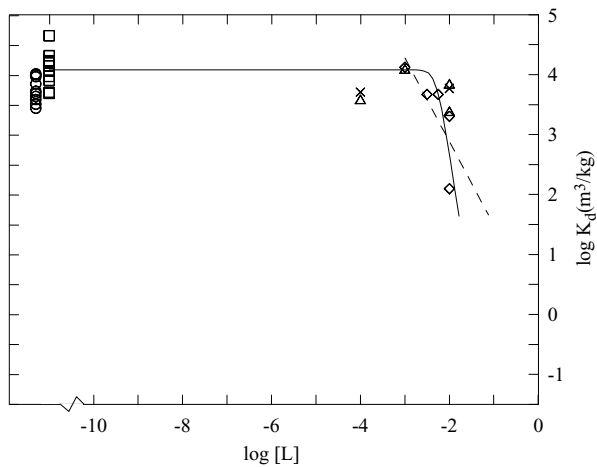
**Figure 4-7.** *Eu sorption with L=oxalic acid, ( $\square$ )  $\text{TiO}_2$ ,  $[\text{L}]=0 \text{ M}$ , ( $\circ$ ) Cement,  $[\text{L}]=0 \text{ M}$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*



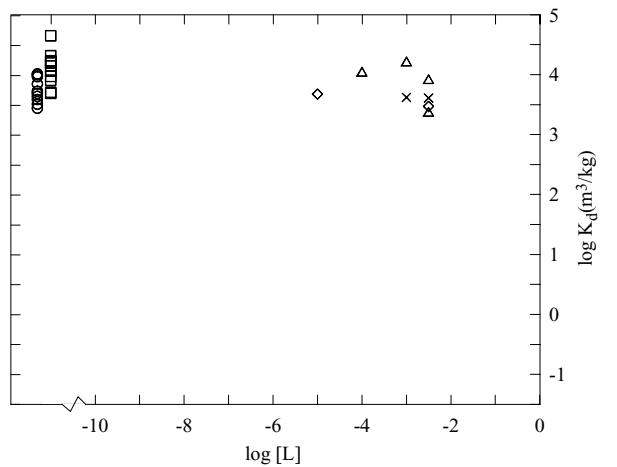
**Figure 4-8.** *Eu sorption with L=fulvic acid, ( $\square$ )  $\text{TiO}_2$ ,  $[\text{L}]=0 \text{ M}$ , ( $\circ$ ) Cement,  $[\text{L}]=0 \text{ M}$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*



**Figure 4-9.** *Eu sorption with L=ISA, ( $\square$ )  $\text{TiO}_2$ ,  $[\text{L}]=0 \text{ M}$ , ( $\circ$ ) Cement,  $[\text{L}]=0 \text{ M}$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*



**Figure 4-10.** *Eu sorption with L=AcAc acid, ( $\square$ )  $\text{TiO}_2$ ,  $[\text{L}]=0 \text{ M}$ , ( $\circ$ ) Cement,  $[\text{L}]=0 \text{ M}$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*



**Figure 4-11.** *Eu sorption with L=TTA, ( $\square$ )  $\text{TiO}_2$ ,  $[\text{L}]=0 \text{ M}$ , ( $\circ$ ) Cement,  $[\text{L}]=0 \text{ M}$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*

### 4.3.2 Cement additives effect on Eu sorption

Cement additives were added to the solutions used in the experiments, in percentage of liquid phase. For simplification and convenience we have used the fraction of liquid phase (*flp*) to express the results from the sorption experiments with cement additives (see Table 4-3).

The sorption of Eu with Sikament 10 (Figure 4-12), is stronger on TiO<sub>2</sub> than on cement. The addition of Sikament 210 (Figure 4-13) and Peramin Conpac 30 (Figure 4-14), reduces the sorption very strongly in the cement system after certain concentration, but in the TiO<sub>2</sub> system the sorption is reduced from the lowest addition of cement additive. With Peramin F (Figure 4-15), we observe lower sorption of europium on cement than on TiO<sub>2</sub>, and the TiO<sub>2</sub>/Ca system resembles the cement system.

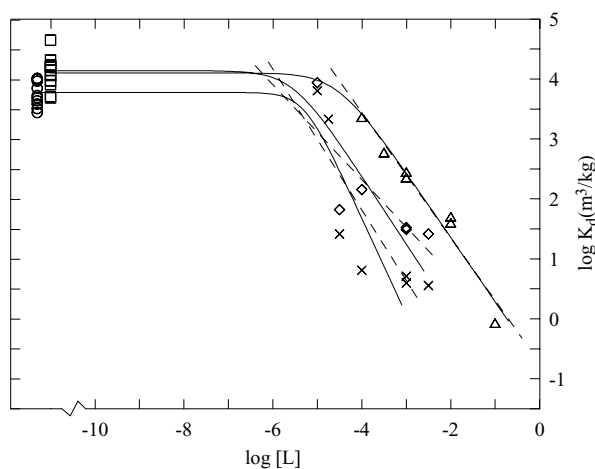
The sorption of Eu<sup>3+</sup> on cement with Glenium 51 as complexing agent is lower than on TiO<sub>2</sub> (Figure 4-16). Glenium 51 is a modified polycarboxylic ether and can form complexes with the cations in the system, lowering the sorption to both sorbent materials. The presence of Ca<sup>2+</sup> in the solutions with TiO<sub>2</sub>, increases the complexation between Glenium 51 and Eu<sup>3+</sup>.

The Eu sorption with Cementa Melcrete is reduced equally for the three systems (Figure 4-17). In this case TiO<sub>2</sub> can be used as an analogue to cement.

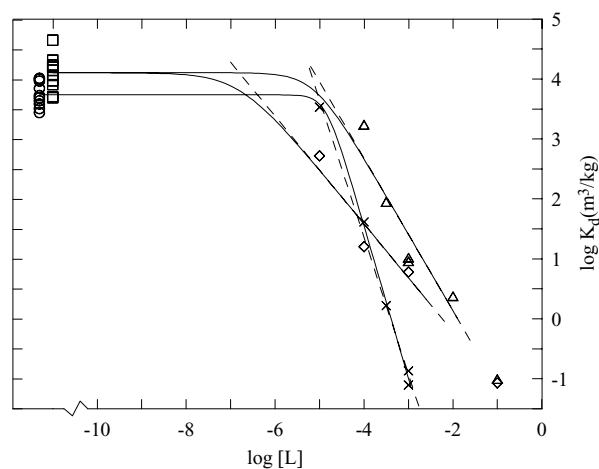
The presence of calcium practically does not affect the sorption of Eu<sup>3+</sup> on TiO<sub>2</sub>, with the presence of Mighty 150 (Figure 4-18), a superplasticiser similar to Cementa Melcrete. The sorption onto cement is though slightly reduced compared to that onto TiO<sub>2</sub>.

**Table 4-3. Fraction of liquid phase (*flp*).**

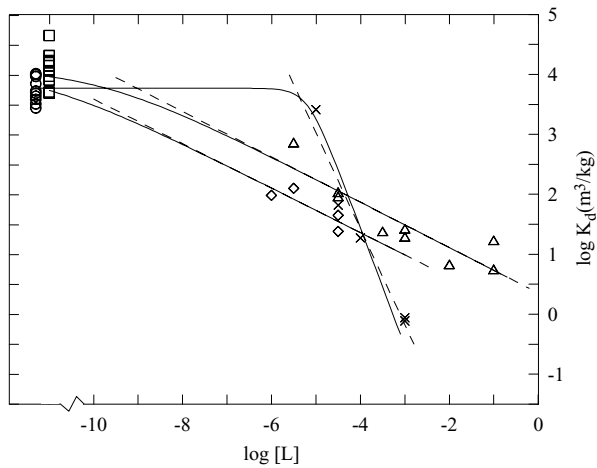
Log <i>flp</i>	<i>flp</i>	% liquid phase
-4	0,0001	0,01
-3	0,001	0,1
-2	0,01	1
-1	0,1	10



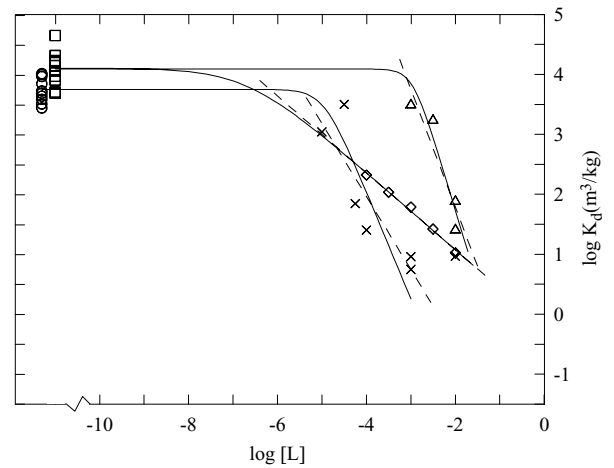
**Figure 4-12.** Eu sorption with L=Sikament 10, (□) TiO<sub>2</sub>, *flp* of L=0 (○) Cement, *flp* of L=0, (Δ) TiO<sub>2</sub>, (◇) TiO<sub>2</sub>, [Ca]=0.002 M, (×) Cement.



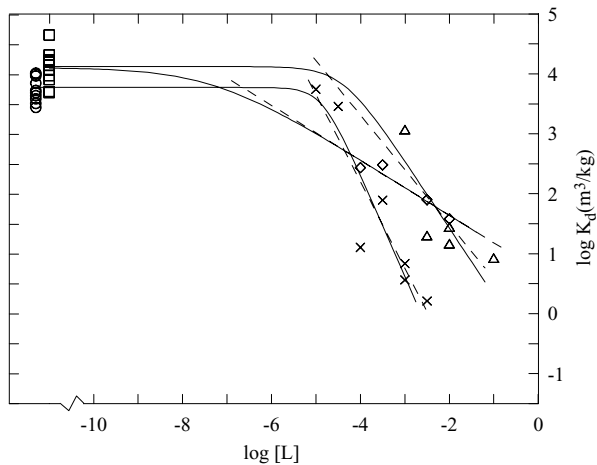
**Figure 4-13.** Eu sorption with L=Sikament 210, (□) TiO<sub>2</sub>, *flp* of L=0, (○) Cement, *flp* of L=0, (Δ) TiO<sub>2</sub>, (◇) TiO<sub>2</sub>, [Ca]=0.002 M, (×) Cement.



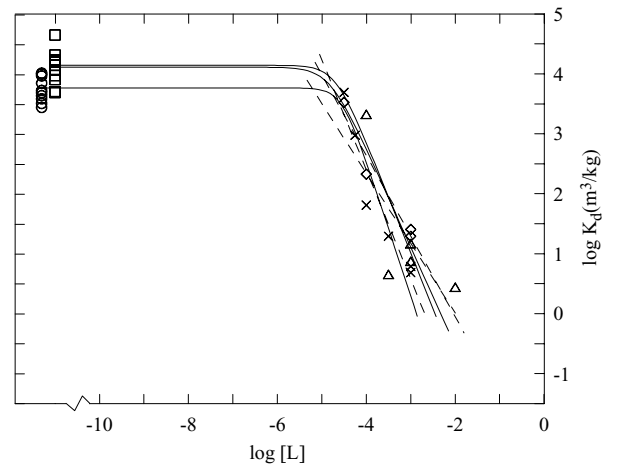
**Figure 4-14.** *Eu sorption with L=Peramin Conpac 30, ( $\square$ )  $\text{TiO}_2$ , flp of  $L=0$  ( $\circ$ ) Cement, flp of  $L=0$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*



**Figure 4-15.** *Eu sorption with L=Peramin F, ( $\square$ )  $\text{TiO}_2$ , flp of  $L=0$ , ( $\circ$ ) Cement, flp of  $L=0$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*



**Figure 4-16.** *Eu sorption with L=Glenium 51, ( $\square$ )  $\text{TiO}_2$ , flp of  $L=0$  ( $\circ$ ) Cement, flp of  $L=0$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*



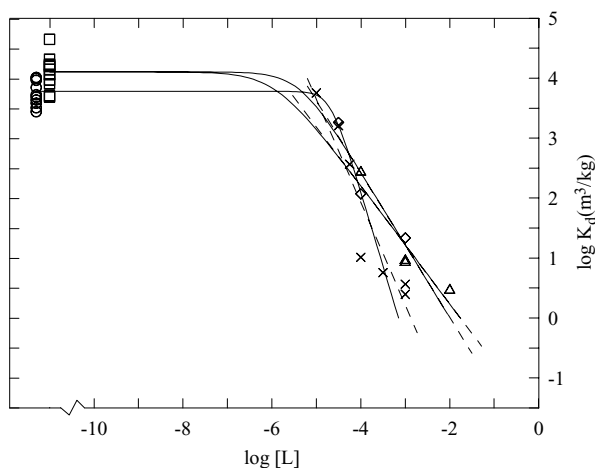
**Figure 4-17.** *Eu sorption with L=Cementa Melcrete, ( $\square$ )  $\text{TiO}_2$ , flp of  $L=0$ , ( $\circ$ ) Cement, flp of  $L=0$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*

### 4.3.3 Cleaning agents effect on Eu sorption

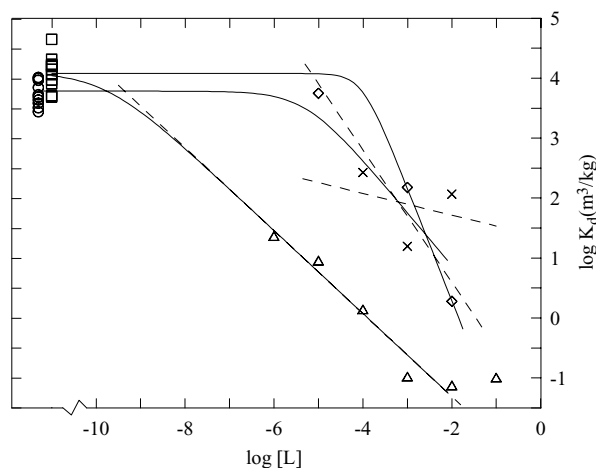
The effect of Clax Delta Balans (Figure 4-19), a cleaning agent, is very strong in the system with  $\text{TiO}_2$ . From the very lowest addition, the  $\log K_d$ -values for  $\text{Eu}^{3+}$  are reduced from 4 to 1, which in percentage of sorbed Eu represents from 99.99 to 90% sorbed Eu. However, it is clear that the presence of  $\text{Ca}^{2+}$  in the solution affects the complexation between  $\text{Eu}^{3+}$  and DTPA since the Eu-sorption is much higher when  $\text{Ca}^{2+}$  is in the system or in a cement environment.

Industrikombi is also a cleaning agent, but it does not complex so strongly to europium as Clax. We don't have complete data for the cement system with different concentrations of Industrikombi, but it did not modify the Eu sorption when 1% of cleaning agent was added (Figure 4-20). However,  $\log K_d$  decreased from 4 to 0.5 when  $\text{TiO}_2$  was the sorbent material by adding from 0.1 to 3.2% of liquid phase.

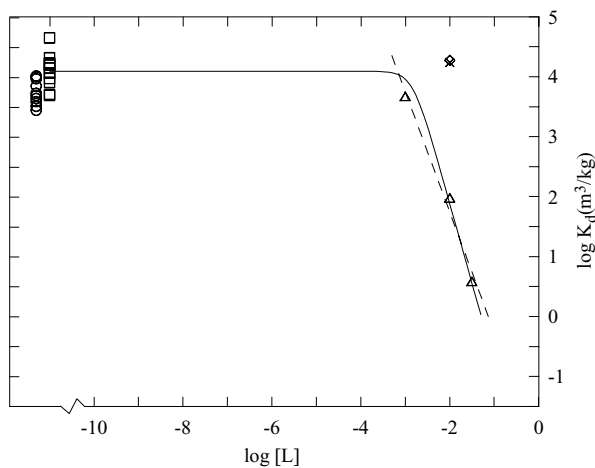
The sorption of Eu on  $\text{TiO}_2$  with Prefect Citron is reduced two orders of magnitude when 1% of cleaning agent was added (Figure 4-21).



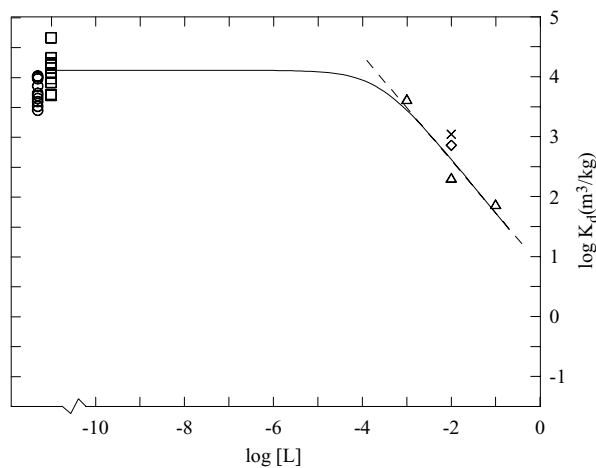
**Figure 4-18.** *Eu sorption with L=Mighty 150, ( $\square$ )  $\text{TiO}_2$ , flp of  $L=0$  ( $\circ$ ) Cement, flp of  $L=0$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*



**Figure 4-19.** *Eu sorption with L= Clax Delta Balans, ( $\square$ )  $\text{TiO}_2$ , flp of  $L=0$  ( $\circ$ ) Cement, flp of  $L=0$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*



**Figure 4-20.** *Eu sorption with L=Industrikombi, ( $\square$ )  $\text{TiO}_2$ , flp of  $L=0$  ( $\circ$ ) Cement, flp of  $L=0$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*

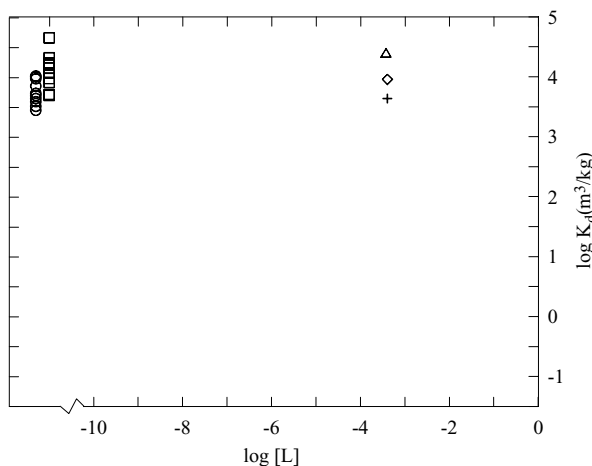


**Figure 4-21.** *Eu sorption with L=Prefect Citron, ( $\square$ )  $\text{TiO}_2$ , flp of  $L=0$  ( $\circ$ ) Cement, flp of  $L=0$ , ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement.*

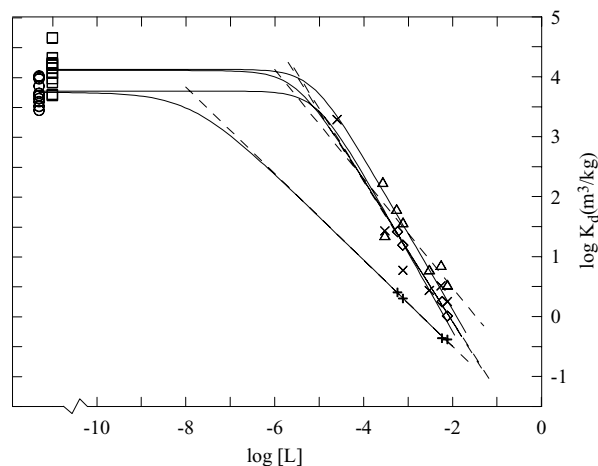
#### 4.3.4 Effect on Eu sorption by the degradation products of the ion exchange resin and the filter aid

The results using the degradation products from Acrisorb LSR 33, an ion exchange resin, can be seen in Figure 4-22. There is no variation on the sorption for all three systems. The concentration of degradation products is given in mol/L TOC (total organic carbon).

The degradation products from Ricem UP2, an acrylonitrile polymer used as a filter aid, reduce the sorption of europium quite independently of the sorbent medium as seen in Figure 4-23.



**Figure 4-22.** *Eu* sorption with  $L$ = Acrisorb LSR33, ( $\square$ )  $\text{TiO}_2$ ,  $[L]=0$  M TOC ( $\circ$ ) Cement,  $[L]=0$  M TOC, ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.01$  M in the degradation step, (+) Cement,  $[\text{Ca}]=0.01$  M in the degradation step.



**Figure 4-23.** *Eu* sorption with  $L$ =Ricem UP2, ( $\square$ )  $\text{TiO}_2$ ,  $[L]=0$  M TOC ( $\circ$ ) Cement,  $[L]=0$  M TOC, ( $\Delta$ )  $\text{TiO}_2$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Ca}]=0.01$  M in the degradation step, ( $\times$ ) Cement (+) Cement,  $[\text{Ca}]=0.01$  M in the degradation step.

#### 4.3.5 Statistical treatment of the *Eu* sorption data

The data was analysed as described in Section 4.2. The results from SPSS regressions can be seen in Tables 4-4 to 4-6, where SD stands for standard deviation,  $D$  is defined in equation (7),  $\beta$  and  $n$  in equation (2), and  $a$  and  $b$  in equation (1).  $K_d$  has the unit  $\text{m}^3/\text{kg}$  and  $[L]$  has the unit  $\text{mol}/\text{dm}^3$ , except for the following: fulvic acid:  $\text{g}/\text{dm}^3$ ; cement additives and cleaning agents: fraction of liquid phase ( $flp$ ); Acrisorb LSR33 and Ricem UP2:  $\text{mol}/\text{dm}^3$  TOC.

In Figure 4-24, we have plotted  $\log(D)/n$ , for the three different sorbent materials and complexing agents ( $D=\beta/A$ ). The reason for plotting  $\log(\beta/A)/n$  instead of  $\log\beta$  is to be able to compare the values for each system, independently of the complexation number ( $n$ ), since we have observed that  $\log\beta$  and  $n$  are interdependent. The figure shows that when  $\text{Eu}^{3+}$  sorption increases, the parameter  $\log(D)/n$  decreases.

Figure 4-25 and Figure 4-26 show all calculated regression curves from the sorption of *Eu* with different organic complexing agents (Figure 4-25) or cement additives and cleaning agents (Figure 4-26).

The sorption vs concentration (volume fraction of liquid phase) of the cement additives is highly similar for the cement system (after 24 h). There is no significant effect at volume fractions of cement additives below  $10^{-6}$  in the aqueous phase. This level would correspond to an initial concentration of the additive of 0.1% of the cement under the present conditions (solid to water ratio of  $1 \text{ g}/\text{dm}^3$ ). Levels of 0.5–3% are common in technical cement, corresponding to volume fractions of the liquid phase of  $10^{-5.3}$  to  $10^{-4.5}$  under the experimental conditions of this study, providing that all of the additive is released from the cement into the water phase. Thus, in a hypothetical worst-case scenario, the maximum levels of cement additives would reduce the sorption of *Eu* on cement by around  $1\pm 0.5$  orders of magnitude (Figure 4-26c). Still, distribution coefficients above  $10^2 \text{ m}^3/\text{kg}$  are obtained (after 24 h), indicating a high degree of sorption even in this unrealistic worst-case (it is expected that not all of the additive would be released from the cement matrix into the water phase).

**Table 4-4. TiO<sub>2</sub>.**

	log K <sub>d</sub> <sup>0</sup>	SD log K <sub>d</sub> <sup>0</sup>	D	SD D	n	SD n	log(D)/n	SD log(D)/n	log β	log [L] <sup>a</sup>	b	a	log [L] <sup>b</sup>	SD log [L]
EDTA	4.12	0.06	8.95E+05	6.72E+05	0.89	0.07	6.71	0.25	20.82	-4.33	-0.86	-1.76	-4.35	0.11
DTPA	4.12	0.06	2.06E+10	3.07E+10	1.05	0.09	9.83	0.30	25.18	-7.82	-1.05	-6.19	-7.81	0.13
NTA	4.12	0.07	9.72E+05	9.00E+05	1.18	0.12	5.06	0.21	20.86	-3.27	-1.14	-1.76	-3.29	0.19
Citric acid	4.12	0.07	6.08E+03	5.93E+03	0.76	0.14	4.98	0.41	18.65	-2.20	-0.74	0.38	-2.20	0.32
Gluconic acid	4.13	0.08	9.00E+07	2.46E+08	1.41	0.28	5.65	0.30	22.82	-4.14	-1.08	-2.41	-4.09	0.39
Oxalic acid													-2.00 <sup>c</sup>	
FA	4.12	0.06	9.73E+03	5.88E+03	0.90	0.10	4.44	0.28	18.86	-2.09	-0.85	0.22	-2.10	0.23
ISA	4.12	0.07	2.85E+04	4.18E+04	1.08	0.24	4.12	0.35	19.32	-2.17	-1.03	-0.24	-2.16	0.21
AcAc													-2.00 <sup>c</sup>	
TTA													-2.50 <sup>c</sup>	
Sikament 10	4.12	0.07	8.04E+04	5.62E+04	1.08	0.11	4.55	0.24	19.78	-2.59	-1.05	-0.73	-2.61	0.27
Sikament 210	4.12	0.09	3.39E+06	3.01E+06	1.28	0.13	5.12	0.27	21.40	-3.46	-1.28	-2.41	-3.46	0.38
Peramin Conpac 30	4.12	0.08	5.74E+03	3.00E+03	0.38	0.06	9.90	1.16	18.63	-4.33	-0.38	0.36	-4.33	0.88
Peramin F	4.10	0.08	2.10E+07	5.81E+07	2.48	0.54	2.95	0.18	22.19	-2.10	-1.97	-2.15	-2.10	0.28
Glenium 51	4.14	0.10	8.91E+04	1.14E+05	1.13	0.25	4.40	0.54	19.82	-2.50	-0.91	-0.32	-2.55	0.75
Cementa Melcrete	4.16	0.15	5.48E+08	1.49E+09	1.87	0.37	4.68	0.36	23.61	-3.53	-1.17	-2.32	-3.70	0.91
Mighty 150	4.12	0.08	7.14E+05	9.89E+05	0.99	0.19	5.92	0.60	20.72	-3.78	-0.99	-1.73	-3.78	0.45
Clax Delta Balans	4.12	0.07	6.53E+06	5.31E+06	0.69	0.08	9.82	0.71	21.69	-6.77	-0.69	-2.70	-6.77	0.54
Industrikombi	4.11	0.07	3.40E+07	7.79E+07	2.66	0.55	2.83	0.23	22.40	-2.04	-2.01	-2.27	-2.12	0.17
Prefect Citron	4.12	0.07	1.97E+03	1.98E+03	0.91	0.22	3.62	0.47	18.16	-1.29	-0.88	0.86	-1.30	0.51
Acisorb LSR33													-3.42 <sup>c</sup>	
Acisorb LSR33 <sup>d</sup>													-3.39 <sup>c</sup>	
Ricem UP2	4.14	0.08	3.65E+06	5.13E+06	1.27	0.20	5.16	0.38	21.43	-3.48	-0.91	-1.34	-3.66	0.39
Ricem UP2 <sup>d</sup>	4.12	0.07	3.81E+06	5.67E+06	1.19	0.24	5.53	0.58	21.45	-3.75	-1.19	-2.46	-3.75	0.08

<sup>a</sup> Log[L] at log K<sub>d</sub>=2, calculated with log K<sub>d</sub> = log K<sub>d</sub><sup>0</sup> - D·log(1+[L]<sup>n</sup>)

<sup>b</sup> Log[L] at log K<sub>d</sub>=2, calculated with log K<sub>d</sub> = a+b·log[L]

<sup>c</sup> Log[L] for the sample with highest [L], when no regression was possible, due to too few samples or when sorption was not influenced in the investigated concentration interval.

<sup>d</sup> 10 mM Ca present in the degradation step.

**Table 4-5. TiO<sub>2</sub> Ca.**

	log K <sub>d</sub> <sup>a</sup>	SD log K <sub>d</sub> <sup>a</sup>	D	SD D	n	SD n	log(D)/n	SD log(D)/n	log β	log [L] <sup>b</sup>	b	a	log [L] <sup>b</sup>	SD log [L]
EDTA	4.08	0.07	9.83E+12	2.86E+13	3.75	0.45	3.47	0.09	27.86	-2.91	-2.24	-4.80	-3.04	0.29
DTPA	4.12	0.07	3.30E+08	3.77E+08	0.95	0.09	8.98	0.34	23.39	-6.75	-0.95	-4.39	-6.75	0.33
NTA	4.09	0.07	2.52E+18	1.05E+19	5.89	0.68	3.12	0.06	33.27	-2.77	-3.47	-7.93	-2.87	0.20
Citric acid	4.12	0.07	1.16E+04	1.81E+04	0.84	0.23	4.85	0.61	18.94	-2.33	-0.82	0.09	-2.33	0.09
Gluconic acid	4.12	0.07	1.10E+11	2.63E+11	1.70	0.20	6.49	0.19	25.91	-5.25	-1.56	-6.20	-5.26	0.14
Oxalic acid													-3.00 <sup>c</sup>	
FA	4.11	0.07	8.89E+09	1.67E+10	3.64	0.41	2.74	0.10	24.82	-2.16	-2.93	-4.51	-2.22	0.18
ISA	4.12	0.07	6.27E+06	1.78E+07	1.83	0.42	3.71	0.21	21.67	-2.56	-1.71	-2.36	-2.55	0.08
AcAc	4.10	0.09	1.00E+11	1.10E+12	4.80	2.33	2.29	0.13	25.87	-1.85	-1.39	0.11	-1.36	0.68
TTA													-2.50 <sup>c</sup>	
Sikament 10	4.15	0.12	2.00E+06	3.65E+06	1.13	0.21	5.55	0.43	21.17	-3.66	-0.79	-0.84	-3.58	0.86
Sikament 210	4.12	0.07	1.36E+06	1.04E+06	0.90	0.09	6.80	0.40	21.00	-4.45	-0.90	-2.01	-4.45	0.43
Peramin Conpac 30	4.12	0.07	1.76E+04	4.05E+04	0.37	0.19	11.35	3.24	19.12	-5.70	-0.37	-0.12	-5.70	0.67
Peramin F	4.12	0.06	2.13E+04	2.23E+04	0.65	0.15	6.70	0.86	19.20	-3.42	-0.64	-0.20	-3.43	0.10
Glenium 51	4.12	0.07	2.51E+03	2.81E+03	0.47	0.16	7.30	1.48	18.27	-2.76	-0.46	0.73	-2.76	0.36
Cementa Melcrete	4.13	0.08	9.25E+07	1.84E+08	1.65	0.24	4.82	0.22	22.84	-3.53	-1.35	-2.74	-3.52	0.23
Mighty 150	4.12	0.08	3.53E+06	8.27E+06	1.22	0.26	5.37	0.37	21.42	-3.64	-1.21	-2.40	-3.64	0.43
Clax Delta Balans	4.09	0.07	3.67E+07	8.06E+07	1.88	0.37	4.02	0.32	22.44	-2.91	-1.10	-1.60	-3.26	0.62
Industrikombi													-2.00 <sup>c</sup>	
Prefect Citron													-2.00 <sup>c</sup>	
Acisorb LSR33														
Acisorb LSR33 <sup>d</sup>														
Ricem UP2														
Ricem UP2 <sup>d</sup>														

<sup>a</sup> Log[L] at log K<sub>d</sub>=2, calculated with log K<sub>d</sub> = log K<sub>d</sub><sup>0</sup> - D·log(1+[L]<sup>n</sup>)

<sup>b</sup> Log[L] at log K<sub>d</sub>=2, calculated with log K<sub>d</sub> = a+b·log[L]

<sup>c</sup> Log[L] for the sample with highest [L], when no regression was possible, due to too few samples or when sorption was not influenced in the investigated concentration interval.

<sup>d</sup> 10 mM Ca present in the degradation step.

**Table 4-6. Cement.**

	log $K_d^0$	SD log $K_d^0$	D	SD D	n	SD n	log(D)/n	SD log(D)/n	log $\beta$	log [L] <sup>a</sup>	b	a	log [L] <sup>b</sup>	SD log [L]
EDTA	3.68	0.11	4.12E+15	1.70E+16	5.74	0.81	2.72	0.08	30.48	-2.43	-4.76	-9.86	-2.49	0.17
DTPA	3.77	0.13	3.62E+06	4.62E+06	0.84	0.10	7.77	0.42	21.43	-5.68	-0.85	-2.81	-5.68	0.71
NTA	3.56	0.11	1.05E+30	1.16E+31	13.11	2.35	2.29	0.05	44.89	-2.17	-3.70	-6.98	-2.42	0.32
Citric acid	3.75	0.06	1.09E+06	1.30E+06	1.73	0.21	3.49	0.16	20.91	-2.48	-1.54	-1.88	-2.51	0.15
Gluconic acid	3.73	0.08	5.46E+16	1.56E+17	3.11	0.28	5.37	0.09	31.61	-4.82	-2.71	-11.26	-4.89	0.16
Oxalic acid													-2.00 <sup>c</sup>	
FA	3.73	0.07	8.80E+08	2.37E+09	4.06	0.67	2.20	0.09	23.81	-1.78	-3.75	-4.73	-1.80	0.06
ISA	3.75	0.06	3.85E+06	4.42E+06	1.76	0.19	3.75	0.14	21.46	-2.75	-1.67	-2.63	-2.77	0.05
AcAc													-2.00 <sup>c</sup>	
TTA													-2.50 <sup>c</sup>	
Sikament 10	3.79	0.17	3.64E+08	9.91E+08	1.62	0.29	5.30	1.33	23.43	-4.20	-1.18	-2.89	-4.15	0.74
Sikament 210	3.75	0.06	2.56E+12	4.00E+12	2.56	0.20	4.85	0.12	27.28	-4.17	-2.29	-7.80	-4.27	0.10
Peramin Conpac 30	3.78	0.10	1.73E+10	3.09E+10	1.98	0.20	5.18	0.18	25.11	-4.28	-1.60	-4.99	-4.35	0.24
Peramin F	3.76	0.14	7.62E+08	2.01E+09	1.79	0.30	4.95	0.25	23.75	-3.97	-1.22	-2.91	-4.02	0.53
Glenium 51	3.79	0.13	1.84E+08	3.80E+08	1.70	0.26	4.85	0.27	23.13	-3.81	-1.45	-3.59	-3.85	0.44
Cementa Melcrete	3.78	0.10	1.82E+10	4.19E+10	2.26	0.28	4.54	0.15	25.13	-3.76	-1.83	-4.91	-3.77	0.23
Mighty 150	3.79	0.14	4.13E+11	1.26E+12	2.48	0.36	4.68	0.19	26.49	-3.96	-1.72	-4.94	-4.03	0.32
Clax Delta Balans	3.80	0.15	5.00E+04	1.22E+05	0.89	0.34	5.28	2.11	19.57	-3.27	-0.18	1.36	-3.52	5.75
Industrikombi													-2.00	
Prefect Citron													-2.00	
Acisorb LSR33													-3.39 <sup>c</sup>	
Acisorb LSR33 <sup>d</sup>														
Ricem UP2	3.77	0.09	4.32E+06	4.62E+06	1.31	0.15	5.06	0.28	21.51	-3.71	-1.17	-2.41	-3.77	0.35
Ricem UP2 d	3.75	0.06	4.92E+05	5.81E+05	0.72	0.19	7.88	1.35	20.56	-5.46	-0.72	-1.94	-5.45	0.14

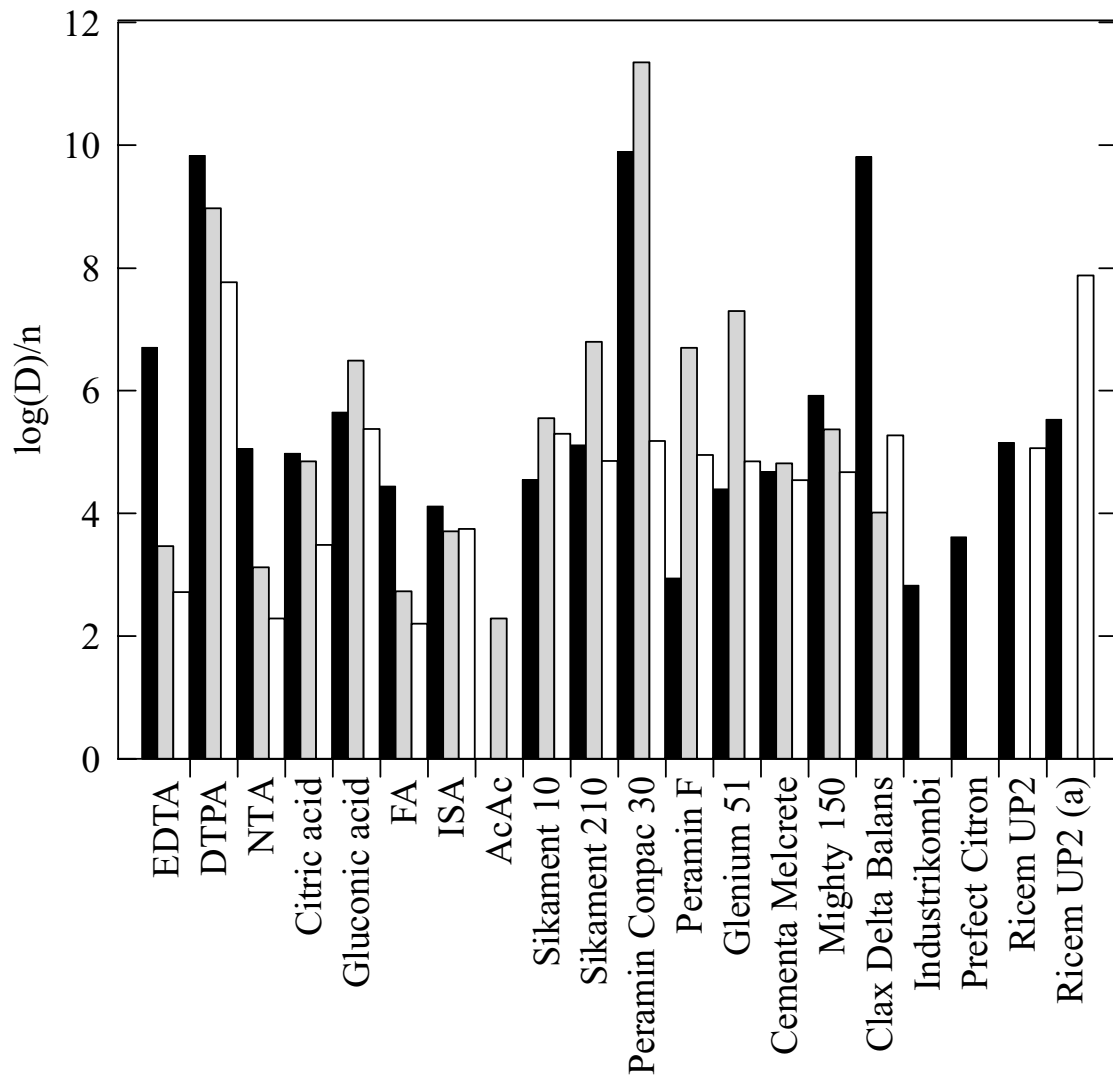
<sup>a</sup> Log[L] at log  $K_d=2$ , calculated with log  $K_d = \log K_d^0 - D \cdot \log(1+[L]^n)$

<sup>b</sup> Log[L] at log  $K_d=2$ , calculated with log  $K_d = a+b \cdot \log[L]$

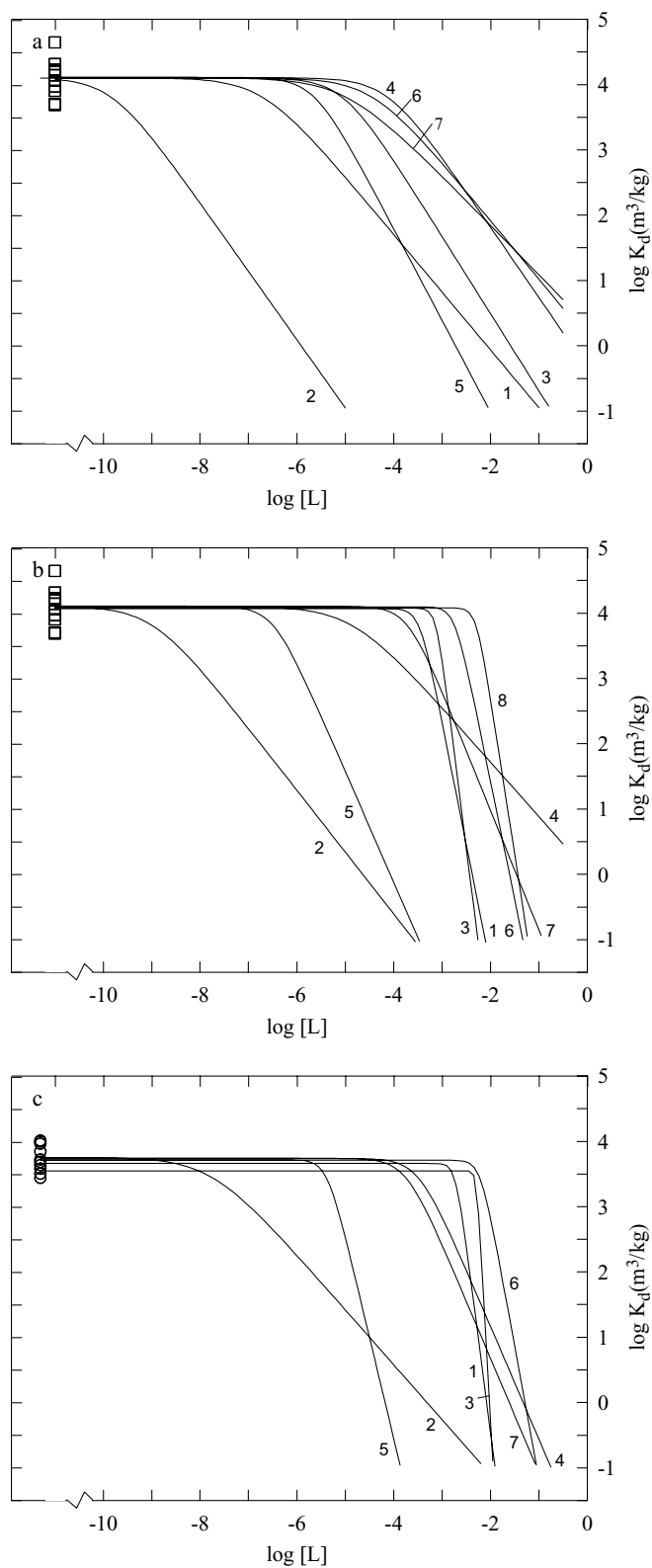
<sup>c</sup> Log[L] for the sample with highest [L], when no regression was possible, due to too few samples or when sorption was not influenced in the investigated concentration interval.

<sup>d</sup> 10 mM Ca present in the degradation step.

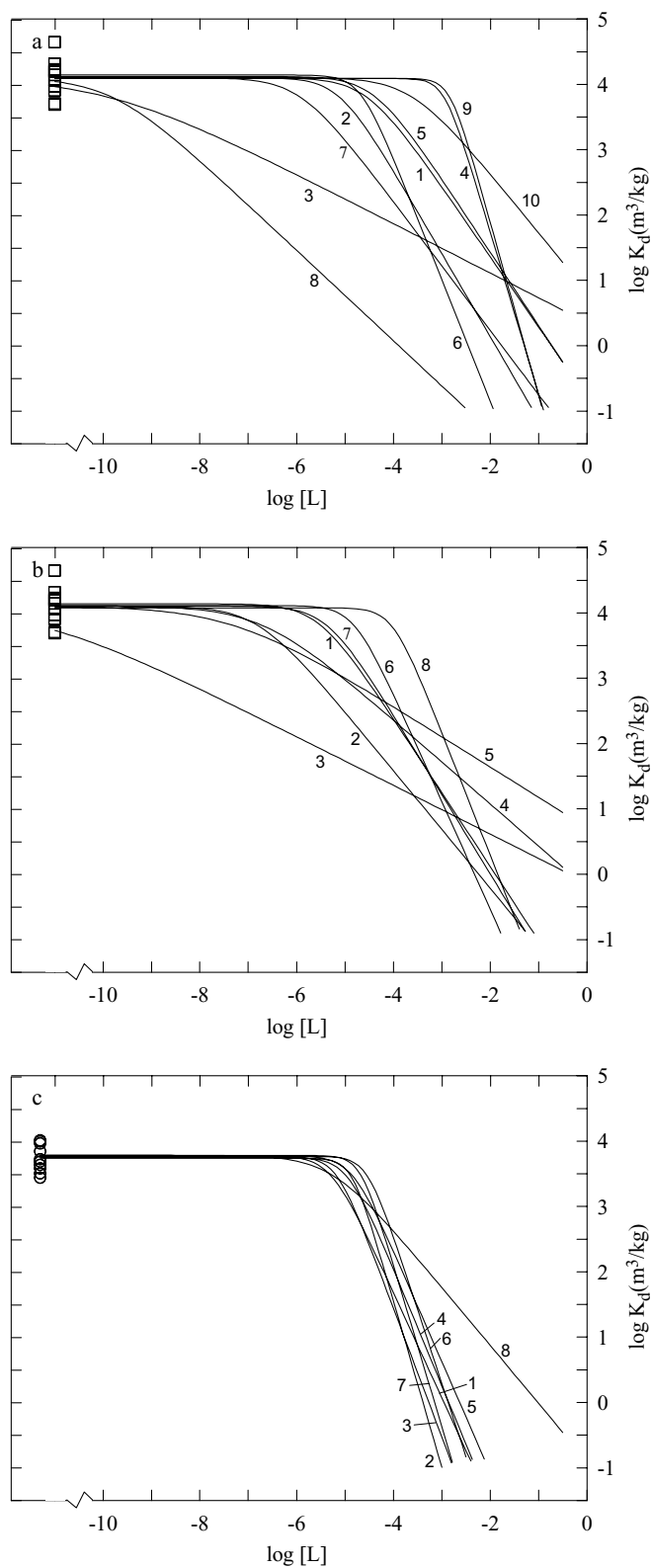




**Figure 4-24.** Calculated values of  $\log(D)/n$  from equation (6). (■)  $\text{TiO}_2$ , (▒)  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( ) Cement.



**Figure 4-25.** Calculated regression lines for the sorption of Eu at pH 12.5 on (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2$  in the presence of 2 mM  $\text{Ca}^{2+}$ , and (c) cement, with different organic molecules (L) at varying concentrations (unit: M, except for FA, where g/L is used). (1) EDTA, (2) DTPA, (3) NTA, (4) Citric acid, (5) Gluconic acid, (6) FA, (7) ISA, (8) AcAc.



**Figure 4-26.** Calculated regression lines for the sorption of Eu at pH 12.5 on (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2$  in the presence of  $2 \text{ mM Ca}^{2+}$ , and (c) cement, with different cement additives and cleaning agents ( $L$ ) at varying concentrations (unit: flp). (1) Sikament 10, (2) Sikament 210, (3) Peramin Compac 30, (4) Peramin F, (5) Glenium 51, (6) Cementa Melcrete, (7) Mighty 150, (8) Clax Delta Balans, (9) Industrikombi, (10) Prefect Citron.

### 4.3.6 Degradation of organics

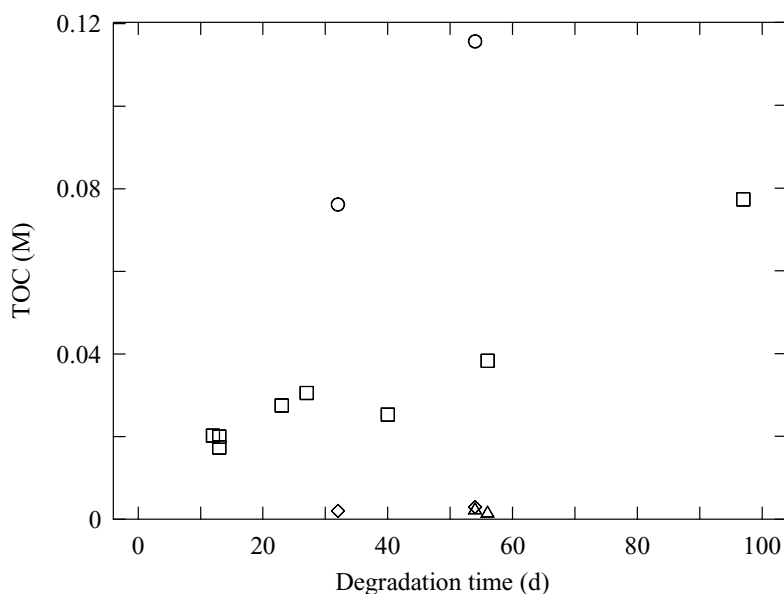
The results from the degradation of the filter aid Ricem UP2 and the ion exchange resin Acrisorb LSR33 at pH 12.5 and 60°C are plotted in Figure 4-27 in terms of TOC (total organic carbon) content versus degradation time. The conditions of these experiments are described in Section 3.2.

The degradation of particularly the product Ricem UP2 as seen in Figure 4-27 led to a significantly reduced Eu-adsorption (Figure 4-23). The degradation of Acrisorb LSR33 was minor. An initial concentration of solid Acrisorb LSR33 of 50 g/L led to a generation of DOC of less than 3 mM (some 70–80 mg/L of dissolved organic matter). No significant effects on the sorption of Eu were observed at 0.4 mM added DOC (approximately 10 mg/L dissolved organic matter), see Figure 4-22.

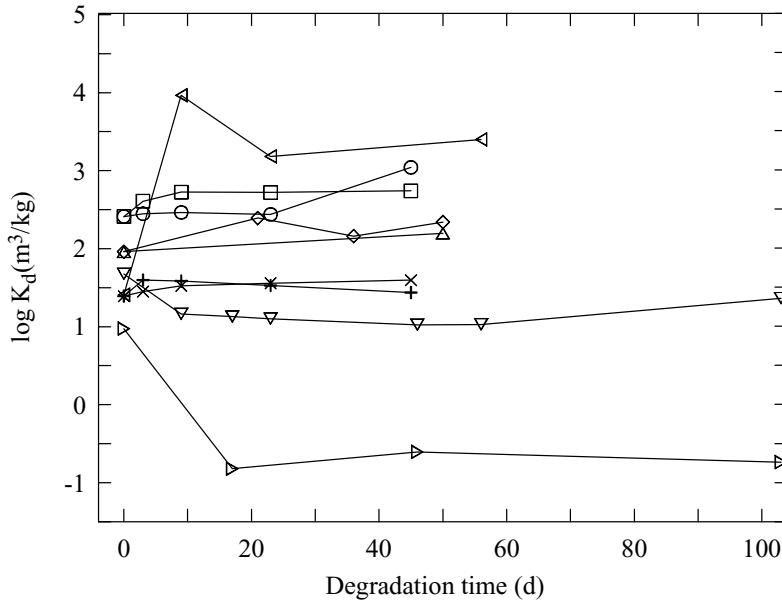
Chelating agents breakdown typically requires longer time scales, more severe chemical conditions, or the presence of catalysts. Hydrolysis of free EDTA via C-N fission requires temperatures in excess of 175°C /Motekaitis et al, 1979/, however some metal complexes are rapidly photodegraded. Rates of EDTA hydrolysis decrease with increasing percentages of total EDTA complexed by the added metal ion. In a similar manner, rates of NTA degradation at high temperatures decrease as the extent of complexation by metal ions is increased.

The results from superplasticizer degradation with time at pH 12.5 and the specified temperature are plotted in Figures 4-28–4-30. The superplasticizers were degraded at pH 12.5,  $flp = 0.1$  and 20, 40 or 60°C. Then 24 h sorption experiments were performed, see Table 3-1. The solid phase was  $TiO_2$ , when cement is not mentioned. The data from the sorption experiments can be found in Appendix II.

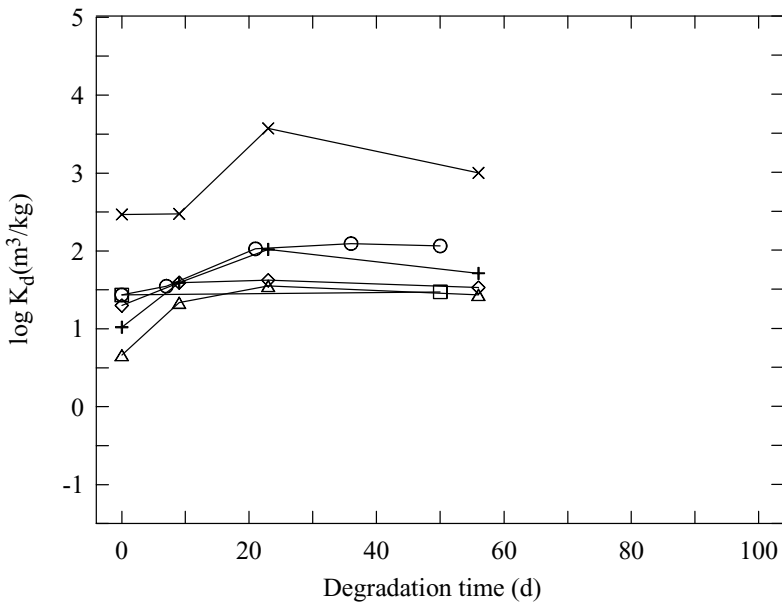
The sorption does not vary or increase much with the degradation of complexing agents as seen in Figures 4-28–4-30, except for Peramin F (Figure 4-28). With the addition of Peramin F with  $flp=10^{-4.5}$  in the cement system there is a sorption increase whereas when a  $flp=10^{-2}$  of Peramin F is added, the sorption decreases.



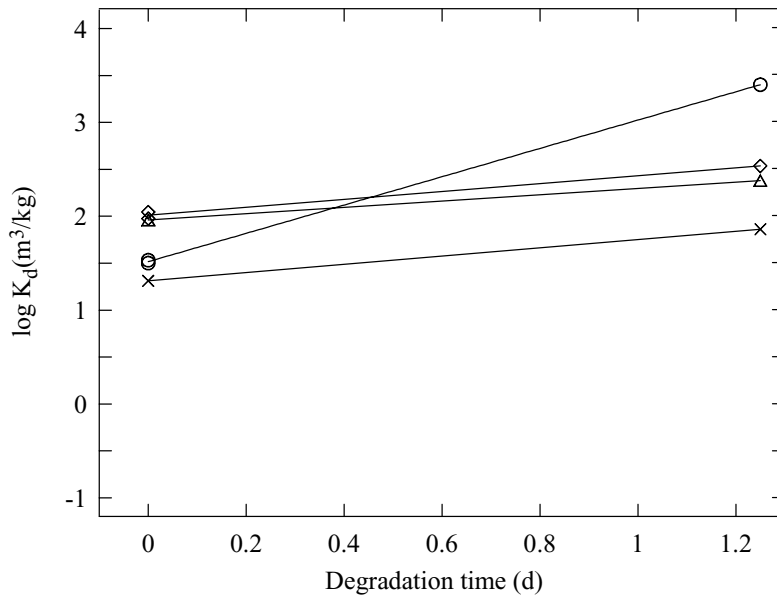
**Figure 4-27.** Degradation of filter aid Ricem UP2 and ion exchange resin Acrisorb LSR33 at pH 12.5, 60°C (□) Ricem UP2, (○) Ricem UP2, [Ca]=0.01 M, (Δ) Acrisorb LSR33, (◇) Acrisorb LSR33, [Ca]=0.01 M.



**Figure 4-28.** The superplasticizers were degraded at pH 12.5,  $flp=10^{-1}$  and the specified temperature. Then 24 h sorption experiments were performed at the specified superplasticizer concentration. The solid phase was  $TiO_2$ , when cement is not mentioned. (□) Sikament 10,  $flp=10^{-3}$ , 20°C, (○) Sikament 10,  $flp=10^{-3}$ , 40°C, (Δ) Sikament 210,  $flp=10^{-3.5}$ , 20°C, (◇) Sikament 210,  $flp=10^{-3.5}$ , 60°C, (×) Peramin Conpac 30,  $flp=10^{-3.5}$ , 20°C, (+) Peramin Conpac 30,  $flp=10^{-3.5}$ , 40°C, (▽) Peramin F,  $flp=10^{-2}$ , 60°C, (<) Cement, Peramin F,  $flp=10^{-4}$ , 60°C, (▷) Cement, Peramin F,  $flp=10^{-2}$ , 60°C.



**Figure 4-29.** The superplasticizers were degraded at pH 12.5,  $flp=10^{-1}$  and the specified temperature. Then 24 h sorption experiments were performed at the specified superplasticizer concentration. The solid phase was  $TiO_2$ , when cement is not mentioned. (□) Glenium 51,  $flp=10^{-2.5}$ , 20°C, (○) Glenium 51,  $flp=10^{-2.5}$ , 60°C, (Δ) Cementa Melcrete,  $flp=10^{-3.5}$ , 60°C, (◇) Cement, Cementa Melcrete,  $flp=10^{-3.5}$ , 60°C, (×) Mighty 150,  $flp=10^{-4}$ , 60°C, (+) Cement, Mighty 150,  $flp=10^{-4}$ , 60°C.



**Figure 4-30.** The superplasticizers were degraded at pH 12.5,  $flp=10^{-1}$  and  $120^{\circ}\text{C}$  during 30 h. Then 24 h sorption experiments were performed at the specified superplasticizer concentration. The solid phase was  $\text{TiO}_2$ . (○) Sikament 10,  $flp=10^{-3}$ , (△) Sikament 210,  $10^{-3.5}$ , (◇) Peramin Conpac 30,  $flp=10^{-4.5}$ , (×) Glenium 51,  $flp=10^{-2.5}$ .

#### 4.3.7 Effect of Equilibration Time on Sorption

The aim of the study was to find a method as fast as possible, to compare the influence of different complexing agents on the sorption of Eu and therefore samples were always taken after one day equilibration. However, some of them were left to equilibrate for different periods of time and we have plotted the sorption of europium with the presence of ISA ( $10^{-2}\text{M}$ ) for the different adsorbent materials. As can be seen in Figure 4-31, the  $K_d$  values increase with time of equilibration to a constant value, that we called the plateau value:  $\log K_d^{\infty}$  ( $\log K_d$  after infinite time).

The complete set of data for different sorption times, for all ligands, concentrations and adsorbent materials can be found in Appendix III.

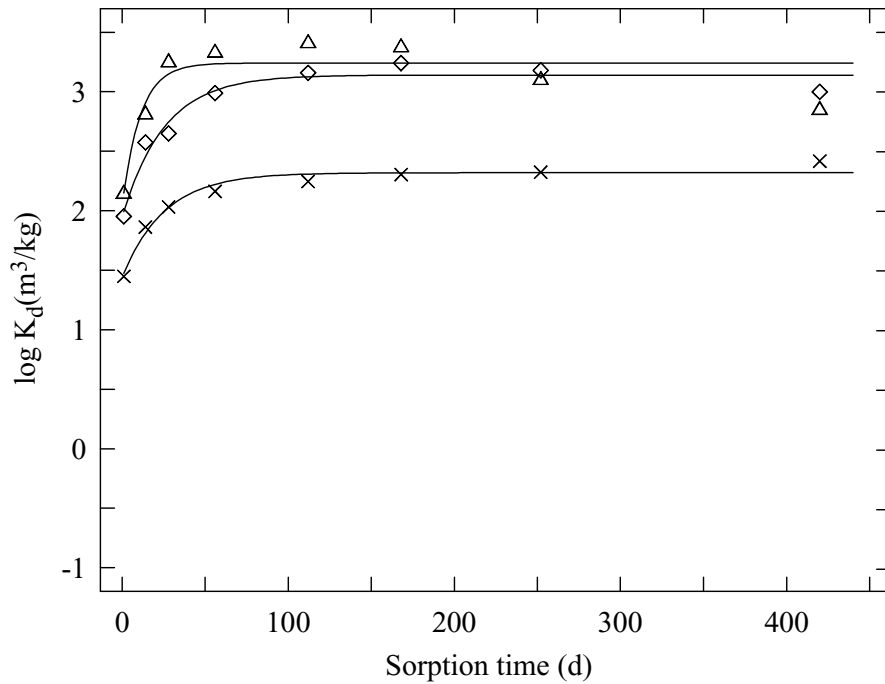
The results were fitted to the following equation:

$$\log K_d = \log K_d^{\infty} - B \cdot e^{-kt} \quad (9)$$

where  $\log K_d^{\infty}$ ,  $B$  and  $k$  are adjustable parameters and  $t$  is time. The equation has no theoretical background but describes the data fairly well and can be used to calculate  $\log K_d^{\infty}$ .

In this section we have plotted  $\log K_d$  after 1, 14, 56, 112, 252 days for all the samples as a function of  $\log K_d^{\infty}$ , where no variation on the value of  $K_d$  was observed (Figure 4-32). It is obvious that 1 d sorption time is not sufficient to do a good comparison between complexing agents, but a preliminary result can be received after 14 d and a final result after 90 days. A continuous mixing of the samples could probably shorten the equilibration time.

After 90 days of equilibration the measured  $K_d$  values are practically the same as after infinite time.



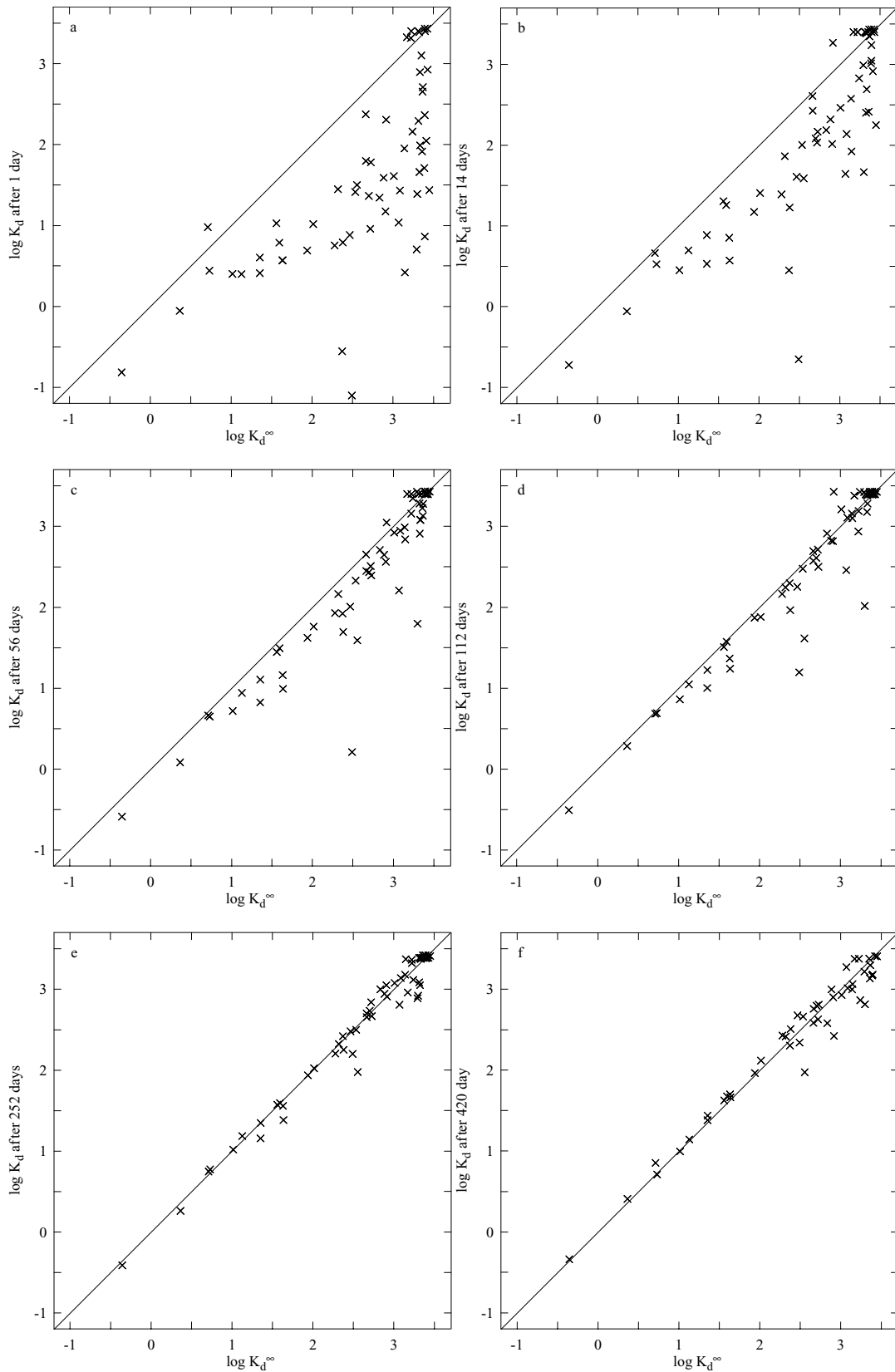
**Figure 4-31.** Sorption of Eu in the presence of isosaccharinic acid: ( $\Delta$ )  $\text{TiO}_2$ , [ISA]= $10^{-2.5}$  M, ( $\diamond$ )  $\text{TiO}_2$ , [ISA]= $10^{-2.5}$  M, [Ca]=0.002 M, ( $\times$ ) Cement, [ISA]= $10^{-2.5}$  M.

#### 4.3.8 Ligand Sorption

The sorption of ligands is shown in Appendix IV expressed as % adsorbed ligand.

Generally, only a minor part (<5%) of the ligands was sorbed to the  $\text{TiO}_2$  (exception gluconic acid  $\approx$ 30%, ISA  $\approx$ 22%).

On the other hand, the sorption to cement was in some cases as high as 75%. In the case of oxalate and perhaps citrate, precipitation reactions are probably the reason for the decrease of ligand concentration in solution.



**Figure 4-32.**  $\log K_d$  after different sorption times are compared to  $\log K_d^\infty$ ,  $\log K_d$  after infinite time, calculated by the equation  $\log K_d = \log K_d^\infty - B \cdot e^{-kt}$ . (a) 1, (b) 14, (c) 56, (d) 112, (e) 252 d, (f) 420 days.



## 5 Discussion

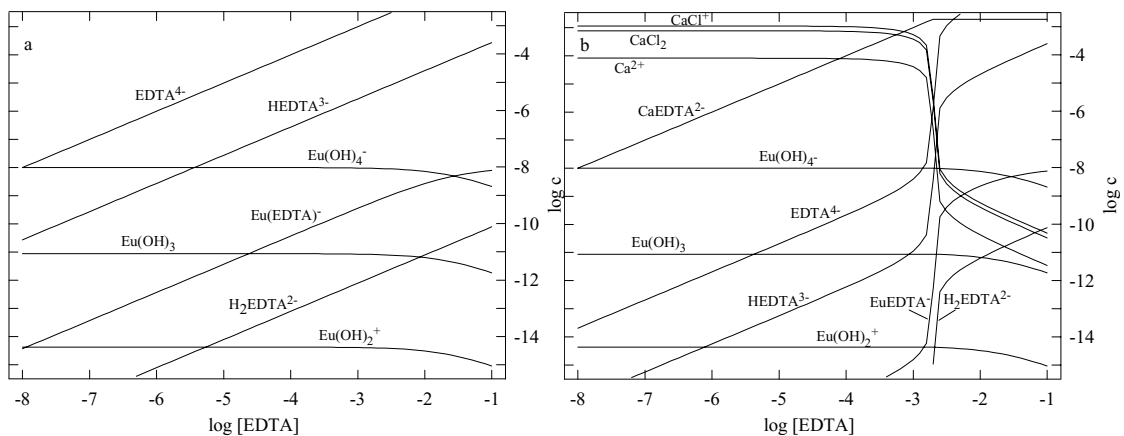
The present study indicated not unexpectedly that the presence of organic ligands in the cementitious environments will affect the sorption of radioactive materials.

Europium was chosen as analogue to trivalent lanthanides and actinides, and from the experiments performed without organic ligands it can be seen that it sorbs very strongly to both  $\text{TiO}_2$  and cement. The main species of europium at pH 12.5 is  $\text{Eu}(\text{OH})_4^-$ , and it is not expected to sorb as such (being negatively charged). However, there is an effective removal of europium from the solution to the surface sites of the adsorbent materials due to surface complexation. Looking at the speciation diagram in solution for  $\text{Eu}^{3+}(10^{-8} \text{ M})$  and EDTA at different concentrations (Figure 5-1a), a gradual increase of the complex  $\text{Eu}(\text{EDTA})^-$  is observed as the concentration of  $\text{EDTA}^{4-}$  also increases. When looking at the speciation diagram in solution for  $\text{Eu}^{3+}(10^{-8} \text{ M})$ ,  $\text{Ca}^{2+}(2 \cdot 10^{-3} \text{ M})$  and EDTA at different concentrations (Figure 5-1b), it is  $\text{Ca}^{2+}$  (in excess) that complexes gradually with  $\text{EDTA}^{4-}$ , and only when all calcium is complexed, EDTA complexes Eu. This type of behaviour was also observed for NTA, D-gluconic acid and fulvic acid.

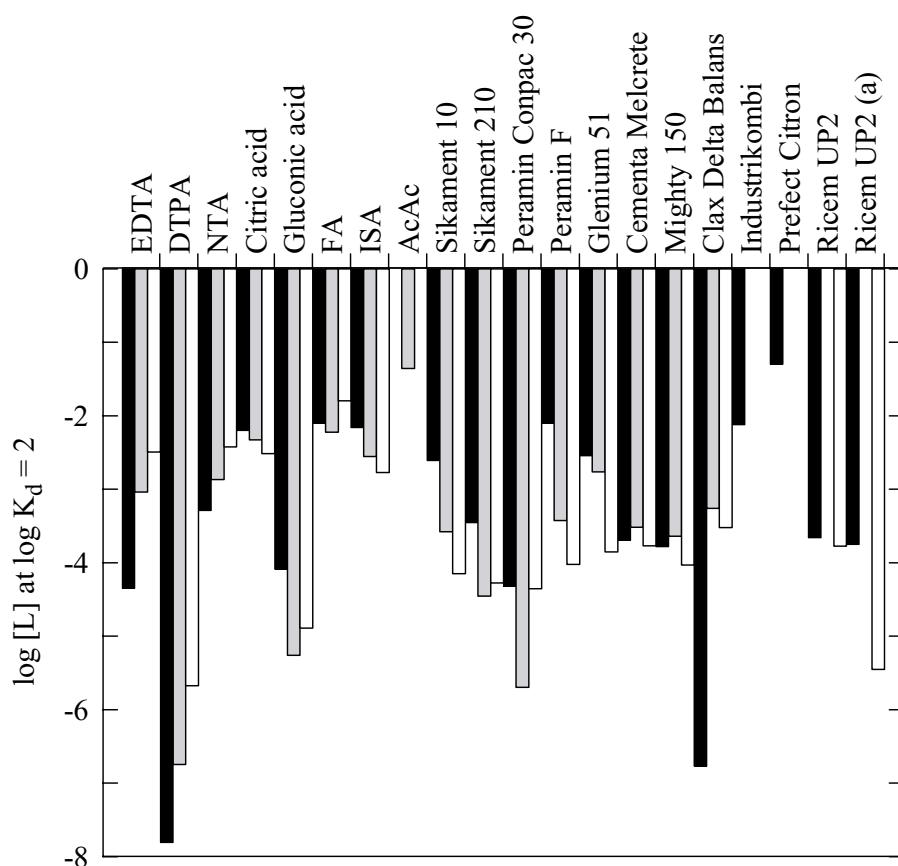
In the results section it was shown that the sorption of Eu on cement as well as on  $\text{TiO}_2$  decreases due to the presence of cement additives at concentration levels expected in fresh cement and concrete of technical quality.

Important information on how the sorption is being affected by the presence of a complexing agent can be obtained by taking a constant  $\log K_d$ -value of 2 and comparing the given values for  $\log [L]$  as seen in Figure 5-2.

In Table 4-4–4-6, the results from the linear regressions can be seen together with the calculated values of  $\log [L]$  when  $\log K_d = 2$ .



**Figure 5-1.** Eu (III) speciation in solution at varying EDTA concentrations (M). (a)  $[\text{Ca}] = 0 \text{ M}$ , (b)  $[\text{Ca}] = 0.002 \text{ M}$ .



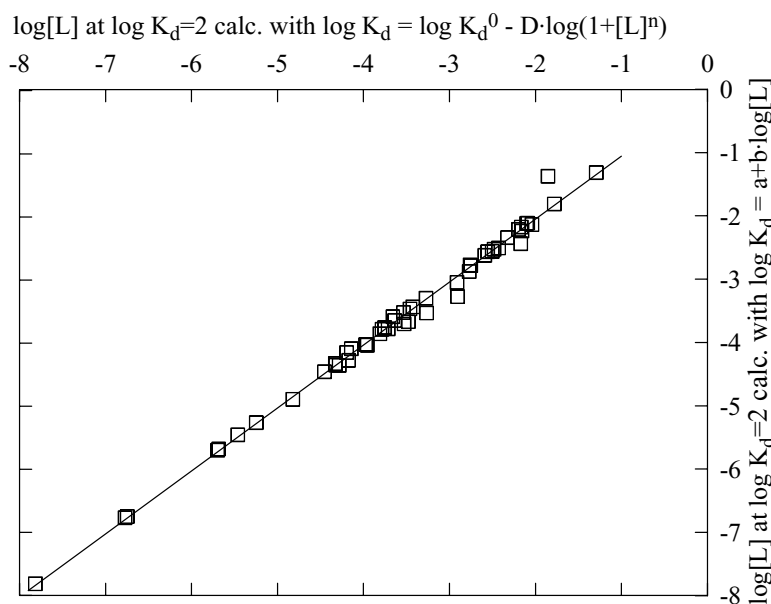
**Figure 5-2.** Calculated values of  $\log [L]$  when  $\log K_d=2$  (from the linear regressions). (■)  $\text{TiO}_2$ , (▒)  $\text{TiO}_2$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( ) Cement.

The effects of the presence of these organic agents and the presence of additives at various concentrations on the distribution of Eu were quantified by different parameters, obtained from the linear regressions ( $a$ ,  $b$  in equation (1)) and the surface-complex competition model ( $D$ ,  $n$  in equations (2) and (7)). Both methods were compared by plotting the calculated values of  $\log [L]$  when  $\log K_d=2$ , using the two different equations ( $\log K_d = \log K_d^0 - D \cdot \log(1+[L]^n)$  versus  $\log K_d = a + b \cdot \log[L]$ ) as seen in Figure 5-3. The good agreement between the two methods clearly demonstrates that both methods can be used to treat this kind of data, if  $\log [L]$  when  $\log K_d = 2$  is used as a comparative parameter. The linear regression method then should be preferred for its simplicity, since the surface-complex competition model (SCCM) needs an initial value to start the iteration.

The influence on Eu sorption of the ligands were estimated and compared to the values of  $\log(D)/n$  and  $\log[L]$  when  $\log K_d = 2$ . The results showed that in most cases  $\log[L]$  when  $\log K_d = 2$  corresponded with the estimation and that the correspondence was worse when  $\log(D)/n$  was used.

Another comparison between systems was done by plotting  $\log[L]$  when  $\log K_d = 2$  for the different solid phases, in order to see if  $\text{TiO}_2$  could be used as an analogue to cement. In Figure 5-4a cement was compared to  $\text{TiO}_2$  and the correlation was very poor. In Figure 5-4b cement was compared to  $\text{TiO}_2$  (2 mM Ca).

The correlation is quite good when  $\text{TiO}_2/\text{Ca}$  (2 mM) is used as analogue to cement. However it is still preferable to use cement as the solid phase, as the systems showed some differences.

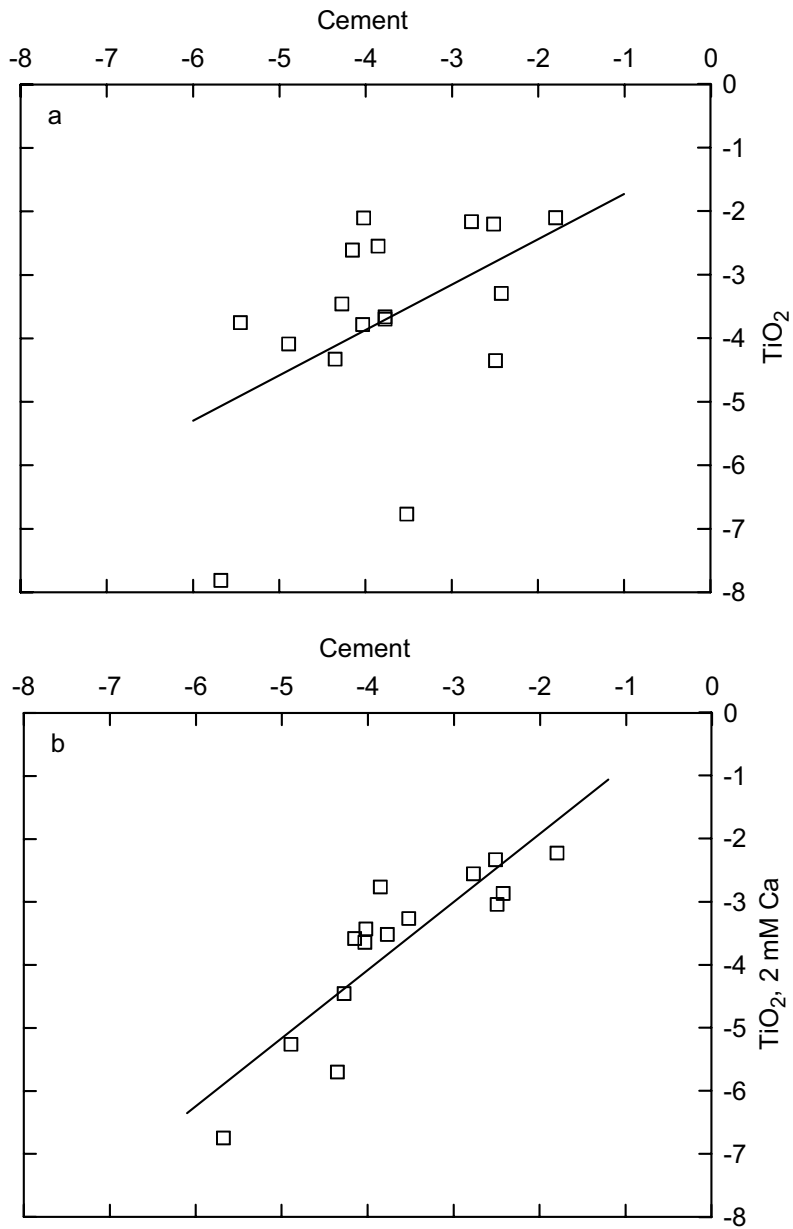


**Figure 5-3.** Comparison of  $\log[L]$  at  $\log K_d=2$ , calculated with  $\log K_d = \log K_d^0 - D \cdot \log(1+[L]^n)$  and  $\log K_d = a+b \cdot \log[L]$ .

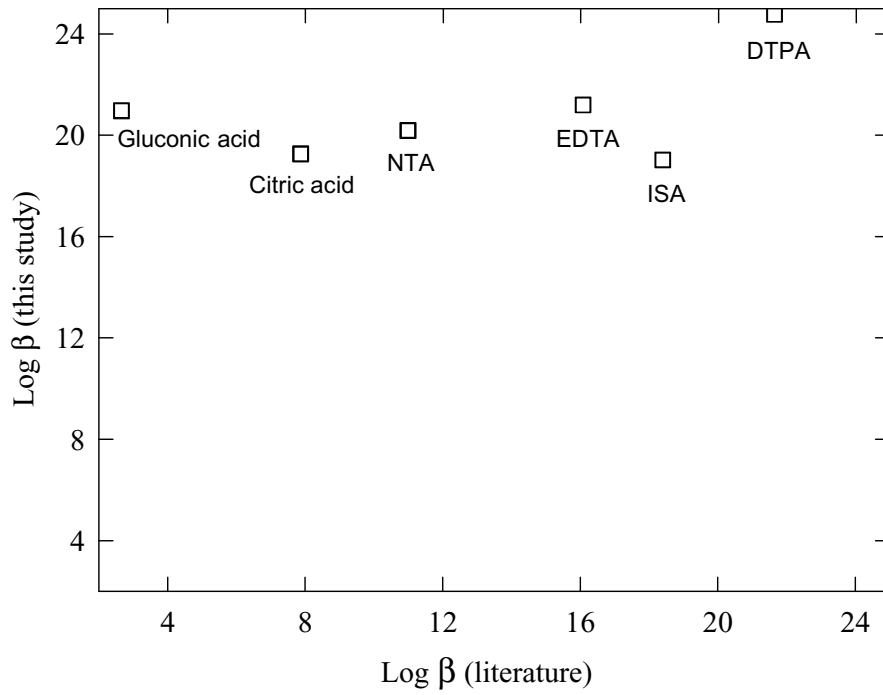
In Figure 5-5 a comparison between  $\log \beta$  from this study and literature values is plotted. Systems with  $\text{TiO}_2$  as solid phase and no added Ca are used for the correlation and the sorption time is 1 d. The literature values are recalculated to an ionic strength of 0.3 M with the method of Truesdell-Jones /Langmuir, 1997/. The poor correlation between  $\beta$  from this study (using the  $\text{TiO}_2$  systems without Ca; the cement systems are too complicated) and literature values shows that the potential of the complexing agents to alter the distribution of radionuclides cannot be assessed solely by looking at the literature  $\beta$  values. Because the literature values represent 1:1 complexes and  $n = 1$  is the most suitable positive integer when using equation (6),  $n$  was set to 1 (in all other calculations  $n$  was an adjustable parameter) and  $A=10^{14.87}$ .

The  $\beta$  value for ISA agreed well with the literature value, while for the other ligands the values obtained in this study were between 3 and 18 orders of magnitude higher.

One reason for this discrepancy could be that equilibrium was not attained.  $\beta$  values calculated from the  $\log K_d^\infty$  (see section 4.3.7; assuming the same  $\log K_d^0$  as after 1 d adsorption time and  $n = 1$ ) lowers  $\log \beta$  with at most 1.8, which means that lack of equilibrium could not explain the high  $\beta$  values after 1 d sorption time. Minor ligand adsorption as observed on  $\text{TiO}_2$  does not either explain the difference between values from this study and literature values.  $\text{TiO}_2$  systems with no Ca added were used when calculating  $\beta$  as this solid phase is stable at high pH and does not disturb the evaluation. No divalent ions were added, which could form complexes with the ligand. The sorption isotherm is approximately linear in the concentration range of interest and sorption is reversible /Dario and Allard, 2003/. At the low Eu concentration it is not likely that polynuclear complexes will form /Allard, 1982/. None of the assumptions in the list above explain the difference between the obtained values and literature values. There is also a great uncertainty of  $A$ , because of the uncertainty of  $\beta_{\text{Eu}(\text{OH})_4^-}$ , which is not measured but calculated according to /Glaus et al, 1997/. Using another value of  $A$  all  $\beta$  values would alter but no better correlation would be obtained. Other possible reasons for the disagreement between the literature and our obtained  $\beta$  values could be the formation of other complexes: with  $n \neq 1$ , or mixed with hydroxide.



**Figure 5-4.**  $\text{Log}[L]$  at  $\text{log } K_d=2$ . Comparison between systems with different solid phases. (a) Cement compared to  $\text{TiO}_2$ , 0 mM Ca, (b) Cement compared to  $\text{TiO}_2$ , 2 mM Ca.



**Figure 5-5.** Comparison between  $\log \beta$  from this study and literature values. Systems with  $\text{TiO}_2$  as solid phase and no added Ca is used. Sorption time: 1 d. Equation (6) with  $n=1$  is used in the calculation. The literature values are recalculated to an ionic strength of 0.3 M with the method of Truesdell-Jones /Langmuir, 1997/.

## 6 Conclusions

Cements are attractive matrices for the immobilisation of radioactive wastes, but they invariably contain additives and the degradation products from these additives. Generally, there is a significant reduction of the sorption (expressed as the distribution coefficient) of Eu on cement as well as on TiO<sub>2</sub> due to the presence of organic ligands and cement additives at concentration levels expected in fresh cement and concrete of technical quality.

The batch sorption method can be used to compare the ability of different organic substances to affect Eu sorption. Calculating the effect of organic substances using complexing constants from the literature would give unreliable results.

If TiO<sub>2</sub> is used instead of cement, Ca (2mM) must be added to the solution, but it is still preferable to use cement as the solid phase, as the systems showed some differences.

The effect on Eu sorption is similar for the seven additives in the cement systems. Short-term effects are reductions of the distribution coefficients by  $1 \pm 0.5$  orders of magnitude under the present experimental conditions. The experiments show, however, that sorption ( $\log K_d$ ) will increase with time by more than 0.4 orders of magnitude after less than 100 d. The effects are more pronounced in the cement systems than in the TiO<sub>2</sub>-systems, but addition of Ca (0.002 M) to the TiO<sub>2</sub>-systems leads to an effect on the sorption more similar to the cement systems.

The effects of the cleaning agents Industrikombi and Prefect Citron on the sorption of Eu on cement and TiO<sub>2</sub> was minor at concentration levels relevant of a cementitious waste deposit. Solid materials, such as ionic exchange resins, are degraded to soluble substances before accomplishing the sorption experiments. Degradation of the ion exchanger (metacrylic polymer) was minor and effects on the sorption not significant.

The filter aid, denoted as inert fibre material (an acrylonitrile polymer) underwent a rapid degradation under alkaline conditions that reached some 15% of the initial load after less than two months (worst case). The degradation products (not characterized) had a pronounced effect on Eu sorption on cement as well as TiO<sub>2</sub> at levels as low as in the mM-range (DOC). It is evident that this agent should not be deposited in a cementitious environment together with trivalent hazardous elements without further studies to characterize these degradation products and to determine their long-term stability under alkaline conditions.

$\log[L]$  at  $\log K_d = 2$  can be used as a first estimation when evaluating the influence of a complexing agent on Eu sorption, but for the final conclusion it is necessary to look at the shape of the complete  $\log K_d$  vs.  $\log[L]$ -curve.

A sorption time of 1 d, which was the time in most experiments, is insufficient, because sorption increases with time and reaches a constant value after 100–200 d. After 14 d a preliminary comparison and after 90 d a final comparison can be done.

The aim of this work was to find a method, as simple and fast as possible, to compare the influence of different complexing agents on the sorption of Eu. This method has been developed and tested successfully. The method can presumably be improved further by investigating the following:

- Examine the sensitivity for  $\text{CO}_3^{2-}$  to see if it is necessary to use a glove box.
- Test if continuous mixing during long time experiments leads to a shorter equilibration time and a final result in less than 90 d.
- Perform similar sorption experiments with other metal ions, to see if the comparison of the ligands results in a similar ranking order.

## **7 Acknowledgements**

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Data from batch sorption experiments ( $[Eu] = 1 \cdot 10^{-8} M$ )

Table AI-1. Results from the batch experiments with 1 d sorption time.

Solid phase	Log (ligand conc.) <sup>a</sup>	[Ca] added (mM)	[Ca] analysed (mM)	pH	log $K_d$ (m <sup>3</sup> /kg) <sup>b</sup>	log $K_d$ (m <sup>3</sup> /kg) <sup>c</sup>	log $K_d$ (m <sup>3</sup> /kg)
<i>No ligand</i>							
TiO2		0		12.46	3.84		4.33
TiO2		0		12.46	3.59		4.08
TiO2		0		12.46	3.63		3.92
TiO2		0		12.44	3.64		4.08
TiO2		0		12.45	3.65		3.99
TiO2		0		12.47	3.77		4.21
TiO2		0		12.47	3.66	3.70	3.70
TiO2		0		12.46	4.19	4.22	4.22
TiO2		0		12.47	4.18	4.24	4.24
TiO2		0		12.47	4.14	4.16	4.16
TiO2		0		12.46	4.17	4.23	4.24
TiO2		0		12.46	4.64	4.66	4.66
TiO2		0		12.51	3.45		3.72
Cem.		0	2.90	12.60	3.30	3.56	3.65
Cem.		0	7.89	12.68	3.60	3.68	3.70
Cem.		0	3.52	12.55	3.18	3.24	3.52
Cem.		0	2.88	12.54	3.59	3.65	4.01
Cem.		0	3.06	12.54	3.52	3.58	3.98
Cem.		0	2.40	12.54	3.15	3.23	3.60
Cem.		0		12.36	3.51	3.94	4.03
Cem.		0		12.36	2.93	3.36	3.45
Cem.		0		12.35	3.12	3.62	3.74
Cem.		0		12.52	3.40	3.74	3.86
<i>EDTA</i>							
TiO2	-3	0		12.49	3.21	3.31	3.31
TiO2	-2.5	0		12.50	2.86	3.02	3.02
TiO2	-2	0		12.50	2.36	2.63	2.63
TiO2	-1	0		12.48	1.61	1.77	1.77
TiO2	0	0		12.45	0.65	0.74	0.74
TiO2	0.5	0		12.36	0.27	0.38	0.38
TiO2	-1	0					1.78
TiO2	-1	2		12.50	3.48	3.65	3.65
TiO2	-0.25	2		12.50	2.73		2.93
TiO2	0	2	1.56	12.46	2.52		2.70
TiO2	0.25	2		12.41	1.26		1.43
TiO2	0.5	2	1.66	12.42	0.07		0.37
TiO2	0.5	2					0.40
Cem.	-1	0	2.62	12.59	3.23	3.38	3.41
Cem.	0.25	0		12.53	2.50	2.56	2.57
Cem.	0.5	0	4.12	12.48	2.59	2.66	2.66
Cem.	0.75	0		12.26	1.52	1.52	1.53
Cem.	1	0	8.61	12.41	-0.65	-0.55	-0.54
Cem.	1	0					-0.82

<sup>a</sup> Unit: M, g/l for FA, volume fraction of liquid phase for the cement additives and cleaning agents.

<sup>b</sup> Corrected for adsorption to the vessel walls according to method 1.

<sup>c</sup> Corrected for adsorption to the vessel walls according to method 2.

Solid phase	Log (ligand conc.) <sup>a</sup>	[Ca] added (mM)	[Ca] analysed (mM)	pH	log K <sub>d</sub> (m <sup>3</sup> /kg) <sup>b</sup>	log K <sub>d</sub> (m <sup>3</sup> /kg) <sup>c</sup>	log K <sub>d</sub> (m <sup>3</sup> /kg)
<i>DTPA</i>							
TiO2	-5	0		12.50	2.08	2.17	2.18
TiO2	-4.5	0		12.48	1.62	1.70	1.71
TiO2	-4	0		12.44	1.16	1.25	1.25
TiO2	-3	0		12.49	-0.10	0.19	0.19
TiO2	-2	0		12.48	-1.32	-1.00	-0.99
TiO2	-1	0		12.48	-1.51	-1.17	-1.17
TiO2	0	0		12.44	-1.55	-1.19	-1.19
TiO2	-4	0					0.98
TiO2	-4	2		12.50	2.26	2.45	2.45
TiO2	-3	2		12.43	0.58		0.90
TiO2	-1	2	1.57	12.47	-0.70		-0.52
TiO2	-4	2					2.29
TiO2	-1	2					-0.56
Cem.	-4	0	3.52	12.54	3.32	3.67	3.75
Cem.	-3.5	0	3.27	12.52	2.75	3.15	3.22
Cem.	-3	0	2.35	12.29	0.89	1.19	1.30
Cem.	-3	0		12.52	1.58	1.81	1.90
Cem.	-2	0	2.59	12.55	1.25	1.42	1.45
Cem.	-1	0	3.01	12.53	0.43	0.56	0.57
Cem.	0.5	0	3.54	12.36	-1.04	-0.34	-0.34
Cem.	-1	0					0.42
<i>NTA</i>							
TiO2	-1.5	0		12.48	3.03	3.11	3.11
TiO2	-1	0		12.47	2.82	2.89	2.89
TiO2	-0.5	0		12.50	2.40	2.52	2.52
TiO2	0	0		12.47	1.39	1.57	1.57
TiO2	0.5	0	0.01	12.45	0.92		1.09
TiO2	-0.5	0					2.37
TiO2	1	0					0.40
TiO2	-0.5	2		12.50	3.58	3.71	3.71
TiO2	0	2	1.59	12.47	3.21		3.38
TiO2	0.25	2		12.50	1.63		1.74
TiO2	0.5	2	1.66	12.45	0.39		0.52
TiO2	0.5	2		12.42	0.29		0.39
Cem.	0	0	3.22	12.52	2.82	3.04	3.09
Cem.	0.25	0		12.56	2.65	2.84	2.86
Cem.	0.5	0	4.39	12.56	3.19	3.28	3.29
Cem.	0.5	0	1.87	12.54	3.03	3.09	3.09
Cem.	0.75	0		12.63	2.88	2.93	2.93
Cem.	1	0	5.56	12.14	-1.02	-0.85	-0.85
Cem.	1	0		12.44	-0.32	-0.29	-0.28
Cem.	1	0					0.41
<i>Citric acid</i>							
TiO2	-1	0		12.47	3.39	3.44	3.45
TiO2	-0.5	0		12.50	2.83	2.99	2.99
TiO2	0	0		12.44	2.26	2.35	2.36
TiO2	1	0		12.11	2.03	2.11	2.11
TiO2	-0.5	0					2.93
TiO2	1	0					1.71
TiO2	-0.5	2		12.48	2.86	2.93	2.93
TiO2	0	2		12.51	2.56		2.60

<sup>a</sup> Unit: M, g/l for FA, volume fraction of liquid phase for the cement additives and cleaning agents.

<sup>b</sup> Corrected for adsorption to the vessel walls according to method 1.

<sup>c</sup> Corrected for adsorption to the vessel walls according to method 2.

Solid phase	Log (ligand conc.) <sup>a</sup>	[Ca] added (mM)	[Ca] analysed (mM)	pH	log K <sub>d</sub> (m <sup>3</sup> /kg) <sup>b</sup>	log K <sub>d</sub> (m <sup>3</sup> /kg) <sup>c</sup>	log K <sub>d</sub> (m <sup>3</sup> /kg)
TiO2	1	2		12.58	1.69		1.71
Cem.	-0.5	0	3.15	12.54	3.34	3.35	3.41
Cem.	0	0	3.30	12.52	2.92	2.95	2.96
Cem.	0.5	0	3.54	12.43	1.85	1.91	1.91
Cem.	1	0	4.00	12.13	1.33	1.38	1.38
Cem.	1	0					1.02
<i>Gluconic acid</i>							
TiO2	-2	0		12.49	3.16	3.31	3.31
TiO2	-1.5	0		12.48	2.45	2.52	2.52
TiO2	-1	0		12.48	1.61	1.70	1.70
TiO2	-0.5	0		12.50	1.56	1.63	1.63
TiO2	0	0		12.47	1.89	1.90	1.90
TiO2	-1.5	0					1.99
TiO2	-3	2		12.51	3.25		3.30
TiO2	-2.5	2		12.50	1.85		2.10
TiO2	-2	2	1.57	12.51	1.52		1.71
TiO2	-1.5	2		12.50	0.66	0.78	0.78
TiO2	-1.5	2					0.86
Cem.	-2.5	0	3.04	12.54	2.91	3.15	3.24
Cem.	-2	0	3.15	12.18	2.91	3.01	3.04
Cem.	-1.75	0		12.53	1.43	1.50	1.54
Cem.	-1.5	0	3.19	12.56	0.94	0.97	1.01
Cem.	-1	0	3.53	12.55	-0.62	-0.50	-0.50
Cem.	-1	0	3.66	12.52	-0.56	-0.45	-0.44
Cem.	-1.5	0					0.70
<i>Oxalic acid</i>							
TiO2	-1	0		12.47	3.79	3.88	3.88
TiO2	0	0		12.46	3.96	4.04	4.04
TiO2	1	0		12.34	3.10	3.27	3.27
TiO2	0	0					3.40
TiO2	0	2		12.48	3.56	3.72	3.72
Cem.	1	0	0.07	12.43	3.21	3.29	3.32
Cem.	0.5	0	1.48	12.50	3.38	3.51	3.57
<i>FA</i>							
TiO2	-4	0		12.50	3.49	3.56	3.56
TiO2	-3.5	0		12.50	2.91	3.02	3.02
TiO2	-3	0		12.50	2.87	3.00	3.00
TiO2	-2.5	0		12.49	2.44	2.56	2.56
TiO2	-2	0		12.49	1.91	1.95	1.95
TiO2	-1.5	0		12.49	1.47	1.50	1.50
TiO2	-1.25	0		12.51	1.23	1.25	1.25
TiO2	-2	0					1.66
TiO2	-3	2	1.56	12.48	3.76		3.91
TiO2	-2.5	2		12.52	3.44		3.50
TiO2	-2	2		12.50	1.31	1.35	1.35
TiO2	-1.5	2		12.51	-0.01		-0.15
TiO2	-2	2					1.04
Cem.	-3	0	3.52	12.55	3.15	3.37	3.44
Cem.	-2	0	3.44	12.55	2.90	2.95	2.95
Cem.	-1.75	0	2.93	12.47	1.60	1.67	1.68
Cem.	-1.5	0	2.78	12.53	0.90	0.96	0.97
Cem.	-2	0					2.65

<sup>a</sup> Unit: M, g/l for FA, volume fraction of liquid phase for the cement additives and cleaning agents.

<sup>b</sup> Corrected for adsorption to the vessel walls according to method 1.

<sup>c</sup> Corrected for adsorption to the vessel walls according to method 2.

Solid phase	Log (ligand conc.) <sup>a</sup>	[Ca] added (mM)	[Ca] analysed (mM)	pH	Log K <sub>d</sub> (m <sup>3</sup> /kg) <sup>b</sup>	log K <sub>d</sub> (m <sup>3</sup> /kg) <sup>c</sup>	log K <sub>d</sub> (m <sup>3</sup> /kg)
<i>ISA</i>							
TiO2	-0.5	0		12.50	3.32		3.42
TiO2	0	0		12.50	2.83		2.97
TiO2	0.5	0		12.48	2.16		2.22
TiO2	1	0		12.51	1.99		2.01
TiO2	0.5	0					2.16
TiO2	-0.5	2		12.49	3.41		3.66
TiO2	0	2		12.49	2.48		2.68
TiO2	0.5	2					1.95
Cem.	-0.5	0		12.54	2.94	3.16	3.19
Cem.	0	0		12.53	2.33	2.45	2.47
Cem.	0.5	0		12.49	1.52	1.56	1.57
Cem.	1	0		12.49	0.66	0.74	0.74
Cem.	0.5	0					1.45
<i>AcAc</i>							
TiO2	-1	0		12.50	3.40	3.60	3.60
TiO2	0	0		12.49	3.97	4.11	4.11
TiO2	1	0		12.41	3.68	3.86	3.86
TiO2	1	0					3.40
TiO2	0	2	1.58	12.47	3.92		4.14
TiO2	0.5	2		12.40	3.35		3.68
TiO2	0.75	2		12.53	3.43		3.68
TiO2	1	2.07		12.40	1.88	2.10	2.11
TiO2	1	2					3.32
Cem.	-1	0	2.71	12.49	3.24	3.61	3.72
Cem.	1	0	3.52	12.39	3.35	3.73	3.78
<i>TTA</i>							
TiO2	-1	0		12.50	3.95	4.06	4.06
TiO2	0	0		12.51	4.08	4.23	4.24
TiO2	0.5	0		12.83	3.77	3.94	3.94
TiO2	0.5	0					3.39
TiO2	0.5	2		12.75	3.29	3.48	3.48
TiO2	-2	2		12.38	3.44		3.69
Cem.	0	0	3.16	12.61	3.47	3.60	3.63
Cem.	0.5	0	2.42	12.70	3.52	3.59	3.62
<i>Sikament 10</i>							
TiO2	-4	0		12.50	3.16	3.38	3.38
TiO2	-3.5	0		12.49	2.59	2.78	2.79
TiO2	-3	0		12.47	2.40	2.46	2.46
TiO2	-2	0		12.48	1.68	1.71	1.71
TiO2	-1	0		12.40	-0.14	-0.06	-0.06
TiO2	-3	0					2.36
TiO2	-2	0					1.61
TiO2	-5	2		12.52	3.80		3.95
TiO2	-4.5	2		12.52	1.98		1.83
TiO2	-4	2		12.49	2.14		2.17
TiO2	-2.5	2		12.52	1.42		1.42
TiO2	-3	2		12.50	1.50	1.53	1.53
TiO2	-3	2					1.50
Cem.	-5	0	3.75	12.52	3.77	3.81	3.82
Cem.	-4.75	0		12.52	3.27	3.33	3.34
Cem.	-4.5	0	3.14	12.52	1.36	1.41	1.42

<sup>a</sup> Unit: M, g/l for FA, volume fraction of liquid phase for the cement additives and cleaning agents.

<sup>b</sup> Corrected for adsorption to the vessel walls according to method 1.

<sup>c</sup> Corrected for adsorption to the vessel walls according to method 2.



Solid phase	Log (ligand conc.) <sup>a</sup>	[Ca] added (mM)	[Ca] analysed (mM)	pH	Log K <sub>d</sub> (m <sup>3</sup> /kg) <sup>b</sup>	log K <sub>d</sub> (m <sup>3</sup> /kg) <sup>c</sup>	log K <sub>d</sub> (m <sup>3</sup> /kg)
Cem.	-4	0	2.88	12.55	0.71	0.78	0.82
Cem.	-3	0	2.96	12.48	0.66	0.70	0.72
Cem.	-2.5	2		12.51	0.49	0.54	0.56
Cem.	-3	0					0.60
<i>Sikament 210</i>							
TiO <sub>2</sub>	-4	0		12.20	3.21		3.25
TiO <sub>2</sub>	-3.5	0		12.48	1.92		1.96
TiO <sub>2</sub>	-3	0		12.48	0.93		0.97
TiO <sub>2</sub>	-2	0		12.48	0.34		0.38
TiO <sub>2</sub>	-1	0		12.38	-1.65		-1.00
TiO <sub>2</sub>	-3	0					1.03
TiO <sub>2</sub>	-5	2		12.50	2.61		2.73
TiO <sub>2</sub>	-4	2		12.50	1.17		1.21
TiO <sub>2</sub>	-1	2.22		12.35	-1.63		-1.07
TiO <sub>2</sub>	-3	2					0.79
Cem.	-5	0	3.22	12.47	3.44	3.50	3.54
Cem.	-4	0	3.16	12.48	1.60	1.62	1.62
Cem.	-3.5	0	3.51	12.53	0.18	0.22	0.23
Cem.	-3	0	2.84	12.48	-1.10	-0.87	-0.86
Cem.	-3	0					-1.10
<i>Peramin Conpac 30</i>							
TiO <sub>2</sub>	-5.5	0		12.51	2.72	2.87	2.87
TiO <sub>2</sub>	-4.5	0		12.50	1.83	1.97	1.98
TiO <sub>2</sub>	-3.5	0		12.49	1.18	1.39	1.39
TiO <sub>2</sub>	-3	0		12.47	1.20	1.30	1.30
TiO <sub>2</sub>	-2	0		12.44	0.78	0.84	0.84
TiO <sub>2</sub>	-1	0		12.23	0.71	0.76	0.76
TiO <sub>2</sub>	-1	0	0.02	12.34	1.21		1.24
TiO <sub>2</sub>	-4.5	0					2.05
TiO <sub>2</sub>	-3	0					1.43
TiO <sub>2</sub>	-6	2		12.52	1.95		1.99
TiO <sub>2</sub>	-5.5	2		12.50	1.76		2.11
TiO <sub>2</sub>	-4.5	2		12.50	1.50	1.66	1.66
TiO <sub>2</sub>	-4.5	2					1.39
Cem.	-5	0	3.03	12.51	2.60	3.20	3.42
Cem.	-4.5	0	3.43	12.52	1.55	1.74	1.83
Cem.	-4	0	1.52	12.55	0.95	1.28	1.28
Cem.	-3	0	3.26	12.49	-0.22	-0.14	-0.11
Cem.	-3	0					-0.06
<i>Peramin F</i>							
TiO <sub>2</sub>	-3	0	0.01	12.48	3.47		3.53
TiO <sub>2</sub>	-2.5	0	0.01	12.43	3.22		3.27
TiO <sub>2</sub>	-2	0	0.02	12.45	1.36		1.44
TiO <sub>2</sub>	-2	0					1.92
TiO <sub>2</sub>	-4	2		12.51	2.45		2.33
TiO <sub>2</sub>	-3.5	2		12.49	1.98		2.04
TiO <sub>2</sub>	-2.5	2		12.48	1.40		1.43
TiO <sub>2</sub>	-2	2		12.46	1.00		1.03
TiO <sub>2</sub>	-3	2					1.80
Cem.	-5	0		12.41	2.96	3.01	3.05
Cem.	-4.5	0		12.52	3.39	3.46	3.51
Cem.	-4.25	0		12.51	1.69	1.79	1.85

<sup>a</sup> Unit: M, g/l for FA, volume fraction of liquid phase for the cement additives and cleaning agents.

<sup>b</sup> Corrected for adsorption to the vessel walls according to method 1.

<sup>c</sup> Corrected for adsorption to the vessel walls according to method 2.

Solid phase	Log (ligand conc.) <sup>a</sup>	[Ca] added (mM)	[Ca] analysed (mM)	pH	Log K <sub>d</sub> (m <sup>3</sup> /kg) <sup>b</sup>	log K <sub>d</sub> (m <sup>3</sup> /kg) <sup>c</sup>	log K <sub>d</sub> (m <sup>3</sup> /kg)
Cem.	-4	0	2.67	12.40	1.24	1.35	1.41
Cem.	-3	0	4.30	12.52	0.91	0.95	0.97
Cem.	-2	0	3.22	12.50	0.93	0.95	0.97
Cem.	-3	0					0.75
<i>Glenium 51</i>							
TiO2	-3	0		12.52	2.75		3.08
TiO2	-2	0		12.50	1.41		1.46
TiO2	-1	0		12.32	0.86		0.94
TiO2	-2.5	0		12.49	1.19		1.31
TiO2	-2	0					1.17
TiO2	-4	2		12.52	2.34		2.45
TiO2	-3.5	2		12.49	2.40		2.49
TiO2	-2.5	2		12.50	1.85		1.91
TiO2	-2	2					1.59
Cem.	-5	0	3.51	12.53	3.09	3.61	3.76
Cem.	-4.5	0	3.39	12.53	2.79	3.30	3.47
Cem.	-4	0	3.49	12.56	0.86	1.01	1.11
Cem.	-3.5	0		12.53	1.32	1.66	1.90
Cem.	-3	0	3.25	12.55	0.58	0.75	0.84
Cem.	-2.5	0	3.69	12.50	0.09	0.19	0.22
Cem.	-3	0					0.57
<i>Cementa Melcrete</i>							
TiO2	-4	0		12.49	3.27		3.34
TiO2	-3	0	0.08	12.37	1.15		1.18
TiO2	-2	0	1.34	12.38	0.44		0.45
TiO2	-3.5	0		12.46	0.59		0.66
TiO2	-3	0					0.88
TiO2	-4.5	2		12.52	0.00		3.54
TiO2	-4	2		12.49	2.26		2.34
TiO2	-3	2		12.49	1.26		1.30
TiO2	-3	2					1.41
Cem.	-4.5	0		12.53	3.58	3.67	3.71
Cem.	-4.25	0		12.53	2.86	2.96	2.99
Cem.	-4	0	2.65	12.38	1.68	1.80	1.82
Cem.	-3.5	0		12.48	1.23	1.28	1.30
Cem.	-3	0	3.46	12.41	0.71	0.78	0.79
Cem.	-3	0					0.69
<i>Mighty 150</i>							
TiO2	-4	0		12.48	2.40		2.47
TiO2	-3	0	0.06	12.34	0.97		0.99
TiO2	-2	0	0.80	12.34	0.48		0.49
TiO2	-3	0					0.96
TiO2	-4.5	2		12.52	3.24		3.27
TiO2	-4	2		12.49	2.04		2.08
TiO2	-3	2					1.34
Cem.	-5	0		12.47	3.63	3.72	3.77
Cem.	-4.5	0		12.53	3.16	3.20	3.22
Cem.	-4.25	0		12.54	2.46	2.54	2.58
Cem.	-4	0	3.01	12.39	0.91	1.00	1.02
Cem.	-3.5	0		12.35	0.70	0.75	0.76
Cem.	-3	0	2.91	12.39	0.36	0.39	0.40
Cem.	-3	0					0.57

<sup>a</sup> Unit: M, g/l for FA, volume fraction of liquid phase for the cement additives and cleaning agents.

<sup>b</sup> Corrected for adsorption to the vessel walls according to method 1.

<sup>c</sup> Corrected for adsorption to the vessel walls according to method 2.

Solid phase	Log (ligand conc.) <sup>a</sup>	[Ca] added (mM)	[Ca] analysed (mM)	pH	Log K <sub>d</sub> (m <sup>3</sup> /kg) <sup>b</sup>	log K <sub>d</sub> (m <sup>3</sup> /kg) <sup>c</sup>	log K <sub>d</sub> (m <sup>3</sup> /kg)
<i>Clax Delta Balans</i>							
TiO2	-6	0	0.01	12.48	1.08		1.38
TiO2	-5	0	0.01	12.54	0.86		0.97
TiO2	-4	0	0.01	12.37	-0.17	0.15	
TiO2	-3	0		12.39	-1.28	-0.97	
TiO2	-2	0		12.55	-1.64	-1.12	
TiO2	-1	0		12.61	-1.91	-0.99	
TiO2	-5	2	1.59	12.48	3.46	3.76	
TiO2	-3	2		12.60	2.42	2.19	
TiO2	-2	2		12.48	0.25	0.29	
Cem.	-4	0		12.53	2.38	2.41	2.44
Cem.	-3	0	1.07	12.52	1.11	1.20	1.20
Cem.	-2	0	0.97	12.64	2.05	2.07	2.07
<i>Industrikombi</i>							
TiO2	-3	0		12.52	3.42	3.69	
TiO2	-2	0	0.02	12.34	1.94	1.99	
TiO2	-1.5	0		11.59	0.46	0.59	
TiO2	-2	2	0.63	12.48	4.28	4.29	
Cem.	-2	0	1.81	12.48	3.91	4.25	4.25
<i>Prefect Citron</i>							
TiO2	-3	0	0.01	12.40	3.50	3.64	
TiO2	-2	0		12.44	2.10	2.33	
TiO2	-1	0		11.91	1.79	1.88	
TiO2	-2	2	1.60	12.46	2.69	2.87	
Cem.	-2	0	3.80	12.48	3.00	3.05	3.05

<sup>a</sup> Unit: M, g/l for FA, volume fraction of liquid phase for the cement additives and cleaning agents.

<sup>b</sup> Corrected for adsorption to the vessel walls according to method 1.

<sup>c</sup> Corrected for adsorption to the vessel walls according to method 2.

## Data from degradation experiments

Table AII-1. Experiments with 1 d sorption time after degradation of the cement additives.

Solid phase	Log (ligand konc.) <sup>a</sup>	pH	Degradation time (d)	Degradation temp.(°C)	log K <sub>d</sub> (m <sup>3</sup> /kg)
<i>Sikament 10</i>					
TiO <sub>2</sub>	-3	12.49	3	20	2.61
TiO <sub>2</sub>	-3	12.49	9	20	2.72
TiO <sub>2</sub>	-3	12.46	23	20	2.72
TiO <sub>2</sub>	-3	12.52	45	20	2.74
TiO <sub>2</sub>	-3	12.49	3	40	2.45
TiO <sub>2</sub>	-3	12.49	9	40	2.46
TiO <sub>2</sub>	-3	12.50	23	40	2.44
TiO <sub>2</sub>	-3	12.51	45	40	3.04
<i>Sikament 210</i>					
TiO <sub>2</sub>	-4	12.20	7	60	3.25
TiO <sub>2</sub>	-3.5	12.53	50	20	2.20
TiO <sub>2</sub>	-3.5	12.49	21	60	2.39
TiO <sub>2</sub>	-3.5	12.53	36	60	2.16
TiO <sub>2</sub>	-3.5	12.54	50	60	2.34
<i>Peramin Conpac 30</i>					
TiO <sub>2</sub>	-4.5	12.51	45	40	2.22
TiO <sub>2</sub>	-3.5	12.49	3	20	1.45
TiO <sub>2</sub>	-3.5	12.48	9	20	1.52
TiO <sub>2</sub>	-3.5	12.49	23	20	1.56
TiO <sub>2</sub>	-3.5	12.51	45	20	1.60
TiO <sub>2</sub>	-3.5	12.49	3	40	1.60
TiO <sub>2</sub>	-3.5	12.49	9	40	1.58
TiO <sub>2</sub>	-3.5	12.49	23	40	1.53
TiO <sub>2</sub>	-3.5	12.51	45	40	1.44
TiO <sub>2</sub>	-3	12.49	3	20	1.28
TiO <sub>2</sub>	-3	12.49	3	40	1.40
<i>Peramin F</i>					
Cem.	-4	12.53	9	60	3.97
Cem.	-4	12.53	23	60	3.18
Cem.	-4	12.54	56	60	3.40
Cem.	-2	12.51	17	60	-0.82
Cem.	-2	12.53	46	60	-0.60
Cem.	-2	12.47	103	60	-0.74
TiO <sub>2</sub>	-2	12.40	9	60	1.16
TiO <sub>2</sub>	-2	12.48	17	60	1.13
TiO <sub>2</sub>	-2	12.46	23	60	1.10
TiO <sub>2</sub>	-2	12.49	46	60	1.02
TiO <sub>2</sub>	-2	12.48	56	60	1.03
TiO <sub>2</sub>	-2	12.46	103	60	1.37
<i>Glenium 51</i>					
TiO <sub>2</sub>	-2.5	12.54	50	20	1.47
TiO <sub>2</sub>	-2.5	12.26	7	60	1.55
TiO <sub>2</sub>	-2.5	12.51	21	60	2.03
TiO <sub>2</sub>	-2.5	12.55	36	60	2.09
TiO <sub>2</sub>	-2.5	12.54	50	60	2.06

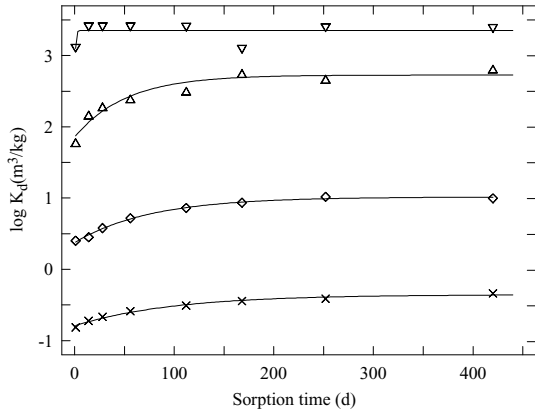
Solid phase	Log (ligand konc.) <sup>a</sup>	pH	Degradation time (d)	Degradation temp.(°C)	log K <sub>d</sub> (m <sup>3</sup> /kg)
<i>Cementa Melcrete</i>					
Cem.	-3.5	12.49	9	60	1.59
Cem.	-3.5	12.53	23	60	1.62
Cem.	-3.5	12.52	56	60	1.53
TiO2	-3.5	12.45	9	60	1.34
TiO2	-3.5	12.46	23	60	1.55
TiO2	-3.5	12.50	56	60	1.44
<i>Mighty 150</i>					
Cem.	-4	12.48	9	60	1.59
Cem.	-4	12.51	23	60	2.02
Cem.	-4	12.53	56	60	1.71
TiO2	-4	12.46	9	60	2.48
TiO2	-4	12.47	23	60	3.57
TiO2	-4	12.51	56	60	3.00

<sup>a</sup> Volume fraction of liquid phase.

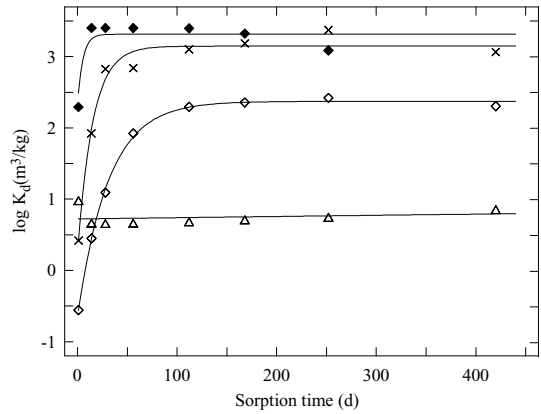
**Table AII-2. Experiments with 1 d sorption time after degradation of Ricem UP2 and Acrisorb LSR 33.**

	pH	TOC (mM)	logK <sub>d</sub> (m <sup>3</sup> /kg)	10 mM in the degradation step
<i>Ricem UP2</i>				
Cem.	12.56	5.505	0.52	
Cem.	12.52	0.767	0.78	
Cem.	12.56	7.674	0.25	
Cem.		3.010	0.44	
Cem.	12.45	0.301	1.44	
Cem.	12.56	0.025	3.30	
Cem.		7.620	-0.38	Ca
Cem.	12.54	0.762	0.31	Ca
Cem.	12.53	5.785	-0.36	Ca
Cem.	12.53	0.579	0.41	Ca
TiO2	12.50	0.551	1.80	
TiO2	12.56	5.505	0.87	
TiO2	12.49	0.767	1.58	
TiO2	12.52	7.674	0.54	
TiO2		3.010	0.79	
TiO2		0.301	1.37	
TiO2	12.52	0.271	2.25	
TiO2	12.53	7.620	0.01	Ca
TiO2	12.52	0.762	1.20	Ca
TiO2	12.53	5.785	0.25	Ca
TiO2	12.53	0.579	1.42	Ca
<i>Acrisorb LSR 33</i>				
Cem.	12.60	0.404	3.65	Ca
TiO2	12.57	0.376	4.42	
TiO2	12.57	0.404	3.97	Ca

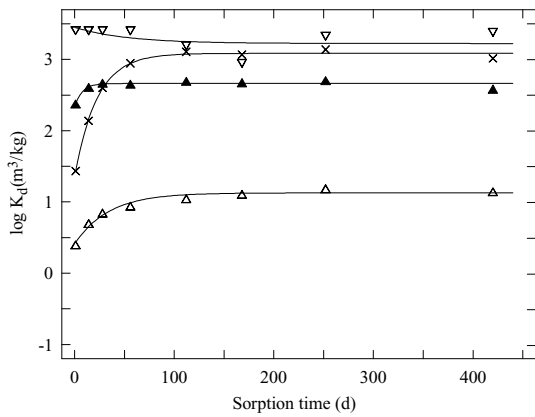
Data from long-time experiments



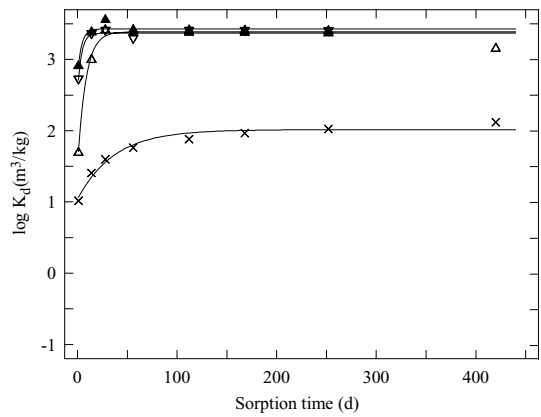
**Figure AIII-1.** ( $\Delta$ )  $\text{TiO}_2$ ,  $[\text{EDTA}] = 10^{-4} \text{ M}$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{EDTA}] = 10^{-2.5} \text{ M}$ ,  $[\text{Ca}] = 0.002 \text{ M}$ , ( $\nabla$ )  $\text{TiO}_2$ ,  $[\text{EDTA}] = 10^{-4} \text{ M}$ ,  $[\text{Ca}] = 0.02 \text{ M}$ , ( $\times$ ) Cement,  $[\text{EDTA}] = 10^{-2} \text{ M}$ .



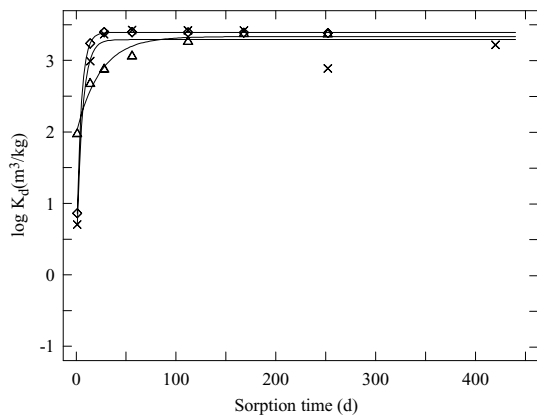
**Figure AIII-2.** ( $\Delta$ )  $\text{TiO}_2$ ,  $[\text{DTPA}] = 10^{-7} \text{ M}$ , ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{DTPA}] = 10^{-4} \text{ M}$ ,  $[\text{Ca}] = 0.002 \text{ M}$ , ( $\blacklozenge$ )  $\text{TiO}_2$ ,  $[\text{DTPA}] = 10^{-7} \text{ M}$ ,  $[\text{Ca}] = 0.002 \text{ M}$ , ( $\times$ ) Cement,  $[\text{DTPA}] = 10^{-4} \text{ M}$ .



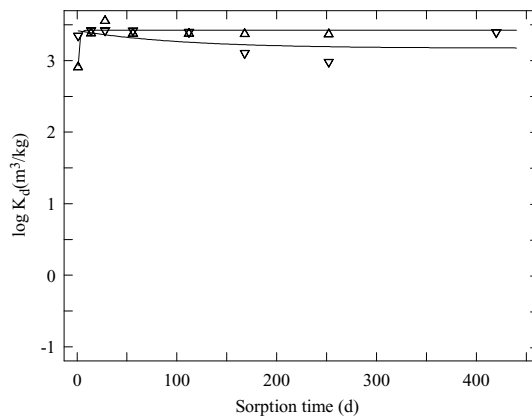
**Figure AIII-3.** ( $\Delta$ )  $\text{TiO}_2$ ,  $[\text{NTA}] = 10^{-2} \text{ M}$ , ( $\blacktriangle$ )  $\text{TiO}_2$ ,  $[\text{NTA}] = 10^{-3.5} \text{ M}$ , ( $\nabla$ )  $\text{TiO}_2$ ,  $[\text{NTA}] = 10^{-3.5} \text{ M}$ ,  $[\text{Ca}] = 0.02 \text{ M}$ , ( $\times$ ) Cement,  $[\text{NTA}] = 10^{-2} \text{ M}$ .



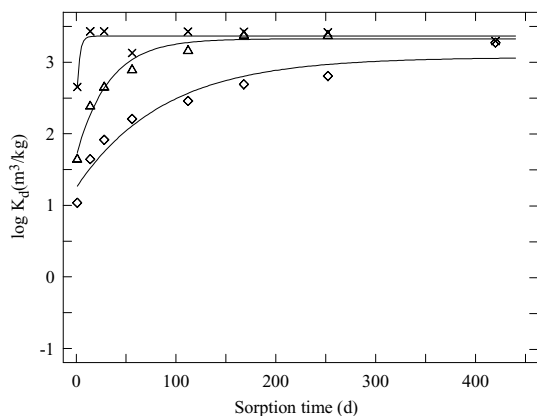
**Figure AIII-4.** ( $\Delta$ )  $\text{TiO}_2$ ,  $[\text{Citric acid}] = 10^{-2} \text{ M}$ , ( $\blacktriangle$ )  $\text{TiO}_2$ ,  $[\text{Citric acid}] = 10^{-3.5} \text{ M}$ , ( $\nabla$ )  $\text{TiO}_2$ ,  $[\text{Citric acid}] = 10^{-3.5} \text{ M}$ ,  $[\text{Ca}] = 0.02 \text{ M}$ , ( $\times$ ) Cement,  $[\text{Citric acid}] = 10^{-2} \text{ M}$ .



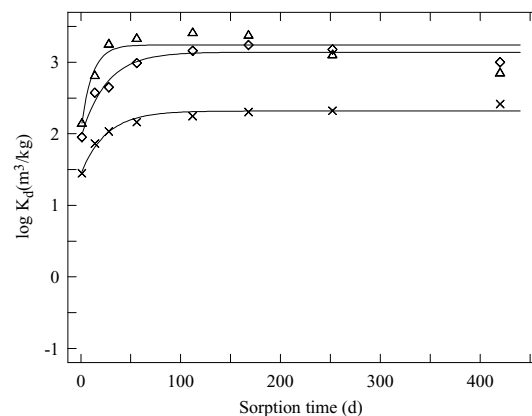
**Figure AIII-5.** ( $\Delta$ )  $\text{TiO}_2$ ,  $[\text{Gluconic acid}]=10^{-4.5}$  M, ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{Gluconic acid}]=10^{-4.5}$  M,  $[\text{Ca}]=0.002$  M, ( $\times$ ) Cement,  $[\text{Gluconic acid}]=10^{-4.5}$  M.



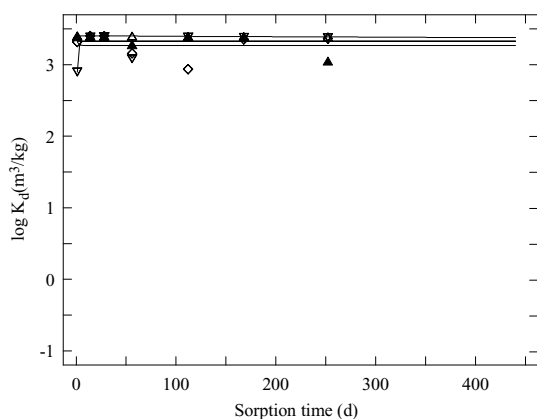
**Figure AIII-6.** ( $\Delta$ )  $\text{TiO}_2$ ,  $[\text{Oxalic acid}]=10^{-3}$  M, ( $\nabla$ )  $\text{TiO}_2$ ,  $[\text{Oxalic acid}]=10^{-3}$  M,  $[\text{Ca}]=0.02$  M.



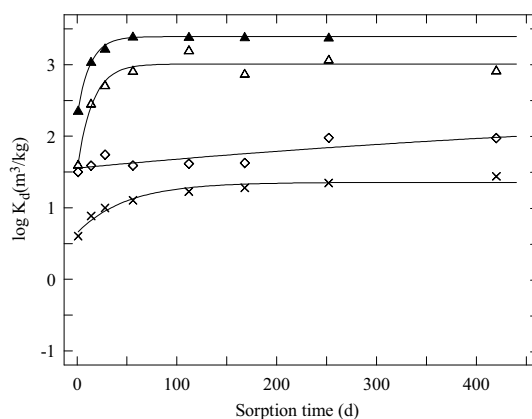
**Figure AIII-7.** ( $\Delta$ )  $\text{TiO}_2$ ,  $[\text{FA}]=10^{-2}$  g/dm<sup>3</sup>, ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{FA}]=10^{-2}$  g/dm<sup>3</sup>,  $[\text{Ca}]=0.002$  M, ( $\times$ ) Cement,  $[\text{FA}]=10^{-2}$  g/dm<sup>3</sup>.



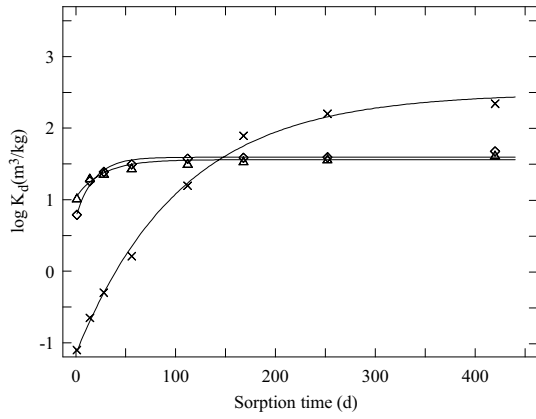
**Figure AIII-8.** ( $\Delta$ )  $\text{TiO}_2$ ,  $[\text{ISA}]=10^{-2.5}$  M, ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{ISA}]=10^{-2.5}$  M,  $[\text{Ca}]=0.002$  M, ( $\times$ ) Cement,  $[\text{ISA}]=10^{-2.5}$  M.



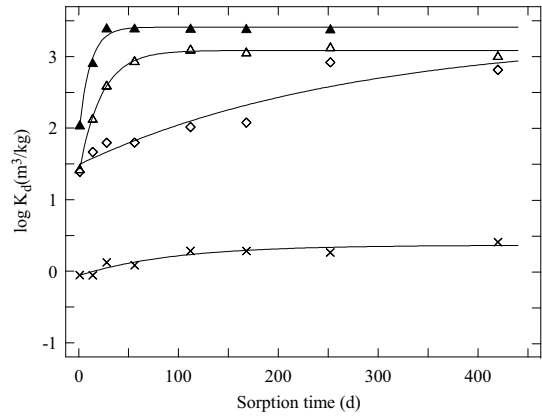
**Figure AIII-9.** ( $\Delta$ )  $\text{TiO}_2$ ,  $[\text{AcAc}]=10^{-2}$  M, ( $\diamond$ )  $\text{TiO}_2$ ,  $[\text{AcAc}]=10^{-2}$  M,  $[\text{Ca}]=0.002$  M, ( $\blacktriangle$ )  $\text{TiO}_2$ ,  $[\text{TTA}]=10^{-2.5}$  M, ( $\nabla$ )  $\text{TiO}_2$ ,  $[\text{TTA}]=10^{-2.5}$  M,  $[\text{Ca}]=0.02$  M.



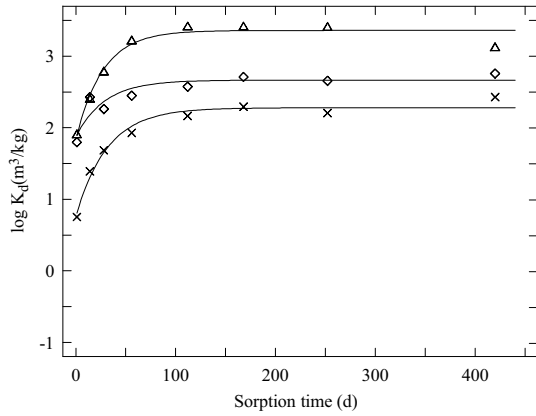
**Figure AIII-10.** ( $\Delta$ )  $\text{TiO}_2$ , Sikament 10,  $\text{flp}=10^{-3}$ , ( $\blacktriangle$ )  $\text{TiO}_2$ , Sikament 10,  $\text{flp}=10^{-2}$ , ( $\diamond$ )  $\text{TiO}_2$ , Sikament 10,  $\text{flp}=10^{-3}$ ,  $[\text{Ca}]=0.002$  M, ( $\times$ ) Cement, Sikament 10,  $\text{flp}=10^{-3}$ .



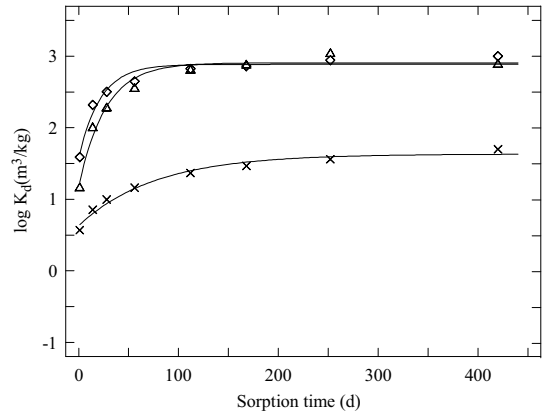
**Figure AIII-11.** ( $\Delta$ )  $\text{TiO}_2$ , Sikament 210,  $\text{flp}=10^{-3}$ , ( $\diamond$ )  $\text{TiO}_2$ , Sikament 210,  $\text{flp}=10^{-3}$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement, Sikament 210,  $\text{flp}=10^{-3}$ .



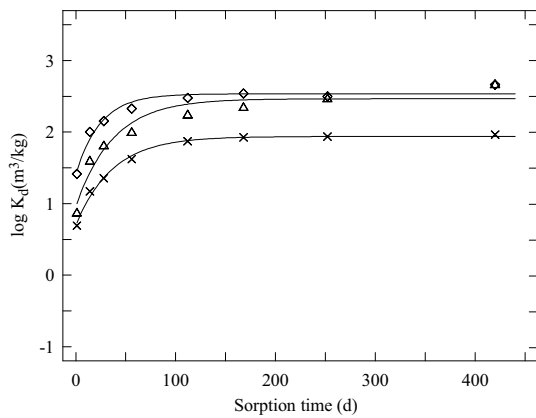
**Figure AIII-12.** ( $\Delta$ )  $\text{TiO}_2$ , Peramin Conpac 30,  $\text{flp}=10^{-4.5}$ , ( $\blacktriangle$ )  $\text{TiO}_2$ , Peramin Conpac 30,  $\text{flp}=10^{-3}$ , ( $\diamond$ )  $\text{TiO}_2$ , Peramin Conpac 30,  $\text{flp}=10^{-4.5}$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement, Peramin Conpac 30,  $\text{flp}=10^{-3}$ .



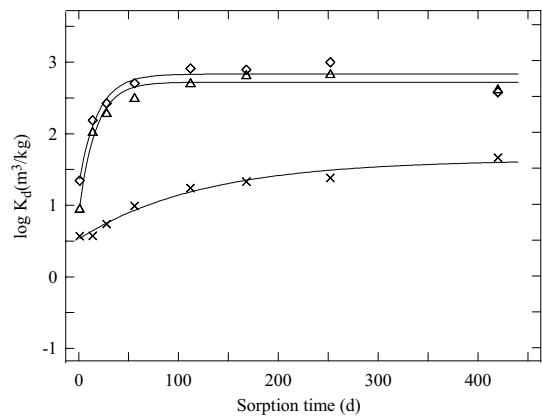
**Figure AIII-13.** ( $\Delta$ )  $\text{TiO}_2$ , Peramin F,  $\text{flp}=10^{-2}$ , ( $\diamond$ )  $\text{TiO}_2$ , Peramin F,  $\text{flp}=10^{-3}$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement, Peramin F,  $\text{flp}=10^{-3}$ .



**Figure AIII-14.** ( $\Delta$ )  $\text{TiO}_2$ , Glenium 51,  $\text{flp}=10^{-2}$ , ( $\diamond$ )  $\text{TiO}_2$ , Glenium 51,  $\text{flp}=10^{-2}$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement, Glenium 51,  $\text{flp}=10^{-3}$ .

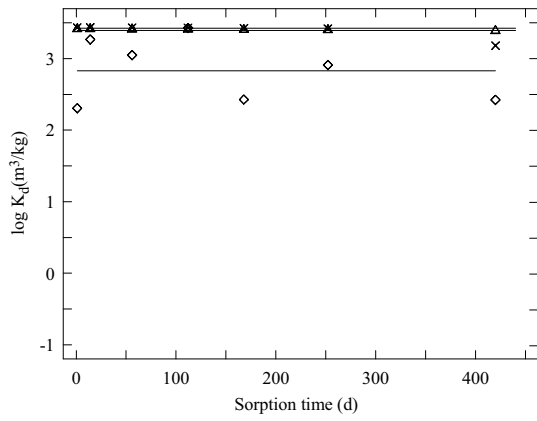


**Figure AIII-15.** ( $\Delta$ )  $\text{TiO}_2$ , Cementa Melcrete,  $\text{flp}=10^{-3}$ , ( $\diamond$ )  $\text{TiO}_2$ , Cementa Melcrete,  $\text{flp}=10^{-3}$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement, Cementa Melcrete,  $\text{flp}=10^{-3}$ .

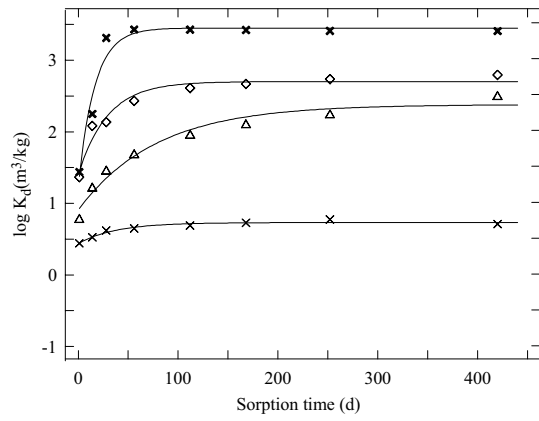


**Figure AIII-16.** ( $\Delta$ )  $\text{TiO}_2$ , Mighty 150,  $\text{flp}=10^{-3}$ , ( $\diamond$ )  $\text{TiO}_2$ , Mighty 150,  $\text{flp}=10^{-3}$ ,  $[\text{Ca}]=0.002 \text{ M}$ , ( $\times$ ) Cement, Mighty 150,  $\text{flp}=10^{-3}$ .





**Figure AIII-17.** ( $\Delta$ )  $\text{TiO}_2$ , Acrisorb LSR33  $[\text{TOC}] = 10^{-3.32} \text{ M}$ , ( $\diamond$ )  $\text{TiO}_2$ , Acrisorb LSR33  $[\text{TOC}] = 10^{-3.32} \text{ M}$ ,  $[\text{Ca}] = 0.002 \text{ M}$ , ( $\times$ ) Cement, Acrisorb LSR33  $[\text{TOC}] = 10^{-3.32} \text{ M}$ .



**Figure AIII-18.** ( $\Delta$ )  $\text{TiO}_2$ , Ricem UP2  $[\text{TOC}] = 10^{-2.52} \text{ M}$ , ( $\diamond$ )  $\text{TiO}_2$ , Ricem UP2  $[\text{TOC}] = 10^{-2.52} \text{ M}$ ,  $[\text{Ca}] = 0.002 \text{ M}$ , ( $\times$ ) Cement, Ricem UP2  $[\text{TOC}] = 10^{-2.52} \text{ M}$ , ( $\times$ ) Cement, Ricem UP2  $[\text{TOC}] = 10^{-3.52} \text{ M}$ .

**Table AIII-1. Data from the long-time experiments.**

Solid phase	log (ligand konc.) <sup>a</sup>	Ca, added (mM)	pH	log K <sub>d</sub> (m <sup>3</sup> /kg)	Sorption time (d)						log K <sub>d</sub> <sup>c</sup> (m <sup>3</sup> /kg)	B <sup>b</sup>	k	sd <sup>c</sup> B	sd <sup>c</sup> k	
					1	14	28	56	112	168						252
<i>EDTA</i>																
TiO2	-2.5	2	12.54	0.40	0.45	0.58	0.72	0.86	0.94	1.02	0.99	1.01	0.64	0.013	0.02	0.00
TiO2	-4	20	12.50	3.10	3.40	3.40	3.40	3.40	3.09	3.39	3.38	3.35	<b>1.00</b>	1.390	0.04	0.50
TiO2	-4		12.51	1.78	2.17	2.28	2.39	2.50	2.75	2.67	2.81	2.73	0.87	0.019	0.07	0.01
Cem.	-2		12.50	-0.82	-0.72	-0.67	-0.59	-0.51	-0.45	-0.41	-0.34	-0.36	0.44	0.010	0.02	0.00
<i>DTPA</i>																
TiO2	-7	2	12.51	2.29	3.40	3.40	3.40	3.39	3.32	3.09	3.38	3.31	<b>1.00</b>	0.192	0.08	0.16
TiO2	-4	2	12.55	-0.56	0.45	1.09	1.92	2.30	2.36	2.42	2.30	2.37	3.03	0.032	0.03	0.00
TiO2	-7		12.52	0.98	0.66	0.66	0.66	0.68	0.71	0.75	0.85	0.71	-0.94	1.250	0.03	263694
Cem.	-4		12.56	0.42	1.92	2.82	2.84	3.10	3.18	3.37	3.06	3.15	2.92	0.065	0.08	0.01
<i>NTA</i>																
TiO2	-3.5	20	12.50	3.40	3.40	3.40	3.40	3.19	2.94	3.32	3.38	3.22	-0.23	0.019	0.11	0.04
TiO2	-3.5		12.51	2.37	2.61	2.67	2.65	2.69	2.67	2.70	2.58	2.66	0.33	0.133	0.02	0.07
TiO2	-2		12.51	0.40	0.70	0.84	0.94	1.05	1.11	1.19	1.14	1.13	0.72	0.029	0.03	0.01
Cem.	-2		12.70	0.41	0.53	0.65	0.82	1.00	1.08	1.16	1.38	1.35	0.91	0.008	0.07	0.00
<i>Citric acid</i>																
TiO2	-3.5	20	12.50	2.71	3.35	3.39	3.28	3.39	3.39	3.39	3.39	3.37	0.86	0.264	0.02	0.20
TiO2	-3.5		12.51	2.93	3.40	3.57	3.40	3.40	3.39	3.39	3.39	3.43	0.65	0.252	0.04	0.36
TiO2	-2		12.58	1.71	3.01	3.43	3.43	3.43	3.42	3.42	3.17	3.39	1.90	0.124	0.05	0.03
Cem.	-2		12.58	1.02	1.41	1.60	1.76	1.88	1.96	2.02	2.12	2.01	0.98	0.027	0.04	0.01
<i>Gluconic acid</i>																
TiO2	-4.5	2	12.51	0.86	3.24	3.40	3.40	3.39	3.39	3.38	3.38	3.39	3.14	0.215	0.00	0.00
TiO2	-4.5		12.52	1.99	2.69	2.89	3.08	3.28	3.39	3.39	3.39	3.33	1.35	0.041	0.06	0.01
Cem.	-4.5		12.61	0.70	2.99	3.37	3.43	3.42	3.42	2.89	3.22	3.29	3.07	0.170	0.09	0.06

<sup>a</sup> Unit: M, g/l for FA, volume fraction of liquid phase for the cement additives, M TOC for Acrisorb LSR 33 and Ricem UP2.

<sup>b</sup> When B is marked with bold numbers, this parameter is set to 1 in the regression due to convergence problems.

<sup>c</sup> Standard deviation calculated by SPSS.

Solid phase	log (ligand konc.) <sup>a</sup>	Ca, added (mM)	pH	log K <sub>d</sub> (m <sup>3</sup> /kg)							log K <sub>d</sub> <sup>o</sup> (m <sup>3</sup> /kg)	B <sup>b</sup>	k	sd <sup>c</sup> log K <sub>d</sub>	sd <sup>c</sup> B	sd <sup>c</sup> k	
				1	14	28	56	112	168	252							420
Oxalic acid																	
TiO2	-3	20	12.49	3.33	3.40	3.40	3.40	3.38	3.08	2.96	3.38	3.17	-0.25	0.010	0.18	0.19	0.02
TiO2	-3		12.51	3.40	3.40	3.40	3.40	3.40	3.39	3.39	3.40	3.40	1.00	22.451	0.00		0.00
FA																	
TiO2	-2	2	12.52	1.04	1.64	1.92	2.21	2.46	2.69	2.81	3.27	3.07	1.82	0.011	0.18	0.21	0.00
TiO2	-2		12.52	1.66	2.40	2.67	2.91	3.18	3.39	3.39	3.33	3.33	1.64	0.031	0.08	0.14	0.01
Cem.	-2		12.57	2.65	3.43	3.43	3.13	3.43	3.42	3.42	3.30	3.36	1.00	0.356	0.04		0.18
ISA																	
TiO2	-2.5	2	12.52	1.95	2.57	2.65	2.99	3.16	3.24	3.18	3.00	3.14	1.20	0.040	0.05	0.12	0.01
TiO2	-2.5		12.52	2.16	2.83	3.27	3.35	3.43	3.39	3.12	2.86	3.24	1.20	0.091	0.10	0.27	0.05
Cem.	-2.5		12.55	1.45	1.86	2.03	2.16	2.25	2.30	2.32	2.42	2.32	0.88	0.039	0.03	0.07	0.01
AcAc																	
TiO2	-2	2	12.38	3.32	3.40	3.40	3.16	2.94	3.35	3.36	3.32	3.22	-0.17	0.031	0.12	0.21	0.10
TiO2	-2		12.39	3.40	3.40	3.40	3.40	3.40	3.39	3.39	3.31	3.31	-0.09	0.001	0.26	0.25	0.00
TTA																	
TiO2	-2.5	20	12.58	2.90	3.39	3.39	3.08	3.38	3.38	3.37	3.33	3.33	1.00	0.829	0.05		0.30
TiO2	-2.5		12.81	3.39	3.39	3.39	3.28	3.38	3.38	3.05	3.32	3.32	1.00	21.960	0.05		0.00
Sikament 10																	
TiO2	-3	2	12.51	1.50	1.59	1.74	1.59	1.62	1.63	1.98	1.97	2.55	1.00	0.001	0.06		0.00
TiO2	-3		12.52	2.36	3.05	3.23	3.40	3.39	3.39	3.39	3.39	3.39	1.11	0.079	0.01	0.03	0.01
TiO2	-2		12.52	1.61	2.46	2.72	2.92	3.21	2.88	3.08	2.93	3.01	1.48	0.065	0.06	0.15	0.01
Cem.	-3		12.58	0.60	0.89	1.00	1.11	1.22	1.28	1.35	1.44	1.35	0.70	0.020	0.04	0.07	0.01
Sikament 210																	
TiO2	-3	2	12.53	0.79	1.26	1.39	1.49	1.57	1.58	1.59	1.67	1.59	0.83	0.055	0.03	0.06	0.01
TiO2	-3		12.54	1.03	1.31	1.37	1.45	1.51	1.54	1.57	1.62	1.56	0.52	0.037	0.03	0.06	0.01
Cem.	-3		12.58	-1.10	-0.65	-0.30	0.21	1.20	1.89	2.20	2.34	2.49	3.64	0.009	0.11	0.11	0.00

<sup>a</sup> Unit: M, g/l for FA, volume fraction of liquid phase for the cement additives, M TOC for Acrisorb LSR 33 and Ricem UP2.

<sup>b</sup> When B is marked with bold numbers, this parameter is set to 1 in the regression due to convergence problems.

<sup>c</sup> Standard deviation calculated by SPSS.

Solid phase	log (ligand konc.) <sup>a</sup>	Ca <sub>i</sub> added (mM)	pH	log K <sub>d</sub> (m <sup>3</sup> /kg)	Sorption time (d)						log K <sub>d</sub> <sup>o</sup> (m <sup>3</sup> /kg)	B <sup>b</sup>	k	sd <sup>c</sup> log K <sub>d</sub> <sup>o</sup>	sd <sup>c</sup> B	sd <sup>c</sup> k	
					1	14	28	56	112	168							252
<i>Peramin Conpac 30</i>																	
TiO2	-4.5	2	12.51	1.39	1.67	1.80	1.80	2.02	2.08	2.81	2.81	3.30	1.81	0.004	0.79	0.74	0.00
TiO2	-4.5		12.52	2.05	2.92	3.40	3.40	3.40	3.39	3.39	3.39	3.41	1.50	0.090	0.03	0.08	0.01
TiO2	-3		12.54	1.43	2.14	2.60	2.95	3.11	3.07	3.01	3.01	3.08	1.73	0.045	0.02	0.05	0.00
Cem.	-3		12.58	-0.06	-0.06	0.12	0.08	0.28	0.28	0.41	0.41	0.36	0.43	0.011	0.06	0.07	0.00
<i>Peramin F</i>																	
TiO2	-3	2	12.52	1.80	2.43	2.26	2.45	2.57	2.71	2.66	2.76	2.66	0.79	0.034	0.08	0.16	0.02
TiO2	-2		12.38	1.92	2.41	2.79	3.23	3.42	3.42	3.42	3.13	3.36	1.52	0.037	0.06	0.13	0.01
Cem.	-3		12.56	0.75	1.39	1.68	1.93	2.16	2.29	2.20	2.43	2.28	1.52	0.032	0.05	0.11	0.01
<i>Glentium 51</i>																	
TiO2	-2	2	12.50	1.59	2.32	2.50	2.65	2.82	2.86	2.94	3.00	2.88	1.31	0.046	0.05	0.12	0.01
TiO2	-2		12.51	1.17	2.01	2.29	2.56	2.82	2.89	3.05	2.90	2.91	1.73	0.037	0.06	0.12	0.01
Cem.	-3		12.56	0.57	0.85	1.00	1.16	1.37	1.47	1.56	1.70	1.63	1.00	0.013	0.05	0.07	0.00
<i>Cementa Melcrete</i>																	
TiO2	-3	2	12.52	1.41	2.00	2.15	2.33	2.48	2.54	2.50	2.66	2.53	1.12	0.041	0.05	0.10	0.01
TiO2	-3		12.48	0.88	1.61	1.82	2.01	2.25	2.36	2.48	2.68	2.47	1.50	0.027	0.09	0.17	0.01
Cem.	-3		12.60	0.69	1.17	1.35	1.62	1.87	1.93	1.94	1.96	1.94	1.24	0.027	0.03	0.05	0.00
<i>Mighty 150</i>																	
TiO2	-3	2	12.61	1.34	2.19	2.42	2.71	2.91	2.89	3.00	2.58	2.83	1.55	0.054	0.07	0.18	0.01
TiO2	-3		12.45	0.96	2.03	2.29	2.51	2.71	2.82	2.84	2.63	2.72	1.83	0.059	0.06	0.14	0.01
Cem.	-3		12.62	0.57	0.57	0.74	0.99	1.24	1.33	1.38	1.66	1.64	1.11	0.008	0.09	0.09	0.00
<i>Acrisorb LSR 33</i>																	
TiO2	-0.32	2	12.56	2.31	3.27	3.05	3.43	3.43	2.43	2.91	2.42	2.92	<b>1.00</b>	0.507	0.17	0.76	0.00
TiO2	-0.32		12.55	3.43	3.43	3.43	3.43	3.42	3.42	3.42	3.41	3.42	<b>1.00</b>	29.616	0.00	0.00	0.00
Cem.	-0.32		12.60	3.43	3.43	3.43	3.43	3.42	3.42	3.42	3.18	3.39	<b>1.00</b>	21.410	0.04	0.00	0.00

<sup>a</sup> Unit: M, g/l for FA, volume fraction of liquid phase for the cement additives, M TOC for Acrisorb LSR 33 and Ricem UP2.

<sup>b</sup> When B is marked with bold numbers, this parameter is set to 1 in the regression due to convergence problems.

<sup>c</sup> Standard deviation calculated by SPSS.

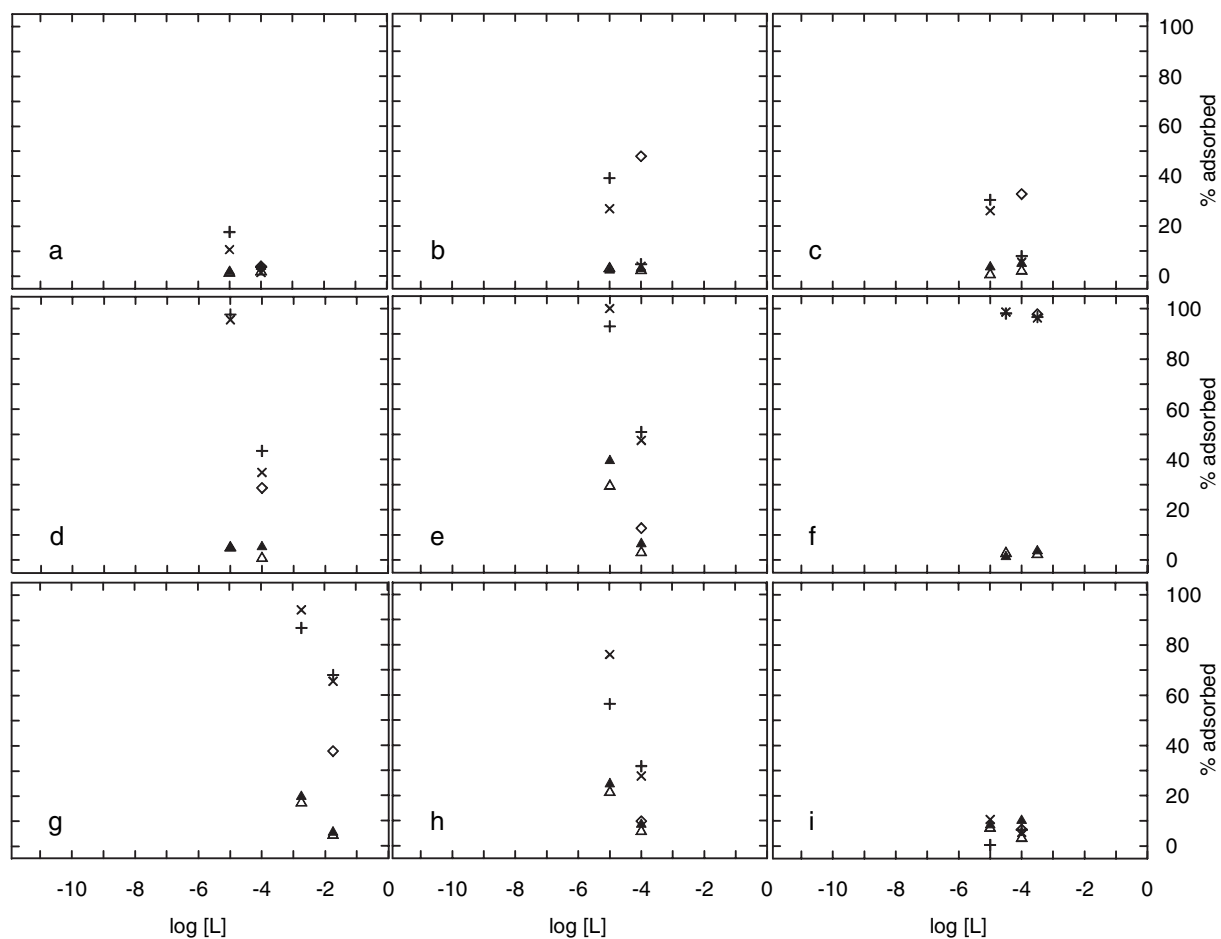
Solid phase	log (ligand konc.) <sup>a</sup>	Ca, added (mM)	pH	log K <sub>d</sub> (m <sup>3</sup> /kg)	Sorption time (d)				log K <sub>d</sub> <sup>c</sup> (m <sup>3</sup> /kg)	B <sup>b</sup>	k	sd <sup>c</sup> log K <sub>d</sub>	sd <sup>c</sup> B	sd <sup>c</sup> k			
					1	14	28	56							112	168	252
<i>Ricem UP2</i>																	
TiO2	-2.5	2	12.57	1.37	2.08	2.13	2.43	2.61	2.67	2.73	2.79	2.70	1.30	0.034	0.06	0.13	0.01
TiO2	-2.5		12.58	0.79	1.23	1.46	1.69	1.96	2.11	2.25	2.51	2.38	1.47	0.013	0.10	0.12	0.00
Cem.	-2.5		12.59	0.44	0.53	0.62	0.65	0.69	0.73	0.77	0.71	0.73	0.29	0.026	0.02	0.03	0.01
Cem.	-3.5		12.57	1.44	2.25	3.31	3.43	3.43	3.42	3.41	3.41	3.45	2.20	0.061	0.08	0.20	0.01

<sup>a</sup> Unit: M, g/l for FA, volume fraction of liquid phase for the cement additives, M TOC for Acrisorb LSR 33 and Ricem UP2.

<sup>b</sup> When B is marked with bold numbers, this parameter is set to 1 in the regression due to convergence problems.

<sup>c</sup> Standard deviation calculated by SPSS. **Appendix IV.** Data from ligand sorption experiments.

## Data from ligand sorption experiments



**Figure AIV-1.** Sorption of ligands as a function of ligand concentration,  $L$  (M; g/L for FA) at a solid:solution ratio of 1 g/L. Sorption time: 1 or 28 d. ( $\Delta$ )  $\text{TiO}_2$ , 1d, ( $\blacktriangle$ )  $\text{TiO}_2$ , 28 d, ( $\diamond$ )  $\text{TiO}_2$ , 0.002 M Ca, 1 d, ( $\times$ ) cement, 1 d, ( $+$ ) cement, 28 d. (a) EDTA, (b) DTPA, (c) NTA, (d) citric acid, (e) gluconic acid, (f) oxalic acid, (g) FA, (h) ISA, (i) AcAc.

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