Review of the Long-term Risks Associated with the Use of Superplasticizers

Miranda Keith-Roach, Lars Olof Höglund

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ABSTRACT

This report provides:

- a critical review of the current understanding of the interactions between polynaphthalene sulphonate (PNS) and polycarboxylate ether (PCE) superplasticizers and cement
- conceptual models developed in Phreeqc to describe superplasticizer uptake and release processes
- estimates of DOC and sulphonate concentrations in the porewater of low pH silica fume grout and concrete prepared with PNS or PCE superplasticizer for use in a spent nuclear fuel repository
- risk-benefit scorecards describing the use of PNS and PCE superplasticizers in low pH silica fume grouts and concretes

The literature review identifies that superplasticizers interact with hydrating cement minerals via adsorption, which results in a superplasticizing effect, and intercalation in organo-mineral phases (OMP). The balance between these interactions depends on the cement porewater sulphate concentration and the timing of superplasticizer addition to the cement. PNS is able to compete more effectively than PCE for adsorption sites, but is also more prone to intercalation into cement minerals. During sorption, the different sized molecular components of the superplasticizer product display different behaviour, with the smaller components tending to remain in the cement porewater to a greater extent, and the polymers binding to the cement. Leaching experiments also detect smaller units in the leachate but the largest amount of DOC in the leachate comes from the material that does not sorb during cement hydration. The chemical or biological degradation of the superplasticizers is limited by the stability of the polymeric backbones, although biodegradable PEG side chains of PCE are expected to be released during alkaline hydrolysis reactions. The effect of superplasticizers on radionuclide solubility and sorption is discussed, and the effect on the long term performance of cementitious materials.

The models suggest that the superplasticizer concentration in the cement porewater will be supported while OMP persist, as sulphate in the groundwater gradually exchanges with the superplasticizer in these phases. After the OMP are removed, long term release of lower concentrations of superplasticizer will be controlled by surface complexation reactions.

Keywords: Polycarboxylate ether; Polynaphthalene sulphonate; Superplasticizer; Conceptual model; Phreeqc, Risk.
Tämä raportti esittää:

- katsauksen nykyisestä tietämystä liittyen polynaftaleenisulfonaatti- (PNS) ja polykarboksylaattiesteripohjaisten (PCE) tehonotkistimien ja sementin välisiin vuorovaikutuksiin.
- Phreeqc-ohjelmalla kehitetyt konseptuaaliset mallit tehonotkistimen sitoutumis- ja vapautumisprosessien kuvaamiseen.
- arviot DOC- ja sulfonaattipitoisuuksista sellaisen matalan pH:n laastin ja PNS- tai PCE-pohjaista tehonotkistinta sisältävän betonin huokosvedessä, joka on tarkoitettu käytettäväksi käytetyn polttoaineen loppusijoituslaitoksessa.
- riski-hyötysuhteeseen perustuvat tuloskortit, jotka kuvaavat PNS- ja PCE-pohjaisten tehonotkistinten käyttöä matalan pH:n laasteissa ja betoneissa.


Malleista voidaan nähdä sementin huokosveden tehonotkistinpitoisuutta tukeva vaikutus OMP-faasien aikana, kun pohjaveden sulfaatti vähitellen korvautuu tehonotkistimella näissä faaseissa. Kun OMP-faasit poistuvat, pinnan kompleksointireaktiot rajoittavat tehonotkistimen pienempien pitoisuksien pitkäaikaisvapautumista.

Avainsanat: Polynkarboksylaattiesteri, polynaftaleenisulfonaatti, tehonotkistin, konseptuaalinen malli, Phreeqc, riski.
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<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>AFm</td>
<td>Calcium sulpho ferri-aluminate e.g. monosulphate</td>
</tr>
<tr>
<td>AFt</td>
<td>Calcium sulpho ferri-aluminate e.g. ettringite</td>
</tr>
<tr>
<td>C₃A</td>
<td>Calcium aluminate</td>
</tr>
<tr>
<td>C₃S</td>
<td>Calcium silicate</td>
</tr>
<tr>
<td>CAH</td>
<td>Calcium aluminate hydrate</td>
</tr>
<tr>
<td>CSH</td>
<td>Calcium silicate hydrate</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
</tr>
<tr>
<td>ESDRED</td>
<td>A cement suitable for the construction of sealing plugs and rock support (shotcrete) in the planned Swiss deep geological repositories for radioactive waste</td>
</tr>
<tr>
<td>HCP</td>
<td>Hardened cement paste</td>
</tr>
<tr>
<td>LAC</td>
<td>Low Alkali Cement</td>
</tr>
<tr>
<td>L/ILW</td>
<td>Low/Intermediate level waste</td>
</tr>
<tr>
<td>LS</td>
<td>Lignosulphonate</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NAGRA</td>
<td>Nuclear waste management organisation of Switzerland</td>
</tr>
<tr>
<td>NUMO</td>
<td>Nuclear waste management organisation of Japan</td>
</tr>
<tr>
<td>OPC</td>
<td>Ordinary Portland Cement</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarboxylate</td>
</tr>
<tr>
<td>PCE</td>
<td>Polycarboxylate ether</td>
</tr>
<tr>
<td>PMS</td>
<td>Polymelamine sulphonate</td>
</tr>
<tr>
<td>PNS</td>
<td>Polynaphthalene sulphonate</td>
</tr>
<tr>
<td>SKB</td>
<td>Nuclear waste management organisation of Sweden</td>
</tr>
<tr>
<td>SP</td>
<td>Superplasticizer</td>
</tr>
<tr>
<td>Sp-ns</td>
<td>Polynaphthalene sulphonate superplasticizer, term used in the modelling</td>
</tr>
<tr>
<td>Sp-pc</td>
<td>Polycarboxylate ether superplasticizer, term used in the modelling</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
</tbody>
</table>
INTRODUCTION

Superplasticizers are cement additives that are used to optimise the workability of the cement and/or allow the materials to be produced at relatively low water:cement ratios (Winnefeld et al. 2007). A low water:cement ratio results in a final product of greater strength and lower porosity.

Cementitious materials are used widely in L/ILW repository concepts. Cement is used to stabilise waste, concrete is used as a waste package material and in technical barriers, grout is used to fill empty space between waste packages and structures, and shotcrete stabilises the rock face and minimise inflow of groundwater during the operational period. Ordinary Portland Cement (OPC) is often seen as advantageous in a L/ILW as it is relatively cheap, is an excellent sorption matrix for many radionuclides and it is the most common type of cement, so there is the most experience related to its short and long-term properties. However, very high pH conditions need to be avoided in spent fuel repositories due to the impact on the bentonite buffer (Bodén and Sievänen 2005), and so the necessary cementitious materials, such as shotcrete, grouting and concrete plugs are made using cements that generate a lower pH (maximum of pH 11). The presence of cementitious materials mean that superplasticizers are inevitable in both L/ILW and spent nuclear fuel repositories (Wieland et al. 2014).

1.1 Chemistry of superplasticizers

Superplasticizers are long chain polymers with functional groups that provide the desired properties. The exact composition of commercial superplasticizers is often unknown (Wieland et al. 2014), but the general types of structure are available. To aid the reader, some of the chemical building blocks of the polymers are given in Table 1-1.

<table>
<thead>
<tr>
<th>Chemical building blocks of relevant polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic acid (prop-2-enoic acid)</td>
</tr>
<tr>
<td>Ether (ethoxyethane)</td>
</tr>
<tr>
<td>Formaldehyde (methanol)</td>
</tr>
<tr>
<td>Maleic acid ((2Z)-But-2-enedioic acid)</td>
</tr>
<tr>
<td>Melamine (1,3,5-Triazine-2,4,6-triamine)</td>
</tr>
</tbody>
</table>
Methacrylic acid (2-Methylprop-2-enoic acid)

Naphthalene

Sulphonate functional group (attached to an organic “R” group)

Vinyl functional group

Superplasticizers interact with cement in the first instance by electrostatic attraction between negatively charged functional groups on the superplasticizer and cement minerals with a positive zeta potential. In a highly alkaline environment, the sorption of Ca\(^{2+}\) ions to negatively charged mineral surfaces creates a positive zeta potential.

First generation superplasticizers were based on modified ligninosulphonates\(^1\). Lignosulphonates are complex polymeric biproducts of the wood and pulp industry with a wide range of molecular masses. They function via electrostatic repulsion but have a relatively poor performance due to the unavoidable variations in their structures (Giraudeau et al. 2009).

The next generation of superplasticizers includes vinyl maleic acid copolymers, sulphonated melamine-formaldehyde condensates (polymelamine sulphonates; PMS) and sulphonated naphthalene-formaldehyde condensates (polynaphthalene sulphonates; PNS) (Winnefeld et al. 2007). Indicative structures are shown in Table 1-2. Both PNS and PMS are linear organic polymers with sulphonate groups at regular intervals. They sorb onto cement particles via their ionic sulphonate groups and increase the fluidity of the cement paste via electrostatic repulsion (Wieland et al. 2014).

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\(^1\) [http://www.theconcreteportal.com/compat.html](http://www.theconcreteportal.com/compat.html)
Table 1-2. Chemical structures of vinyl maleic acid copolymers, sulphonated melamine formaldehyde and sulphonated naphthalene formaldehyde

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignosulphonate (Giraudeau et al. 2009)</td>
<td><img src="image" alt="Lignosulphonate" /></td>
</tr>
<tr>
<td>Vinyl copolymers (Giraudeau et al. 2009)</td>
<td><img src="image" alt="Vinyl copolymers" /></td>
</tr>
<tr>
<td>Sulphonated melamine-formaldehyde condensate (Andersson et al. 2008)</td>
<td><img src="image" alt="Sulphonated melamine-formaldehyde" /></td>
</tr>
<tr>
<td>Sulphonated naphthalene-formaldehyde condensate (Andersson et al. 2008)</td>
<td><img src="image" alt="Sulphonated naphthalene-formaldehyde" /></td>
</tr>
</tbody>
</table>

In the 1990s, polycarboxylate (PC) superplasticizers were introduced. PC superplasticizers are synthesised specifically for purpose and lower concentrations are therefore generally required, compared to other superplasticizers. They also have the benefits of adding strength to the final material and reducing the amount of water.
required in the cement mix beyond that of earlier superplasticizers. The most common PC superplasticizers are polycarboxylate ethers (PCE), polyacrylic or polymaleic acid polymers with long polyethylene glycol (PEG) (also referred to as polyoxyethylene and polyethylene oxide) sidechains. The generic structure for PCE is shown in Figure 1-1, in this case with a methacrylic-acid based backbone. Commercial PCE superplasticizers have a characteristic “comb” shape (Marchon et al. 2013, Winnefeld et al. 2007).

Figure 1-1. Chemical structure of the sodium salt of a polycarboxylate ether (from NDA 2015)

PCE superplasticizers bind to cement particles via their polymeric backbone and hinder coagulation through steric effects caused by the long polyoxyethylene side chains of the polymer (Janowska-Renkas 2015) and, to a lesser degree, electrostatic repulsion (Wieland et al. 2014). This results in effective fluidisation of the cement, and they are therefore commonly used in shotcrete and to make high performance concrete (Wieland et al. 2014). Wieland et al. (2014) showed experimentally that PCE-type superplasticizers generally gave rise to a stronger retardation of hydration processes than PNS-type superplasticizers, which was in agreement with earlier studies. The efficiency of PCE superplasticisers depends on the type, length and arrangement of the polymer backbone and sidechains, and the frequency of functional groups (Janowska-Renkas 2015).

1.2 Components of superplasticizer products

Commercial superplasticizer products and superplasticizers synthesised for experiments contain a mixture of molecules, including the large polymers that give the cement the desired properties as well as oligomers, monomers and unreacted reagents (Yamamoto et al. 2008; Herterich et al. 2003; Janowska-Renkas 2015). The sorption properties of these different molecules vary, thus the organic material remaining in solution generally does not have the same composition as the organic material sorbed. The polymers tend to sorb to a greater extent than monomers and dimers (Winnefeld et al. 2007, Fujita et al. 2008, Yamamoto et al. 2008).

Sorption of superplasticizers is often measured via analysis of the dissolved organic carbon (DOC) of the porewater, which does not differentiate between the different organic components of the product used. However, gel permeation chromatography

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2 http://pubs.acs.org/cen/coverstory/8241/8241process2.html
(GPC) has been used in a number of studies to separate out the components and characterise the molecules that remain in solution. This information is important for understanding sorption processes (Chapter 2), for interpreting the results of leaching and degradation experiments (Chapters 3 and 4) and for assessing the impact of the superplasticizer on the sorption of radionuclides (Chapter 5).

1.3 Cementitious materials in nuclear waste repositories

As cementitious materials are used for a variety of purposes in L/ILW and spent fuel repositories, the mechanical and chemical properties required of the cement vary. For example, a high early fluidity is needed for shotcrete while high mechanical strength is needed for barriers, and the acceptable pH of the cement leachate varies according to the type of repository.

Standard cement is Ordinary Portland Cement (OPC), and the typical unhydrated cement clinker minerals\(^3\) and components are (SKB 2014):

- Tricalcium silicate, C\(_3\)S.
- Dicalcium silicate, C\(_2\)S.
- Tricalcium aluminate, C\(_3\)A.
- Tetracalcium aluminate ferrite, C\(_4\)AF.
- Calcium sulphate (gypsum), C\(_6\)H\(_2\) (added as a retardant to the cement).
- Alkali hydroxides, Na + K.

Table 1-3 gives some characteristics of the calcium silicate and aluminate minerals.

Table 1-3. Main phases of Portland cement and their characteristics (from Griesser 2002)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>C(_3)S</th>
<th>C(_2)S</th>
<th>C(_3)A</th>
<th>C(_4)AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount in CEM I</td>
<td>40 - 80</td>
<td>0 - 30</td>
<td>3 - 15</td>
<td>4 - 15</td>
</tr>
<tr>
<td>Reactivity</td>
<td>High</td>
<td>Low</td>
<td>Very high</td>
<td>Low</td>
</tr>
<tr>
<td>Impurities</td>
<td>Al(_2)O(_3), Fe(_2)O(_3), MgO</td>
<td>Al(_2)O(_3), Fe(_2)O(_3), Na(_2)O, K(_2)O, SO(_3)</td>
<td>Fe(_2)O(_3), Na(_2)O, K(_2)O, (MgO)</td>
<td>MgO, SiO(_2), TiO(_2)</td>
</tr>
<tr>
<td>Technical name</td>
<td>Alite</td>
<td>Belite</td>
<td>Aluminate phase</td>
<td>Ferrite phase</td>
</tr>
<tr>
<td>Heat of hydration [J/g]</td>
<td>500</td>
<td>250</td>
<td>1340</td>
<td>420</td>
</tr>
<tr>
<td>Contribution to strength</td>
<td>High at early stages</td>
<td>High at late stages</td>
<td>High at very early stages</td>
<td>Very low</td>
</tr>
</tbody>
</table>

The addition of water to anhydrous cement clinker initiates energetic hydration reactions and produces new minerals that give the cement its mechanical strength. The

\(^3\) Abbreviations commonly used in cement science for the clinker components: C = CaO, S = SiO\(_2\), A = Al\(_2\)O\(_3\), F = Fe\(_2\)O\(_3\), H = H\(_2\)O, C\(_6\)H\(_2\) = CaSO\(_4\)·2H\(_2\)O, N = Na\(_2\)O, K = K\(_2\)O
main binding phases of hydrated cement are calcium silicate hydrates (CSH) and calcium hydroxide (CH). Complex calcium sulpho ferri-aluminates known as AFt and AFm⁴ are also major hydration products resulting from reactions involving calcium aluminate, calcium alumino-ferrite, and calcium sulphate. Calcium sulphate is added to the clinker to promote the formation of the AFt ettringite rather than calcium aluminate hydrates (CAH). CAH are undesirable as early hydration products as they lead to the rapid setting of the cement. Ettringite crystals create a protective layer on the clinker materials, creating the “dormant phase” when the cement can be transported and emplaced. CSH and CAH minerals then form and cause the cement to stiffen. Although the early hydration reactions are most energetic, reactions continue for many months after the cement hardens.

The properties of cement are controlled by the balance of different clinker materials. Sulphate resistant cement contains lower amounts of C₃A, while low alkali cement contains low amounts of alkali hydroxides. Low pH cements are usually made using pozzolans such as silica fume, fly ash or blast furnace slag. Pozzolans are aluminous and siliceous materials that react with calcium hydroxide to form cements with little or no free Portlandite (Ca(OH)₂). When the Ca:Si molar ratio of the cement mix is less than ~1.6, CSH-gel will form in the fully hydrated concrete instead of Portlandite and the pH will be less than 12.5. Decreasing the Ca:Si ratio would further decrease the pH.

Silica fume is an amorphous polymorph of silicon dioxide used to increase the strength and decrease the porosity of OPC concrete. The particles are ultrafine, approx. 10 to a few 100 nm particle size and can therefore fill the intergranular space in concrete and achieve a denser packing (Plank et al. 2009). It is a very reactive pozzolan and forms calcium silicate hydrates (El-Didamony et al. 2013). Silica fume is commonly used for creating low pH cement for nuclear waste repositories. Its addition to cement, however, increases the water demand, the heat of hydration and therefore the total shrinkage (El-Didamony et al. 2013).

Fly ash is a fine coal combustion product. It consists mostly of alumina-silicate glass with some crystalline constituents, such as quartz and various iron oxides (Marchon et al. 2013), and can contain unburnt carbon. It is used as a replacement or partial replacement for cement clinker materials and produces cement that is stronger and more resilient to chemical attack, including sulphate attack. Fly ash can usually replace up to 35% of the cement; the amount is limited by its slow hydration and variable quality (Marchon et al. 2013).

Blast furnace slag can also be used as a partial replacement for OPC clinker materials. It contains CaO (30-50%), SiO₂ (28-38%), Al₂O₃ (8-24%), and MgO (1-18%). The main advantages of using blast furnace slag are reduced alkali–silica reactions, a higher resistance to chloride ingress and therefore reinforcement corrosion, and higher resistance to attacks by sulphate and other chemicals. Blast furnace slag may contain calcium sulphide and this may render it unsuitable for use in a spent nuclear fuel repository.

⁴ AFt = C₆(A,F)X₃Hy (y = 32 for ettringite) and AFm = C₄(A,F)X₂Hy (y = 12 for monosulfate), where C = CaO, H = H₂O, A = Al₂O₃, F = Fe₂O₃ and X = CaSO₄.
The partial replacement of OPC with silica fume, fly ash or blast furnace slag reduces the amount of clinker minerals and thus the minerals that contribute to a high porewater pH, i.e. alkali metal hydroxides and portlandite (calcium hydroxide). In order to produce a low pH cement (pH 11 or less in the pore fluids) using OPC silica fume cement and slag based mixes, Bodén and Sievänen (2005) found that the minimum content of SiO₂ in mixes should be close to or above 50 weight-% of total binder materials or Ca/Si molar ratio should be close to or less than 0.80.

1.4 Other cement additives

Grinding agents are used in the milling of cement to produce a fine powder in order to optimise the particle size distribution and reduce the cost of grinding. They bind to the cement particle surfaces and reduce agglomeration. Propylene glycol, diethylene glycol, triethanolamine and even PCEs are used as grinding agents (Weibel and Mishra 2014). Posiva have supplied information that triethanolamine, acetic acid, triisopropanolamine and diethyleneglycol are used in different mixes. Typically, 50-200 g/tonne cement is used, if they are used at all. The cement grinding agents therefore contribute to the organic content of the cement and its porewater (Wieland et al. 2014), and may contain molecules that resemble components of superplasticizers.

1.5 Concerns over superplasticizers

The first reason for concern over the use of superplasticizers is that they are organic materials with functional groups that may be able to reduce the sorption of radionuclides to cementitious materials or the host rock. A joint project between the nuclear waste management organisations of Switzerland (Nagra), Japan (NUMO), Sweden (SKB) and Finland (Posiva) aimed to classify superplasticizers on the basis of their impact on radionuclide sorption (Andersson et al. 2008). They identified the following questions as important for classifying the risks posed by different types of superplasticizer:

- Do the organics leach out of the cement paste or not?
- How much organic material leaches and when?
- What kind of organic degradation products are formed?
- Do the organics leached affect radionuclide sorption?

Further to this, the following issues are also relevant:

- Do the superplasticizers sorb to other components of the repository?
- Do the superplasticizers negatively affect cement mineralogy and/or degradation?
- Could the organic material stimulate microbial activity, particularly sulphate-reduction to sulphide?
- Could the sulphonate content of PNS and PMS increase sulphate in the system, and thus enhance cement degradation and sulphide production?
1.6 Aims and report structure

The first aim of this report is to review the literature to establish the state of the art knowledge on the:

- Sorption of superplasticizers to cement phases
- Chemical and biological stability of different types of superplasticizer
- Leaching of superplasticizers and their degradation products from cementitious materials
- Degradation mechanisms and products
- Potential influence on radionuclide mobility
- Potential influence on other aspects of repository performance

The next aim is to use the information in the literature review to develop conceptual models for the uptake of superplasticizers into hydrating cements and their release as the cement porewater exchanges with the surrounding groundwater. The models are intended to aid our understanding of these complex processes and to give an insight into long term trends. The final aim is to compile risk-benefit scorecards for PNS and PCE superplasticizers in low pH grout and concrete.
2 Sorption of Superplasticizers to Cementitious Materials

2.1 Introduction

When considering the results of superplasticizer sorption experiments, a few important general observations are helpful. The first is that different components of superplasticizer products have different sorption properties (Section 1.2), and this means that the sorption of the actual polymeric superplasticizer may be greater than indicated by DOC measurements. Additionally, the amount of superplasticizer used in experiments is important. At low concentrations, sorption of superplasticizers to cement increases linearly with the amount added. However, as the amount added increases and surface sites are increasingly taken, the extent of sorption decreases to reach a plateau at the point of surface saturation. Optimal fluidity is achieved with a saturated surface but this increases the amount of the superplasticizer that remains in solution. As the point of surface saturation is dependent on the superplasticizer and the cement used, experimental results may reflect different points in the sorption profile. Lothenbach et al. (2007), for example, acknowledged that the low level of PCE superplasticizer sorption observed in their experiments (55%) reflected the high dosage of PCE used.

Studying the sorption of superplasticizers to cement is further complicated by the changing mineralogy of the cement clinker as it hydrates. This means that the extent of sorption and the sorption mechanism can be affected by the time the superplasticizer is added to the cement mix. Superplasticizers can be adsorbed to the surfaces of the cement minerals, which results in an increased workability of the cement paste, or incorporated into early cement hydration products (Flatt and Houst 2001, Griesser 2002). Incorporation has also been referred to as “consumption” by Alonso and Puertas (2015), and is largely a wasteful process that increases the required dosage of superplasticizer to achieve particular cement properties. Since superplasticizers that remain in solution have no impact on the workability of the cement paste (Griesser 2002), it is important that uptake onto cement particles occurs efficiently and predominately through adsorption. In this report, sorption is used to describe adsorption + incorporation, i.e. when the processes have not been examined separately.

Sorption processes are also affected by the zeta potentials of the mineral components (e.g. Plank and Hirsch 2007). Calcium ions play an important role in creating positive zeta potentials that allow adsorption of superplasticizers (Griesser 2002). C₃A has the most positive zeta potential of the cement clinker minerals at about +10 mV (Alonso and Puertas 2015), while ettringite has the most positive zeta potential of the early cement hydration phases, followed by monosulphate and syngenite (Plank and Hirsch 2007). In this chapter, sorption processes are first discussed for PNS and PCE superplasticizers, and then the influence of adding fly ash, silica fume or slag on the sorption processes is discussed.
2.2  Sorption to cement

2.2.1  PNS superplasticizers

The kinetics of PNS superplasticizer sorption during cement hydration is fast and incorporation into early hydration products is an important factor. The relatively high charge density of PNS superplasticizers influences its sorption to cement minerals (Griesser 2002) and the sulphonate group can undergo reactions with minerals in the place of sulphate (Onofrei and Gray 1989).

Onofrei and Gray (1989) investigated the binding of a PNS type superplasticizer in hardened silica fume blended sulphate resistant Portland cement using electron-microautoradiography and scanning electron microscopy. The majority of the superplasticizer was observed to be associated with CAH phases and calcium-rich CSH phases, which form during the hydration of C3S, C2S and C3A in the clinker. Plank and Hirsch (2007) examined the distribution of PNS between different hydrated cement minerals and found that it was associated with ettringite to the greatest extent, and with monosulphate to a lesser extent. This was true for both the mass concentration and the surface concentration of ettringite and monosulphate. Both ettringite and monosulphate are reaction products of C3A, indicating that C3A is particularly important.

A common method to show sorption during the initial hydration processes is to delay the addition of the superplasticizer by a few minutes and see how this affects the amount sorbed compared with when the superplasticizer is added immediately. Uchikawa et al. (1995) investigated sorption of four superplasticizers to C3A and C3S. PNS sorbed effectively to a C3A phase, and delayed addition reduced the amount sorbed from 94.3% to 20.1%. Sorption to a C3S phase was about 5 times lower (26% sorbed), and this was not affected by a delay in the addition of the PNS (27% sorbed). Using OPC cement, the delay in addition of PNS had a lesser but still significant effect (55% vs 70%). The influence of the timing of PNS addition on its sorption has also been observed by Mannonen (1996), who found that when a PNS superplasticizer was added to the cement mix one minute after the water, the percentage sorbed was reduced to a half or third of the amount bound when the water and superplasticizer were added simultaneously. Plank and Hirsch (2007) found that a 2-hour delay decreased PNS sorption to OPC by about 40%. These results show that PNS sorption occurs to a large degree in the first minute(s) of cement hydration.

The sorption processes that occur in the first minute or so of C3A hydration, however, involve incorporation of the PNS superplasticizer to a significant degree, which reduces its superplasticizing effect. Well defined PNS organo-mineral intercalation compounds have been identified by XRD analysis of the reaction products of lime, sodium aluminate and varying amounts of PNS (Fernon et al. 1997). These were described as layered double hydroxides where PNS anions have replaced some of the hydroxyl groups. A lower amount of C3A in the clinker can therefore reduce the amount of PNS superplasticizer required to achieve a given fluidity (Griesser 2002). Delayed addition of the superplasticizer to the cement mix is another method for limiting PNS incorporation and improve the flow and properties of cement. For example, El-Didamony et al. (2013) found that delayed addition of a PNS superplasticizer up to 7.5 minutes increasingly improved the fluidity, total porosity and bulk density of a sulphate...
resisting cement paste containing silica fume. Therefore, the optimum time to add PNS superplasticizers could be the start of the dormant period, when the initial C₃A hydration reactions have taken place and the cement is about to be worked (Flatt and Houst 2001). Flatt and Houst (2001) suggested that this is often not practical, but this no longer seems to be the case: El-Didamony et al. (2013) report that the development and use of delayed addition has become increasingly important and the Technical Data Sheet for Pantarhit® LK (FM) PNS superplasticizer states that it should be added to ready-mixed concrete.

The sulphate concentration of cement porewater plays an important role in the sorption of PNS and its influence on cement properties. Sulphate and PNS compete for the same binding sites, particularly on C₃A (Griesser 2002). Sulphate hinders PNS incorporation into hydrating C₃A phases (Kim et al. 1999), and lowers the dosage required for optimal dispersion. However, sulphate also competes for sorption sites on cement minerals, which can reduce the necessary adsorption of the superplasticizer. Griesser (2002) summarised his results in Figure 2-1, note that a high relative yield value is equivalent to a low cement fluidity, i.e. is undesirable. At low sulphate concentrations, there is a high degree of superplasticizer incorporation, which increases the yield (i.e. decreases fluidity). As the sulphate added increases, the superplasticizer is incorporated to a lesser degree and adsorbed to a greater extent, improving performance. The optimal sulphate concentration is shown at point B in Figure 2-1. As the sulphate concentration increases further, adsorption of the superplasticizer is inhibited, again increasing the yield of the cement.

![Figure 2-1. Distribution of superplasticizers as a function of the sulphate ion concentration in the dormant period. The minimal relative yield value is reached at maximum SP_{ads} (position B). The figure is divided into a low (I), intermediate (II) and a high (III) sulphate sector (from Griesser 2002).](image-url)
Experiments on aged, hardened cement avoid incorporation processes and give an insight into adsorption of solution phase superplasticizers onto cement in the actual repository. Glaus et al. (2006) found that the UV/Vis spectra of PNS and LS superplasticizer in the supernatant of sorption experiments and the original superplasticizers differed, i.e. that particular species were sorbed preferentially. The data were normalised to produce a one site Langmuir sorption isotherm: the sorption capacity of the cement for PNS and LS was 81 and 43 g/kg, respectively, while the sorption-affinity constant (K) of the superplasticizers were 19 and 2.1 L/g, respectively. The desorption profiles of the superplasticizers did not follow the Langmuir model, and suggested that most of the superplasticizer is either irreversibly sorbed or that the desorption kinetics are very slow in the timeframe of the experiments. This suggests that superplasticizer-cement interactions are strong even without chemisorption processes associated with cement hydration.

2.2.2 PCE superplasticizers

PCE superplasticizers also show rapid sorption to hydrating cement. For example, Winnefeld et al. (2007) synthesised 9 polymaleic acid-based PCE superplasticizers and found that their sorption to OPC was complete within 5 minutes. However, PCE superplasticizer generally sorb to a lesser degree to cement than PNS superplasticizers (Griesser 2002, Wieland et al. 2014, Uchikawa et al. 1995, Alonso and Puertas 2015). Wieland et al. (2014) found that 10-20% of the PCE superplasticizer used in OPC remained in the porewater, compared to 2-5% of the PNS. As more PNS was used in the OPC, the superplasticizer-relatedDOC in the porewater was at a concentration of tens of mM for both.

There is contrasting evidence of the extent to which and how PCE superplasticizers are bound to cement particles. Some studies show that C3A and its hydration products are less important for PCE than PNS superplasticizers, and that incorporation occurs to a lesser extent. For example, Hanehara and Yamada (1999) found that the delay of a PCE superplasticizer only had a small influence on the fluidity of a cement. Uchikawa et al. (1995) found that a PCE superplasticizer sorbed to a similar extent to individual C3A and C3S phases and that the time of addition had a negligible effect on the amount sorbed. Delayed addition to OPC cement had a small effect on the amount sorbed (61 vs 66% sorbed) in this study.

However, Griesser (2002) found that delaying the addition of a PCE superplasticizer by 90 seconds improved the workability of cement. The cement was selected due to its high C3A content and the results indicated that PCE was incorporated into hydrating minerals to an extent. Giraudeau et al. (2009) identified intercalation of PCE superplasticizers in AFm crystallites. Plank et al. (2010) found that PCE organo-mineral phases form at 75 °C in the absence of sulphate and that they intercalate during C3A hydration. A high level of steric hindrance, e.g. long side chains, however can limit intercalation. The formation of PCE organo-mineral phases has also been identified in calcium aluminate cement (Ng et al. 2013). Small-angle X-ray scattering (SAXS) analysis and XRD identified that the plane distance increased by ~10.2 – 10.5 nm when organo-mineral phases formed, compared to the corresponding minerals formed in the absence of PCE, which have a d-spacing of ~1 nm (Ng et al. 2013). Additionally, Ferrari et al. (2017) showed that a greater amount of orthorhombic C3A in cement
reduced the effect of four PCE superplasticizers. Alonso and Puertas (2015) report that the C₃A in OPC clinker is normally the cubic form, although small amounts of the orthorhombic form may also be present.

This contrasting evidence may reflect differences in the chain lengths (e.g. Plank et al. 2010) and the charge density of the PCE superplasticizers used. For example, Plank and Hirsch (2007) found that delayed addition (2 hours) had little impact on the sorption of two PCE superplasticizers to hydrated cement minerals, but did affect a third PCE superplasticizer. The two superplasticizers that were not affected had relatively high side chain densities and therefore low charge densities. The higher charge density of the third PCE appeared to result in it interacting to a greater extent with the hydrating phases, which is consistent with the earlier discussion of the positive zeta potential of C₃A. Alonso and Puertas (2015) also found a relationship between charge density and PCE superplasticizer sorption to cubic C₃A. They investigated the adsorption of three PCE superplasticizers with different backbone chain lengths (MW 37 000 – 189 000) and polycarboxylate:ester group ratios from 0.4 – 1.9, and a PNS superplasticizer. All four superplasticizers showed a linear relationship between the amount adsorbed and the amount added per gram of solid in the absence of sulphate. The authors stated that this is an indication of the coexistence of the precipitation, adsorption and uptake of the admixture into the aluminate hydrate layers. Sorption of the PCE with the highest charge density was less than that of the PNS superplasticizer investigated. Ng et al. (2013) also found that PCE superplasticizers with a lower charge density incorporated into calcium aluminate cement minerals to a lesser extent than those with a high charge density.

Winnefeld et al. (2007) synthesised 9 comb-shaped maleic acid PCE superplasticizers. The superplasticizers with shorter side chains and a lower density of PEG side chains showed the greatest sorption to cement, due to their relatively high charge density. While 100% of polymethacrylic acid sorbed to the cement, the highest sorption of a PM superplasticizer observed was 87%, presumably due to the lower charge density. Superplasticizers with short side chains and high side chain densities only led to small improvements in the workability of cement paste. Short side chains offer a limited steric effect to hinder particle aggregation, while a high density of sidechains results in a low charge density of the superplasticizer and therefore reduces its sorption to the cement particles. Polymers with the same structure (and therefore charge density) but different numbers of repeat units were compared and the polymer fractions with a high molecular weight sorbed preferentially.

Sulphate is important for limiting PCE superplasticizer incorporation into organic mineral phases and for removing PCE from these phases (Plank et al. 2010). Giroudeau et al. (2009) identified that exposure of PCE superplasticizers intercalated in AF₅₉ crystallites to sulphate resulted in the dissolution and precipitation of new phases, together with the release of some of the superplasticizer. It would be sterically difficult for superplasticizers to replace sulphate within pre-formed sulphate minerals, due to the smaller size of the inorganic minerals (e.g. Ng et al. 2013).

Sulphate also affects PCE superplasticizer adsorption. It has been shown that, at low superplasticizer doses, the PCE superplasticizer with the highest charge density
(carboxylate:ester ratio) and PNS were most able to compete with the sulphate ions (Alonso and Puertas 2015). As a result, the superplasticizers delayed the peak heat of hydration. This agrees with Zimmermann et al. (2009) who suggested that sulphate sensitivity of PCE superplasticizers is directly proportional to the mean length of the ether side chains and inversely proportional to the ionic charge. Wieland et al. (2014) found that the sulphate porewater concentration was lowest in the absence of superplasticizer, higher with PCE and highest with PNS in OPC and a low pH cement (silica fume). This is consistent with the general trend that PNS competes to the greatest extent with sulphate. Griesser (2002) observed an increase of up to 20 % in the sulphate porewater concentration with PCE, PNS and PMS superplasticizers. Therefore, sulphate and PCE superplasticizers appear to compete for the same binding sites.

2.3 Influence of alternative cement components

2.3.1 Sulphate resistant cement

Sulphate resistant cement contains lower amounts of C₃A minerals and so incorporation of PNS and even PCE in organic cement minerals is expected to be lower than in OPC.

2.3.2 Low alkali cement

Low alkali cement contains smaller quantities of K⁺ and Na⁺, which are normally present as readily soluble sulphates (Flatt and Houst 2001). The readily soluble sulphate in the clinker is therefore low. This can lead to greater incorporation of superplasticizers into the AF₃₅ phases and the requirement for the addition of higher superplasticizer concentrations (Flatt and Houst 2001). For example, Kim et al. (1999) found that PNS capable of fluidising OPC had little fluidising effect on low alkali cement.

2.3.3 Silica fume

The inclusion of silica fume to make a high performance low porosity concrete or a low pH cement affects the surfaces available for superplasticizer sorption. In cement paste, silica fume interacts with dissolved calcium ions to gain an overall positive surface charge allowing sorption of superplasticizers (Plank et al. 2009). The addition of 16% silica fume to low alkali Portland cement significantly increased the dose of each of 6 PCE superplasticizers tested to achieve the same spreading properties (Plank et al. 2009). For example, with methacrylate ester superplasticizers, the dosage required was up to 0.4% of the cement, and up to 2.45 % of the cement mixed with one type of silica fume. It was not possible to disperse cement mixed with a second type of silica fume using any of the three most effective methacrylate ester superplasticizers synthesised; the surface area of this silica fume was 50% greater than the first, contained 15% more carbon and had less regular-shaped particles, and was found to develop a more positive zeta potential due to sorption of Ca⁡⁺ ions. Kakinuma et al. (2008, in Plank et al. 2009) had shown that irregular-shaped silica fume particles can significantly increase the required dosage of PCE superplasticizers. The methacrylate ester superplasticizers were also found to be able to disperse the first type of silica fume on its own, but not the second type. Despite this, they were seen to adsorb effectively and to an equal extent to both types of silica fume.
Higher doses of a different type of PCE, based on allylether, were required in the cement on its own (Plank et al. 2009). However, the desired spread in the cement paste could be achieved even with the second type of silica fume blended in the cement, using a dosage of slightly more than twice that used for the cement on its own. Furthermore, two of the three allylether-based superplasticizers were able to disperse both silica fume types on their own. In this case, the two that achieved best dispersion were those that adsorbed most effectively to the silica fume. Although they sorbed equally to the two types of silica fume, higher doses were required to achieve the desired spread with the second type of silica fume. Therefore, compatibility between the silica fume and superplasticizer is important to minimize the wastage of sorbing superplasticizer without it having an effect.

Fujita et al. (2008) found that a PCE superplasticizer sorbed to fly ash silica fume cement to a greater extent than to OPC. The possible reasons for this were discussed as being the unburnt carbon content of the fly ash silica fume cement, since fly ash itself sorbs about half of the amount of superplasticizer sorbed by OPC and the large surface area of silica fume that can bind a large amount of superplasticizer.

The observations of Onofrei et al. (1989) that PNS was associated with CAH phases and calcium-rich CSH in a hardened silica fume blended cement suggests that PNS sorption to silica fume is relatively low despite its large surface area. This is generally consistent with PNS reacting more specifically with C₃A and its hydration products, compared to PCE superplasticizers.

Wieland et al. (2014) examined the sorption of PNS and PCE superplasticizers to three types of cement, which were described as OPC, low alkali and low pH (shotcrete-type) cements. The amount of PNS or PC remaining in the porewater after 28 days hydration were fairly similar for the three cements. However, since higher superplasticizer concentrations were added to the low alkali cement and the low pH cement formulations compared to OPC, a greater proportion of the superplasticizer sorbed to these hydrated cements and the final concentration of sorbed superplasticizer was higher. Possible reasons given for this were the large amount of ettringite and the presence of silica fume in the low pH cement as well as the lower pH of both cements, since the high hydroxide and low Ca²⁺ concentration of the OPC affects the zeta potential of the cement minerals and thus may reduce sorption of the negatively charged superplasticizers. They used the results to estimate Rₐ values for the sorption of superplasticizers, which were low:

- Ordinary Portland Cement: PC = 8.5 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}; PNS = 3.8 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}
- Low pH cement: PC = 1.2 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}; PNS = 1.5 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}
- Low alkali cement: PC = 3.3 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}; PNS = 1.7 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}

2.4 Sorption to bentonite

Interactions between superplasticizers and bentonite had not been investigated in the open literature when Hakanen and Ervanne (2006) carried out their review of superplasticizers. Since then, Wang et al. (2012) have found that a PCE superplasticizer sorbs rapidly to natural bentonite, reaching equilibrium within ~10 minutes. At pH ~11, ~70 mg/g of superplasticizer sorbed to the bentonite and the amount decreased with
decreasing pH to a minimum at pH 6. Sorption was also found to be greater at higher temperatures (30 – 60 °C). This study therefore suggests that superplasticizers that desorb from cement in a spent fuel repository and come into contact with bentonite will be sorbed to a significant extent.
3 LEACHING OF SUPERPLASTICIZERS FROM CEMENTITIOUS MATERIALS

The leach profiles of superplasticizers from hydrated cement initially reflect the relatively low molecular mass components of the commercial product that sorb to a lesser extent than the polymers themselves (see Section 1.2). Subsequent leaching is very low within the constraints of the experiments. This has been seen in the release of radiolabelled PNS superplasticizer from a Canadian Type 50 high performance grout containing 10% silica fume by dry mass, which was dominated by the material in the pore space and from concomitant dissolution of the C3S and C3A hydrated phases (Onofrei and Gray 1989). The cumulative release over 30 days of leaching from the solid sample with the water renewed 5 times was about 10^{-16} kg/m², low in comparison to the loading in the solid phase (10^{-13} to 10^{-12} kg/m²). The components of PNS that leached from ground cement over 5 days at 60 °C differed from the original PNS product used, and only the polyethylene glycol chains from a PCE superplasticizer were observed in solution (Herterich et al. 2003). Herterich et al. (2004) suggested that the polyethylene glycol was released by alkaline hydrolysis of the carboxylate-ester bond, leaving the polycarboxylate/polyacrylate backbone bound to the cement. Hydrolysis of carboxylate esters is an expected reaction at high pH (e.g. Section 4.1).

A low proportion of PCE superplasticizer leached within 56 days, with five renewals of the deionised water leachate, from concrete monolithic self-compacting cement concrete bodies that had been hardened for three days (Herterich et al. 2004). Less PCE superplasticizer leached from hardened cement containing fly ash and no limestone, compared to hardened cement containing limestone and no fly ash. This concrete also had the lowest water:cement ratio, and therefore had the smallest pores. Again, the polymer was seen to be sorbed more strongly than other components of the commercial product. Between 0.3 - 1.9% of the active component leached over 56 days, and the amount leached decreased over time. The concentration of the superplasticizer-related material in the first leach solution phase, which is most affected by the superplasticizer remaining in the porewater, was generally 2-3 times the concentration of subsequent leaches. The superplasticizer leached from hardened cement containing fly ash and no limestone (lowest w/c ratio) decreased further in the 5th and 6th water change. The maximum TOC concentrations in the leachates were 1-2 mg/L, and about 60% of the TOC came from concrete admixtures.

This general trend has also been observed in the field by Ruckstuhl et al. (2002), who examined the leaching of PNS from grout, and saw that monomers and dimers leached into the groundwater but oligomers consisting of more than four repeat units were not observed in the groundwater. This was considered to reflect the different binding properties of the molecules. Acrylate, methacrylate and 2-hydroxyethyl methacrylate from an acrylate-based grouting agent have been seen to leach quickly during the construction of a tunnel in Norway (Sverdrup et al. 2000). The highest concentrations of these chemicals in the drainage water (4-5 mg/L) occurred during the injection of the materials, and then the concentrations dropped rapidly to <0.3 mg/L.
Yamamoto et al. (2008) examined the leaching of the PMS superplasticizer SP40 from OPC and Mighty 150 (PNS superplasticizer) and Glenium 51 (PCE superplasticizer; now known as MasterGlenium 51) from low pH silica fume cement prepared with slightly different water:cement ratios. The cement containing Glenium 51 was prepared with a lower amount of water (1.2:1 rather than 1.4:1). Both OPC and low pH silica fume cement were also prepared without superplasticizer for comparison. Leaching was carried out over 56 days at a L/S ratio of 4:1 and the leachate included superplasticizer material that did not sorb as the cement underwent hydration. Leaching of fresh low pH silica fume cement with deionised water and synthetic groundwater released an equal concentration of organic matter from the cements prepared with PCE and PNS superplasticizers, despite the use of ~3 times as much PNS. Relatively little extra organic matter (~20 mg/L) was seen to leach compared to the cements prepared without superplasticizer. Saline water did not affect the amount of PCE leached, but increased the amount of PNS released and slightly reduced release of PMS. The additional release of PNS dimers into saline water is consistent with the observation that the sulphonate groups compete for binding sites with \( \text{SO}_4^{2-} \). The leachates from 56 days were analysed by GPC and there was no evidence of the polymers or oligomers. Smaller organic molecules were detected that were representative of constituents of the materials (e.g. melamine constituent, dimer of naphthalene sulphonate) or unreacted monomers (e.g. methacrylate polyethylene glycol). In all cases, the polymers have a higher affinity for the cement, as seen in sorption experiments.

Hardened cement was ground to <100 µm and leached at L/S ratios of 10, 50, 100 and 1000 for a fixed time period of 38 weeks (Yamamoto et al. 2008). These experiments gave similar overall results to the fresh cement leach tests, but showed that more organic matter leached from the low pH silica fume cement with PNS than from that with PCE at all L/S ratios and in all waters. Taking the leaching of background organic matter from the cement grinding agents into account, the leaching of the PNS was substantially higher than the PCE. It was argued that this reflects the greater amount of PNS required compared to PCE. Since the results from the fresh cement and deionised water or groundwater at L/S 4 did not show this trend, it appears that L/S ratios of 10 and more cause alterations in the cement mineralogy that enhance release of the PNS superplasticizers, as suggested by Onofrei et al. (1992). The pH of the experiments supports this. Fresh cement leached with deionised water and groundwater at L/S 4 resulted in a leachate of around pH 12 after 56 days, while in the hardened cement leachates with L/S 10 – 1000, the leachates were between ~pH 10.6 and 10.9. With saline water, the pH was lower in both cases and lowest in the hardened cement experiments with L/S 10-1000. The pH of the porewater did not vary significantly between L/S 10 and 1000. Groundwater samples from boreholes containing leachate from a low pH cement grouting experiment at Onkalo were also analysed and there was no evidence of PNS superplasticizers leaching, or their degradation products. PCE superplasticizers had not been used in the grouting experiment.

Yamamoto et al. (2008) presented NUMO’s contribution to an international project on superplasticizers, published in Andersson et al. (2008). Chalmers Technical University found similar results to Yamamoto et al. (2008) with more PNS (Mighty 150) leaching from low pH grout than PCE (Glenium 51) at L/S of 20 (see approximate values in Table 3-1) and that the amount leached did not change outside experimental variations.
from 7 to 42 days of leaching. The results from Helsinki University suggested that PCE (Glenium 51) did not leach from OPC at L/S of 10 over a 6-week period, but increased the organic carbon leached from low pH grout by 6 mg/L. The increase effectively doubled the amount of organic carbon leached relative to the cement prepared without superplasticizer. PNS (Mighty 150) resulted in additional organic leaching from both OPC (by 10 mg/L) and low pH grout.

Table 3-1. Approximate results for leaching from the low pH grout from the different laboratories contributing to Andersson et al. (2008). Background TOC leached from cement prepared with superplasticizer has been subtracted from the TOC values.

<table>
<thead>
<tr>
<th>Institution</th>
<th>L/S</th>
<th>Water</th>
<th>PNS leached (mg/L TOC)</th>
<th>PCE leached (mg/L TOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NUMO (fresh cement)</td>
<td>4</td>
<td>Groundwater</td>
<td>18</td>
<td>19</td>
</tr>
<tr>
<td>NUMO (fresh cement)</td>
<td>4</td>
<td>Saline</td>
<td>33</td>
<td>19</td>
</tr>
<tr>
<td>NUMO</td>
<td>10</td>
<td>Groundwater</td>
<td>31</td>
<td>7</td>
</tr>
<tr>
<td>NUMO</td>
<td>10</td>
<td>Saline water</td>
<td>28</td>
<td>3</td>
</tr>
<tr>
<td>Chalmers</td>
<td>20</td>
<td>Saline water</td>
<td>27</td>
<td>17</td>
</tr>
<tr>
<td>Helsinki University</td>
<td>10</td>
<td>Saline water</td>
<td>16</td>
<td>6</td>
</tr>
</tbody>
</table>
4 CHEMICAL AND BIOLOGICAL STABILITY OF SUPERPLASTICIZERS

Commercial superplasticizers contain unreacted reagents, monomers, dimers and short chain oligomers as well as the polymers that give the product its superplasticizing function. The smaller molecules are most likely to remain in the porewater during the hydration of cement (Section 2). The stability of these smaller molecules is therefore relevant as well as the stability of solution phase and bound polymers.

The chemistry of the superplasticizer degradation products affect their potential for radionuclide complexation. The likely chemical- and biodegradation mechanism and products are therefore discussed in this chapter.

4.1 Chemical degradation mechanisms and products

The generic chemical structure of PCE superplasticizers provides an insight into the reactive sites where degradation processes are most likely to occur. The PEG side chain is most vulnerable to nucleophilic attack, at the carbonyl carbon of the ester group. This carbon is bound to two electron-withdrawing oxygens, and thus has a delta positive charge. The high hydroxide concentration of cement porewater is expected to lead to nucleophilic attack at this carbon and the resulting hydrolysis reaction would produce a carboxylic acid (attached to the polycarboxylate back bone) and hydroxide (PEG). Alkaline hydrolysis of ester groups is a well-documented chemical process. This reaction would remove the polyethylene glycol side chains from the polycarboxylate backbone, and was suggested to be responsible for PEG determined in cement porewater in Hertereich et al. (2004). The PNS chain and PC backbone are more resistant to degradation and, although further reactions may occur, evidence for this has not been identified.

One difficulty in experimental studies is differentiating between the unreacted PEG in the superplasticizer product used and the PEG degradation product, especially when the amount of PEG determined is a small amount of the total superplasticizer added, as it was in Hertereich et al. (2003, 2004). Another limitation is that experiments are short with respect to the evolution of radioactive waste repositories. For example, experiments by Yilmaz et al. (1993) were carried out for 20 days, and in this time a commercial PNS superplasticizer treated with 1 M KOH did not degrade. Further, the rate of degradation can vary between sorbed and dissolved species.

Glaus et al (2006) carried out longer term experiments, the longest identified in the literature review. They prepared OPC with LS and PNS superplasticizers and allowed the cement to age to ~20 months. The superplasticizers were extracted from the crushed material using 1 M Na2CO3 and it was found that the uv/vis spectra had not altered with respect to the original superplasticizer solution, i.e. the main structural components had been conserved. The technique is not, however, capable of detecting a decrease in the degree of polymerisation, as it detects chromaphores - functional groups that absorb light in the uv and visible regions. The uv/vis spectra of superplasticizers in the porewater showed changes from 4 to 20 months, suggesting that the functional groups of the compounds in the porewater are more prone to change than those that are sorbed.
This is consistent with the smaller molecules in the superplasticizer mix that tend to sorb to a lesser extent being more prone to chemical degradation than the polymers.

Polyacrylates are used as co-builders in household detergents (FDA 2010), and studies have shown that polymers with a molecular weight of 4500 precipitate in soil and sewage treatment systems, and sorb to particles. They are resistant to chemical degradation.

### 4.2 Biodegradation

Products can be defined as "readily biodegradable" to show that they will rapidly be degraded in the environment, while "inherently biodegradable" shows that that can be biodegraded under conditions that strongly promote biodegradation. Lignosulphonates are inherently biodegradable, PMS and PNS do not fulfil the criteria for being readily biodegradable, and PC range from not readily biodegradable to poorly biodegradable (Deutsche Bauchemie e. V. 2011). Under repository conditions, with low microbial populations, anaerobic conditions and a relatively high pH, degradation of the polymers is therefore expected to be very slow. However, most processes in a fairly stagnant repository system are very slow and the long time scales involved mean that degradation cannot be excluded. Although this section focusses on PNS and PCE, the melamine component of PMS superplasticizers has been found to be degraded by bacteria isolated from a paddy field (Tagaki et al. 2012).

Many biodegradation reactions take place after the molecule has passed into the microbial cell. This is clearly difficult for polymers, thus biodegradation mechanisms for the superplasticizer polymers are likely to involve the release of enzymes, known as exoenzymes.

#### 4.2.1 PNS

Anaerobic Clostridium sp have been found to use naphthalene-2,6-disulphonate as a sulphur source for growth (Cook et al. 1999). The desulphonation of naphthalene-2-sulphonate by Pseudomonas sp C22 is shown in Figure 4-15. The first step of the reaction involves $\text{H}^+$ ions, suggesting that this will be challenging under highly alkaline conditions. Following desulphonation, degradation of naphthalene-1-sulphonate and naphthalene-2-sulphonate merges into the Pseudomonas sp naphthalene degradation pathway, which also involves the 1,2-dihydroxynaphthalene molecule. This degradation pathway breaks the naphthalene structure and produces pyruvate (CH$_3$COCOO$^-$ involved for example in the Kreb’s cycle), and either gentisate, a well-known metabolic intermediary based on a benzene ring with two alcohol groups and a carboxylate group, or catechol, a benzene ring with two alcohol groups, together with formic acid. Microbial degradation of naphthalene has been identified under denitrifying, SO$_4^{2-}$ reducing, and Mn(IV) or Fe(III) reducing conditions (Gascoyne 2002).

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5 [http://eawag-bbd.ethz.ch/nphs/nphs_map.html](http://eawag-bbd.ethz.ch/nphs/nphs_map.html)
Ruckstuhl et al. (2002) examined the aerobic biodegradation of components of a PNS commercial product that leached from fresh cement at a tunnel construction site. Monosulphonated monomers degraded faster than disulphonated analogues, which was in keeping with other results in the literature. Degradation of oligomers was not observed over the 100 day experiment.

Sulphonated naphthalene formaldehyde condensates were found to be biodegraded by aerobic bacteria from textile industry activated sludge wastewater at pH 7.2 (Cheriaa et al. 2008). The condensates are similar to PNS superplasticizer but with an average of 7-8 condensed monomers. Biodegradation was found to involve cleavage of the CH$_2$ bridging bonds followed by cleavage of the naphthalene rings.

Bacteria from granitic groundwater were not able to degrade the PNS superplasticizer Disal under aerobic conditions (Haveman et al. 1986). Part of a relatively high concentration (200 g/L) of Disal was biodegraded under nitrate-reducing conditions, particularly by *Pseudomonas* sp. (Haveman et al. 1996). *Pseudomonas* sp. are not normally able to degrade polymers (Gascoyne 2002), but Disal presumably contains unreacted precursor molecules, monomers and dimers that are more readily degradable. Gascoyne (2002) suggested that cooperation with another type of bacteria may allow the full biodegradation of PNS superplasticizers.

To summarise, following the cleavage of the CH$_2$ bridging bonds in the PNS polymeric chain, the PNS oligomers, dimers and monomers are expected to be biodegradable, at least under favourable pH conditions. The degradation of the stable polymeric chain is therefore expected to be the slowest step in the degradation process.
4.2.2 PCE superplasticizers

PCE superplasticizers are expected to undergo abiotic alkaline hydrolysis reactions at the ester group that binds the PEG chains to the polymer backbone relatively quickly in the context of groundwater flow and repository evolution. The biodegradability of the resultant PEG and poly(meth)acrylate is therefore relevant here.

PEG have been seen to be degraded by bacteria in soil (Haines and Alexander 1975, Abdalla et al. 2005), river sediments (Obradors and Aguilar 1991) and sewage (Huang et al. 2005, Dwyer and Tiedje 1986). The smaller polymers and oligomers are generally biodegraded more easily than the longer polymers. Dwyer and Tiedje (1986) also reported that anaerobic depolymerisation of PEG results in the production of acetaldehyde, which can be used further by microorganisms.

Haines and Alexander (1975) identified that the soil bacteria *Pseudomonas aerugirosa* excreted an enzyme that degrades PEG with a molecular weight (MW) of up to 20 000, and identified ethylene glycol as a metabolite. They also found that under their experimental conditions ethylene glycol was degraded most quickly, within 2 days, followed by di-, tri-, and tetaethylene glycols and PEG of MW 400, for which extensive attack was evident by day 5. PEG of MW 1000 – 10 000 showed extensive degradation by the last sampling point of 20 days. A number of bacteria able to utilize PEG of MW 20 000 as sole carbon source were isolated from soil, including gram-positive rods, gram-negative rods occurring singly and in chains, and gram-variable isolates. Huang et al. (2005) demonstrated degradation of PEG of MW 600, 6000 and 20 000 under both aerobic and anaerobic conditions.

Suzuki et al. (1978) found that although microorganisms in a river bed mud did not degrade PEG (MW 8000) or polyacrylate (MW 410 000), degradation occurred following ozonisation of the materials to reduce the molecular weight of the polymer units (MW 250). Peregrina et al. (2013) isolated *Pseudomonas* sp or *Bacillus* sp from the paper production process that could degrade polymethacrylate, while Kawai (1995) proposed a mechanism for bacterial degradation of polyacrylate (MW 1000). These studies indicate that microbial degradation of the poly(meth)acrylate backbone may also be possible if it is degraded to smaller units by another process.

The PEG in PCE superplasticizers appears to have a MW of ~1000 and are therefore likely to be biodegradable. Acrylic acid and methacrylic acid are also readily biodegradable, for example > 60% and 86%, respectively, were degraded in 28 days under laboratory test conditions (Sverdrup et al. 2000). Therefore, the cleavage of the stable polyacrylate/polymethacrylate chain is expected to be the slowest part of the degradation process.
4.3 Summary of possible degradation products

The possible degradation products of PNS and PCE superplasticizers are summarised in Table 4-1.

Table 4-1. Summary of possible degradation products from PNS and PCE superplasticizers

<table>
<thead>
<tr>
<th></th>
<th>PNS</th>
<th>PC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reagents and synthetic biproducts</strong></td>
<td>Naphthalene sulphonate monomers and dimers Oligomers</td>
<td>Readily degradable ethylene glycol Polyethylene glycol of different molecular weights Acrylic or methacrylic acid Monomers, dimers, oligomers</td>
</tr>
<tr>
<td><strong>Degradation products</strong></td>
<td>Naphthalene sulphonate monomers and dimers 1,2-dihydroxynaphthalene Sulphate Readily degradable carboxylic acids such as pyruvate, gensite and formate Catechol Carbon dioxide</td>
<td>Polyethylene glycols of different molecular weights Polycarboxylate polymer, oligomer, dimer and monomer Readily degradable acrylate, methacrylate, acetaldehyde and other low weight organics Carbon dioxide</td>
</tr>
</tbody>
</table>
5 POTENTIAL FOR RADIONUCLIDE COMPLEXATION AND IMPACT ON RADIONUCLIDE SOLUBILITY AND SORPTION

There is concern that superplasticizers may increase the transport of radionuclides out of a repository. This chapter first looks at evidence that superplasticizers enhance radionuclide solubility, i.e. form complexes with radionuclides, and then examines whether this effect manifests in an ability to reduce radionuclide sorption to a) cement and b) granite and bentonite.

5.1 Effect on radionuclide solubility

The literature leaves no doubt that superplasticizers can increase the solubility of some radionuclides, although all experiments are carried out at relatively high superplasticizer concentrations. For example, a variety of superplasticizers increased the solubility of Ni(II), Am(III), Pu(IV) and, to a lesser extent, U(VI) by up to three orders of magnitude when added at 0.3% to cement-equilibrated water (NDA 2015). Greenfield et al. (1998) found that 0.3 and 3% solutions of a PNS lignosulphonate (HS-100) and a polycarboxylate polymer (HS-700) increased the solubility of Tc(IV), U(IV), Pu(IV) and Am(III) in cement –equilibrated water (pH 12.0-12.4). The solubility of Am(III) was affected to the greatest degree by both superplasticizers, by up to 5 orders of magnitude. There were differences in the relative effects of the two superplasticizers on the different radionuclides, particularly at the lower superplasticizer concentration.

Wieland et al. (2014) carried out experiments using cement water and a cation exchange resin (DOWEX 50 W X-4) and showed that a PC-type superplasticizer (Glenium 51 BASF AG, Switzerland) reduced the sorption of Ni to the resin, while a PNS superplasticizer (Rheobuild 1000, BASF AG, Switzerland) reduced the sorption of Ni(II) and Eu(III). The sorption of Th(IV) was not affected in these experiments.

5.2 Effect on radionuclide sorption to cement

Several studies have examined the effect of superplasticizers on the sorption of radionuclides to cement. The general picture is that radionuclide sorption is reduced when superplasticizers and radionuclides are mixed with hardened cement paste (HCP), i.e. when the solution-phase concentration of the superplasticizer is much higher than expected in an actual cement porewater. However, when the results have been extrapolated to conditions in a real cement, an effect is thought to be unlikely. The validity of the extrapolation methods has not, however, been established. The experimental evidence is discussed below.

Glaus et al. (2003) developed a screening procedure for assessing whether concrete admixtures may affect the sorption of radionuclides on cement. They found that commercially available superplasticizers were generally able to reduce the sorption of Eu(III) and Th(IV) to crushed hardened OPC paste when added at high solution concentrations (2 g/L) and relatively high L/S ratio (ratio not given). The use of superplasticizers in the preparation of hardened cement paste did not affect the sorption of radionuclides to the HCP (L/S ratio not given). They also found no evidence to
suggest that the superplasticizers degraded to products with higher complexing power over ~4 months.

Wieland et al. (2014) found that neither a PCE nor a PNS superplasticizer had a significant effect on Ni, Eu(III) and Th sorption to HCP. This was assessed in two types of experiment. The first was a set of batch experiments with superplasticizer added to the solution phase and the second involved squeezing cement porewater from the hydrated cement and diluting it to give the expected ratio of “HCP to ligand concentration” in a repository for batch experiments. Since the porewater squeezed out from the cement contains the ligands at the equilibrium concentration, it is not clear how the dilution achieves its aim. The batch experiments were carried out with L/S ratio of 40 for Ni and 4000 for Eu(III) and Th to maximise the chance of statistically robust radioactivity determinations. The initial concentrations in the batch experiments were: $^{63}$Ni = $1.40 \cdot 10^{-9}$ M, $^{152}$Eu = $1.50 \cdot 10^{-9}$ M and $^{228}$Th = $2.48 \cdot 10^{-10}$ M, to keep the experiments under saturated with respect to any solubility-limiting phases.

For Eu(III), the first set of batch experiments involved 0.25 g/L hardened cement paste and up to 30.8 (PCE) and 35 (PNS) mM DOC from the admixture. The second set of experiments involved 0.25 g/L hardened cement paste and a 100- or 1000-fold dilution of the superplasticizer in the porewater squeezed out of the cement after 28 days or 360 days (42-63 mM DOC prior to dilution). The DOC concentration in the porewater squeezed out of the cement was higher than the DOC concentration used in the first set of batch experiments. Therefore, the experiments did not directly address the impact of superplasticizers at cement porewater concentrations on radionuclide sorption. Wieland et al. (2014) discussed the possibility that superplasticizers could also enhance sorption of radionuclides through the formation of ternary surface complexes. However, an increase in radionuclide sorption due to the superplasticizers was not observed in the experiments.

Dario et al. (2004) investigated the impact of seven superplasticizers used by SKB on the sorption of Eu(III) to OPC cement, using a solid/liquid ratio of 1 g/L. The results are summarised in Table 5-1. The Kd of Eu(III) on its own was 300 - 1000 times greater than the value of 10 m$^3$/kg applied by SKB, and was about 30 - 100 times higher than the Kd found by Wieland et al. (2014) for Eu(III) in similar experiments. The initial concentration of $^{152}$Eu(III) was $1 \cdot 10^{-8}$ M, which may exceed the solubility of Eu(III) in cement porewater. Ochs et al. (1997) reported measured Eu(III) solubility ranges from <6.6$ \cdot 10^{-10}$ M in simulated cement porewater at the Portlandite state of degradation and 1.8 - 2.7$ \cdot 10^{-9}$ M in simulated fresh cement porewater, and that this agreed well with thermodynamic calculations. It is therefore possible that Eu(III) precipitation occurred in the absence of the superplasticizers.

All of the superplasticizers began to exhibit an effect on Eu(III) sorption in the concentration range 0.001-0.01 % of the solution phase, or 0.01 - 0.1 g/L (Dario et al. 2004). Since the products contain ~40% superplasticizer by mass, and applying the assumption that the molecules are 50% carbon by mass, this relates to effects in the DOC concentration range 0.2 - 2 mM. It was concluded that if all of the superplasticizer leached out from the cement, the liquid phase superplasticizer concentration would be below the level that affects the sorption of radionuclides seen with the 1 g/L cement
However, as with the other studies, this requires assumptions in the extrapolation of the effects to repository conditions. In longer term experiments with 15 or 18 mM DOC of the different superplasticizers, there was a tendency for the Kd to increase over about 100 days and then reach an equilibrium value that was well below that of Eu(III) on its own (Table 5-1).

Table 5-1. Effect of superplasticizers on Eu(III) sorption to OPC (inferred from figures in Dario et al. 2004). The Kd of Eu(III) in the absence of superplasticizer is ~3 000-10 000 m³/kg

<table>
<thead>
<tr>
<th>Superplasticizer</th>
<th>Polymer description</th>
<th>Manufacturer</th>
<th>Solution phase concentration when effect is seen on Eu(III) sorption (% liquid phase)</th>
<th>Approximate Kd (m³/kg) of Eu(III) with 0.01 % superplasticizer in solution after 24 hours</th>
<th>Approximate Kd (m³/kg) of Eu(III) with 0.1 % superplasticizer in solution after 1 and 420 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sikamen t 10</td>
<td>Vinyl maleic acid copolymer</td>
<td>Sika AG, Switzerland</td>
<td>~0.003</td>
<td>~6</td>
<td>4 and 28</td>
</tr>
<tr>
<td>Peramin F</td>
<td>Melamine sulphonate</td>
<td>Perstorp AB, Sweden</td>
<td>~0.005</td>
<td>~20</td>
<td>5.6 and 270</td>
</tr>
<tr>
<td>Sikamen t 210</td>
<td>Naphthalene sulphonate</td>
<td>Sika AG, Switzerland</td>
<td>Between 0.001 - 0.01</td>
<td>~40</td>
<td>0.08 and 220</td>
</tr>
<tr>
<td>Cementa Melcrete</td>
<td>Naphthalene sulphonate</td>
<td>Cementa AB, Sweden</td>
<td>~0.007</td>
<td>~60</td>
<td>4.9 and 91</td>
</tr>
<tr>
<td>Mighty 150</td>
<td>Naphthalene sulphonate</td>
<td>Cementa AB, Sweden</td>
<td>~0.003</td>
<td>~10</td>
<td>3.7 and 46</td>
</tr>
<tr>
<td>Peramin Conpac 30</td>
<td>Polycarboxylate ether</td>
<td>Perstorp AB, Sweden</td>
<td>Between 0.001 – 0.003</td>
<td>~19</td>
<td>0.9 and 2.6</td>
</tr>
<tr>
<td>Glenium 51</td>
<td>Polycarboxylate ether</td>
<td>Master Builders Inc. USA</td>
<td>Between 0.003 – 0.01</td>
<td>~10</td>
<td>3.7 and 50</td>
</tr>
</tbody>
</table>

Dario et al. (2004) also carried out equivalent experiments using complexing agents that are present in L/ILW repositories, including EDTA and citrate. Both of these began to influence Eu(III) sorption to cement at concentrations between 10⁻⁴ – 10⁻³ M, which is equivalent to 1-10 mM DOC (EDTA) or 0.6 – 6 mM DOC (citrate). The superplasticizers therefore had an effect on Eu(III) sorption (and possibly dissolution) at DOC concentrations that are similar, if not lower, than those of citrate and EDTA.
The NDA (2015) carried out a variety of experiments examining the effect of superplasticizers on radionuclide sorption to cement. The superplasticizers that enhanced radionuclide solubility (Section 5.1) were not able to enhance radionuclide transport through concrete blocks prepared with superplasticizers and radionuclides. They also carried out desorption experiments after crushing concrete prepared in the same way. They applied a two-stage leaching process, first using a L/S ratio of 2 and then of 8 L/kg. There was no evidence that the superplasticizers enhanced radionuclide migration or leaching from the concrete. Furthermore, the NDA (2015) investigated the effect of a range of cement additives (PCE superplasticizer and adjuncts) on the solubility, mobility, and migration of selected radionuclides and the effect of gamma irradiation on mobility and leaching of selected radionuclides. None of the results indicated that the superplasticizers decrease radionuclide sorption to cement.

5.3 Effect on radionuclide sorption to granite and bentonite

Andersson et al. (2008) described experiments investigating the effect of superplasticizers on Eu(III) sorption to crushed granite, using Kivetty granite from Finland. The experiments were carried out at Helsinki University and Chalmers University and there were some systematic differences in their data. This was thought to be due to the different experimental approaches (Table 5-2). Although Chalmers used a higher Eu(III) concentration, they determined lower Rd values and values for sorption to the vessels, i.e., precipitation did not appear to occur. The use of centrifugation at Chalmers and centrifugation and filtration at Helsinki University left some uncertainty as to whether centrifugation alone was sufficient to remove colloids in the Chalmers experiments or whether filtration removed dissolved Eu(III) species at Helsinki University, i.e., which results reflect the actual Rd values. However, it was also possible that the lack of a washing procedure for the crushed granite at Helsinki University left smaller particles in solution that led to higher Eu(III) sorption. Holgersson (2013) subsequently evaluated the impact of these experimental variations and his results suggest that sorption of $^{152}$Eu to the filters led to the overestimation of the Rd. The results from Chalmers (Andersson et al. 2008) showed that the Rd of Eu(III) decreased by 1-2 orders of magnitude with PCE superplasticizers added at about 0.1 and 1 g commercial product/L, pH 7-10. For Glenium 51, the lower concentration was equivalent to 0.036 g/L of the superplasticizer or 1.7 mM organic carbon. PNS superplasticizers had a more limited effect on Eu(III) sorption to granite.

Becker and Lippold (2016) studied the effect of Glenium 51 PCE superplasticizer on Eu(III) sorption to bentonite ($10^{-6}$ M Eu (III); 0.1 g/L superplasticizer; L/S 200; pH 5.8) and found that the superplasticizer increased Eu(III) sorption by about 5%. Further experiments are planned at higher pH.
Table 5-2. Main differences in experimental conditions in sorption studies performed by Chalmers and Helsinki University (Andersson et al. 2008).

<table>
<thead>
<tr>
<th>Method description</th>
<th>Chalmers</th>
<th>Helsinki University</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu concentration (M)</td>
<td>$10^{-6}$</td>
<td>$10^{-10}$ and $10^{-9}$</td>
</tr>
<tr>
<td>S:L</td>
<td>1:20</td>
<td>1:100</td>
</tr>
<tr>
<td>Shaking</td>
<td>Manual</td>
<td>Automatic</td>
</tr>
<tr>
<td>Vessels</td>
<td>Plastic</td>
<td>Glass</td>
</tr>
<tr>
<td>Leaching time (d)</td>
<td>200</td>
<td>42</td>
</tr>
<tr>
<td>Separation of phases</td>
<td>Centrifugation</td>
<td>Centrifugation and filtration</td>
</tr>
<tr>
<td>Storage</td>
<td>Glove box (N$_2$)</td>
<td>Outside glove box</td>
</tr>
<tr>
<td>Measurements</td>
<td>LSC</td>
<td>Gamma spectrometry</td>
</tr>
<tr>
<td>Wall adsorption</td>
<td>Empty tube</td>
<td>After removal of crushed rock and solution desorption with 0.1 M HCl overnight</td>
</tr>
<tr>
<td>Initial pH of water</td>
<td>8.5, 9, 10</td>
<td>7, 9, 10*</td>
</tr>
<tr>
<td>Pretreatment</td>
<td>Water exchanges</td>
<td>No treatment</td>
</tr>
</tbody>
</table>

* Not measured during the experiments
6 POTENTIAL IMPACT OF SUPERPLASTICIZERS ON THE LONG TERM DEGRADATION OF CEMENTITIOUS MATERIAL

The use of superplasticizers increases the strength and lowers the porosity of cementitious materials, and therefore is expected to be largely beneficial in their long term function. El-Didamony et al. (2013) showed the relationship between an increasing amount of PNS superplasticizer (0 – 2 mass %) and increased bulk density of cement paste, and lower porosity.

Wieland et al. (2014) discussed the potential for superplasticizers to affect the cement surface, mineral composition as well as and the chemical border of the cement-water system (such as pH, Eh). However, neither PCE nor PNS superplasticizers resulted in a discernible difference in the kind or amount of hydration products formed after 28 days of hydration, within the sensitivity of XRD. This was in agreement with Lothenbach et al. (2007), who found that although a PCE superplasticizer delayed early C\textsubscript{3}S dissolution and therefore Portlandite and CSH formation, it had no significant effect on the amount or type of hydrates formed after 6 days. \textsuperscript{29}Si NMR measurements showed that the silicate chain length of the CSH phases was unaffected in both a low alkali cement and a low pH cement formulation (ESRED cement) by the presence of the two superplasticizers (Wieland et al. 2014). The superplasticizers that remained in the pore solution also had little influence on the elemental composition of the pore fluids.

Three superplasticizers, a PNS, PMS and LS were found to reduce the porewater concentration of Cl\textsuperscript{-} in OPC (Yilmaz et al. 1992). Chloride attacks the steel reinforcement in structural concrete, and corrosion of the steel leads to crack formation in the concrete. A lower porewater Cl\textsuperscript{-} concentration is therefore beneficial for long term structural concrete performance.
7 CONCEPTUAL MODELS DESCRIBING THE FATE OF SUPERPLASTICIZERS IN CEMENT

This chapter explores simplified models of the following
- Diffusion-controlled release of superplasticizers from the plug as a function of \( Kd \)
- Adsorption of superplasticizers to cement
- Combined uptake of superplasticizers into organic mineral phases and surface sorption sites
- Release of superplasticizers from organic mineral phases and surface sorption sites into brackish groundwater, as a function of porewater exchange

The aim of this Chapter is to build a conceptual model that supports the understanding of the complex processes affecting the uptake and release of superplasticizers from cement. All parameter values have been selected arbitrarily thus the trends in the results are important, rather than the numeric values.

7.1 Diffusion-controlled release of superplasticizers from the plug as a function of \( Kd \)

In cement-stabilised waste in a L/ILW repository, the superplasticizers will be in the same medium as the radionuclides, and all radionuclides will need to pass through cementitious barriers in order to reach the far field. Therefore, the influence of superplasticizers in the cement itself is the critical question. In a spent fuel repository, the canisters containing the spent fuel are surrounded by bentonite and are separated from the cement. Therefore, the outward flux of superplasticizers into the groundwater in the repository is critical, together with their effect outside the cement.

Therefore, in this section, a simple model is presented that describes the release of superplasticizers from the plug by diffusion. The plug is selected as the largest cementitious component of the spent fuel repository, thus diffusion from the plug will be slower than from other cementitious components. The model accounts for the effects of linear adsorption, i.e. the impact of a \( Kd \)-value that will act to retard the release of the superplasticizer. The plug geometry here is based on the plug design presented within the DOPAS project (D4.5, Holt and Koho, 2016), see Figure 7-1. Note that this is not the reference plug design for Olkiluoto.
In the simplified interpretation of the plug geometry applied, it is assumed that the plug has a cylindrical cross-section of radius 2.25 m and length 6 m. It is further assumed that the radial diffusion from the plug into the surrounding rock is negligible. Both ends of the plug, i.e. at $x = 0$ m and $x = 6$ m, the concentration is kept at zero. The diffusion is described by the model presented by Carslaw and Jaeger (1959), Eq 1:

$$C_{av} = \frac{8V_0}{\pi^2} \cdot \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \frac{D_e}{(s_p+1-s_p)K_d \rho_s} \cdot \left( \frac{(2n+1)^2 \pi^2}{\theta^2} \right)$$  \hspace{1cm} \text{Eq 1}

where:

- $C_{av}$ = the average concentration of SP in the concrete plug (kmol/m$^3$ porewater)
- $V_0$ = the volume of the plug (m$^3$)
- $D_e$ = the effective diffusivity of SP in the concrete plug (m$^2$/s)
- $s_p$ = the porosity of the concrete plug (m$^3$/m$^3$)
- $K_d$ = distribution coefficient to represent a linear sorption isotherm (m$^3$/kg)
- $\rho_s$ = solid density of the concrete plug (kg/m$^3$)
- $t$ = time (years)
- $L$ = half-length of the plug (m)

The cumulative released amount is calculated from:

$$N_{released} = \varepsilon_p \cdot V_0 \cdot (C_0 - C_{av}) \hspace{1cm} \text{Eq 2}$$

where:

- $C_0$ = the initial concentration of SP in the concrete plug (kmol/m$^3$ porewater)
Figure 7-2 shows the cumulative amount of superplasticizer released over time for different Kd-values. The rate of diffusive release is obtained by differentiation of the cumulative release; Figure 7-3 shows the release rate over 100 000 years, while Figure 7-4 shows the results over the first 1000 years.

The results illustrate that if the Kd is zero, superplasticizer release is rapid and the plug is essentially depleted of superplasticizers within the first 5000 years. However, if sorption to the cement minerals is strong, a slow but consistent release of superplasticizers may continue over several tens of thousands of years. In all cases, the rate of release decreases by an order of magnitude over the first 50 years. The profiles shown for the higher Kd values are most representative for superplasticizer material that binds to the cement during cement hydration (see Section 3), while the very low Kd values are more representative of superplasticizer material that does not bind.

**Figure 7-2.** Cumulative amounts of superplasticizer released from the plug by diffusion over time for different Kd-values. 0-100 000 years.
Figure 7-3. Rate of release of superplasticizers from the plug by diffusion versus time for different Kd-values. 0-100 000 years.

Figure 7-4. Rate of release of SPs from the plug by diffusion versus time for different Kd-values. 0-1 000 years.

7.2 Adsorption models for superplasticizers in cement

In this section, different conceptual models are used to describe the adsorption of superplasticizers in cement. The Kd model, Langmuir and Freundlich sorption isotherms and a surface complexation model are used. The Langmuir, Freundlich and surface complexation model address competition from sulphate for surface sorption.
sites. The effects of hydrolysis and different pH-dependent reactions, and hypothetical weak-type and strong-type adsorption sites are also included in the surface complexation model.

In the calculations, the concrete porewater is initially equilibrated with the cement minerals, but any subsequent mineral reactions are disregarded. The porewater, including hypothetical adsorption sites, is then reacted with increasing amounts of sulphate to illustrate the competition for sorption sites in the concrete. The parameters applied in each model are, however, arbitrary and were selected purely to demonstrate the different concepts.

### 7.2.1 Linear isotherm – Kd-model

The Kd-model assumes that sufficient sorption sites are available for all species in the system and that there is a linear dependence between concentration in adsorbed phase and the concentration in the porewater. Figure 7-5 shows the Kd model, calculated in Phreeqc, with a constant dissolved superplasticizer concentration of 1 mM Sp_ns and varying sulphate concentration. The actual Kd values applied were selected arbitrarily, so it is the trends that are important. Since the concentration of Sp_ns is constant, the amount sorbed is also constant. The sulphate concentration, in contrast, gradually increases. This is accompanied by a steady increase in the amount of adsorbed sulphate.

![Figure 7-5](image)

**Figure 7-5.** Adsorption of superplasticizer and sulphate assuming a linear sorption isotherm (Kd-value) with no competition between the superplasticizer and sulphate for sorption sites. The sulphate concentration has been varied in the calculations.

The Kd-values for Sp_ns and sulphate do not vary as the sulphate concentration changes.

---

6 Sp_ns denotes a superplasticizer of naphtalene sulphonate type
7.2.2 Langmuir isotherm

The model for the Langmuir isotherm applied here considers competition between the superplasticizer and sulphate for adsorption sites. The competitive form of the Langmuir isotherm is given by Eq 3 and Eq 4:

\[
\theta_{SP} = \frac{K_{I,SP}[SP]}{1+K_{I,SP}[SP]+K_{I,SO_4}[SO_4]} \quad \text{Eq 3}
\]

\[
\theta_{SO_4} = \frac{K_{I,SO_4}[SO_4]}{1+K_{I,SP}[SP]+K_{I,SO_4}[SO_4]} \quad \text{Eq 4}
\]

where:
- \( \theta_{SP} \) = the fraction of the adsorption sites occupied by SP
- \( \theta_{SO_4} \) = the fraction of the adsorption sites occupied by sulphate
- \( K_I \) = the equilibrium constants for the adsorption reaction of SP and sulphate respectively
- \([\quad]\) = the concentration of SP and sulphate respectively

The adsorbed amount of SP and sulphate respectively is given by Eq 5 and Eq 6:

\[
A_{Adx,SP} = S_0 \cdot \theta_{SP} \quad \text{Eq 5}
\]

\[
A_{Adx,SO_4} = S_0 \cdot \theta_{SO_4} \quad \text{Eq 6}
\]

where:
- \( S_0 \) = the total concentration of adsorption sites

An example calculation of the competitive adsorption behaviour of Sp_ns and sulphate as described by the Langmuir isotherm is shown in Figure 7-6. This was calculated in Phreeqc using a constant concentration of 1 mM Sp_ns Phreeqc and arbitrary parameter values for the sorption isotherms. As the sulphate concentration increases, there is a gradual increase in adsorbed sulphate and the amount of adsorbed superplasticizer decreases. The Kd-values for Sp_ns and sulphate evaluated from the results are presented in Figure 7-7. The Kd-values vary with the sulphate concentration due to the competition for sorption sites.
**Figure 7-6.** Adsorption of superplasticizer and sulphate according to a Langmuir sorption isotherm that accounts for competition between the superplasticizer and sulphate for sorption sites. The sulphate concentration has been varied in the calculations. Note the logarithmic y-axis.

**Figure 7-7.** Kd-values of the superplasticizer and sulphate calculated from a Langmuir sorption isotherm that accounts for competition between the superplasticizer and sulphate for sorption sites.
7.2.3 Modified Freundlich isotherm

The Freundlich isotherm has been modified to account for the effects of competition for adsorption sites between SP and sulphate. The Freundlich isotherm has the general form according to Eq 7 and Eq 8:

\[ A_{\text{Ads},SP} = S_0 \cdot K_{1,SP}[SP]^n \]  
\[ A_{\text{Ads},SO_4} = S_0 \cdot K_{1,SO_4}[SO_4]^m \]

where:
\( A_{\text{Ads}} \) = adsorbed amount of SP and sulphate respectively
\( S_0 \) = the total concentration of adsorption sites
\( K_1 \) = the equilibrium constants for the adsorption reaction of SP and sulphate respectively
\([ \ )\] = the concentration of SP and sulphate respectively
\( n, m \) = empirical exponents

The results of example Phreeqc calculations, using arbitrary parameter values for the sorption isotherms, demonstrates the competitive adsorption between Sp_{ns} and sulphate. The calculated results are shown in Figure 7-8. The Kd-values for Sp_{ns} and sulphate evaluated from the results are presented in Figure 7-9. The Kd-values vary with the sulphate concentration due to the competition for sorption sites.

**Figure 7-8.** Adsorption of the superplasticizer and sulphate according to a modified Freundlich sorption isotherm that takes into account competition between the superplasticizer and sulphate for sorption sites. The sulphate concentration has been varied in the calculations which is shown by the slight gradual increase in adsorbed sulphate. A logarithmic concentration scale is used on the y-axis.
7.2.4 Adsorption by surface complexation

The surface complexation model applied here accounts for basic protolysis reactions of the surface complexes, adapting the principles presented by Dzombak and Morel (1990). The model also accounts for the competition between the superplasticizer and sulphate for adsorption sites, the effects of hydrolysis and different pH-dependent reactions. Both weak-type and strong-type adsorption sites have been included in the model. There is no thermodynamic data available to describe surface complexation of SP in cement system. However, a selection of hypothetical surface complexation species have been assembled in Table 7-1 as a basis for the demonstration of a model concept in Phreeqc.

The results of the Phreeqc calculations demonstrate competitive adsorption between Sp_ns and sulphate (Figure 7-10). Two predominant surface complexes are identified for the parameters selected in this example, m_Cal_wOHSp_ns^ and m_Cal_wOHSO_4^2, the gradual change in their relative abundance with increasing groundwater sulphate concentration illustrates the competition for adsorption sites. A more detailed presentation of the variation of the amount of the individual surface complexes at gradually increasing sulphate concentrations is presented in Figure 7-11. The Kd-values for Sp_ns and sulphate evaluated from the results are presented in Figure 7-12. The evaluated Kd-values vary with the sulphate concentration due to the competition for sorption sites.
<table>
<thead>
<tr>
<th>Species acronym</th>
<th>Reaction formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal_s</td>
<td>Cal_sOH</td>
<td>Surface master species, strong site</td>
</tr>
<tr>
<td>Cal_w</td>
<td>Cal_wOH</td>
<td>Surface master species, weak site</td>
</tr>
<tr>
<td>Cal_wO⁻</td>
<td>Cal_wOH = Cal_wO⁻ + H⁺</td>
<td>Surface protolysis, weak site</td>
</tr>
<tr>
<td>Cal_wOH₂⁺</td>
<td>Cal_wOH + H⁺ = Cal_wOH₂⁺</td>
<td>Surface protolysis, weak site</td>
</tr>
<tr>
<td>Cal_sO⁻</td>
<td>Cal_sOH = Cal_sO⁻ + H⁺</td>
<td>Surface protolysis, strong site</td>
</tr>
<tr>
<td>Cal_sOH₂⁺</td>
<td>Cal_sOH + H⁺ = Cal_sOH₂⁺</td>
<td>Surface protolysis, strong site</td>
</tr>
<tr>
<td>Cal_sSO₄⁻</td>
<td>Cal_sOH + H⁺ + SO₄⁻² = Cal_sSO₄⁻ + H₂O</td>
<td>Sulphate surface complex, strong site</td>
</tr>
<tr>
<td>Cal_wSO₄⁺</td>
<td>Cal_wOH + H⁺ + SO₄⁻² = Cal_wSO₄⁺ + H₂O</td>
<td>Sulphate surface complex, weak site</td>
</tr>
<tr>
<td>Cal_sOHSO₄⁻²</td>
<td>Cal_sOH + SO₄⁻² = Cal_sOHSO₄⁻²</td>
<td>Sulphate surface complex, strong site</td>
</tr>
<tr>
<td>Cal_wOHSO₄⁻²</td>
<td>Cal_wOH + SO₄⁻² = Cal_wOHSO₄⁻²</td>
<td>Sulphate surface complex, weak site</td>
</tr>
<tr>
<td>Cal_sSp_ns</td>
<td>Cal_sOH + H⁺ + Sp_ns⁻ = Cal_sSp_ns⁻ + H₂O</td>
<td>Naphtalene sulphonate SP surface complex, strong site</td>
</tr>
<tr>
<td>Cal_wSp ns</td>
<td>Cal_wOH + H⁺ + Sp ns⁻ = Cal_wSp ns⁻ + H₂O</td>
<td>Naphtalene sulphonate SP surface complex, weak site</td>
</tr>
<tr>
<td>Cal_sOHSp_ns⁻²</td>
<td>Cal_sOH + Sp_ns⁻ = Cal_sOHSp_ns⁻²</td>
<td>Naphtalene sulphonate SP surface complex, strong site</td>
</tr>
<tr>
<td>Cal_wOHSp ns⁻²</td>
<td>Cal_wOH + Sp ns⁻ = Cal_wOHSp ns⁻²</td>
<td>Naphtalene sulphonate SP surface complex, weak site</td>
</tr>
<tr>
<td>Cal_sSp_pc</td>
<td>Cal_sOH + H⁺ + Sp_pc⁻ = Cal_sSp_pc⁻ + H₂O</td>
<td>Polycarboxylate SP surface complex, strong site</td>
</tr>
<tr>
<td>Cal_wSp pc</td>
<td>Cal_wOH + H⁺ + Sp_pc⁻ = Cal_wSp_pc⁻ + H₂O</td>
<td>Polycarboxylate SP surface complex, weak site</td>
</tr>
<tr>
<td>Cal_sOHSp pc⁻²</td>
<td>Cal_sOH + Sp_pc⁻ = Cal_sOHSp pc⁻²</td>
<td>Polycarboxylate SP surface complex, strong site</td>
</tr>
<tr>
<td>Cal_wOHSp pc⁻²</td>
<td>Cal_wOH + Sp_pc⁻ = Cal_wOHSp pc⁻²</td>
<td>Polycarboxylate SP surface complex, weak site</td>
</tr>
</tbody>
</table>

Cal denotes Calcium aluminate hydrate surface sites
_s is a strong-type surface site
_w is a weak-type surface site
O, OH, H refer to element symbols
Sp_ns is a functional unit group of sulphonate in the naphtalene sulphonate superplastiziser
Sp_pc is a functional unit group of carbonate in the polycarboxylate superplastiizer
Figure 7-10. Adsorption of a superplasticizer and sulphate according to a surface complexation model that takes into account the competition between the superplasticizer and sulphate for sorption sites. The sulphate concentration has been varied in the calculations. A linear concentration scale is used on the y-axis.
Figure 7-11. Distribution of the superplasticizer and sulphate between different surface species in the surface complexation model that takes into account the competition between the superplasticizer and sulphate for sorption sites. The sulphate concentration has been increased in 20 steps in the calculations. A logarithmic scale is used on the y axis.

Figure 7-12. Kd-values for the superplasticizer and sulphate calculated using a surface complexation model that considers the competition between the superplasticizer and sulphate for sorption sites. The sulphate concentration has been varied in the calculations.
7.3 Combined intercalation and adsorption of SPs in cement

7.3.1 Introduction

Practical experience and results from experimental investigations (Chapter 2), show that superplasticizers may interact with the hydrating cement minerals. If superplasticizers are mixed with the cement at an early stage of the hydration they may form solid precipitates, known as organo-mineral phases (OMP) or intercalates. This leads to a high consumption of superplasticizers to obtain the desired flow properties of the concrete. The OMPs are primarily formed by reaction of superplasticizers with calcium aluminate hydrates, such as $C_3A H_6$. The OMPs formed by reaction with superplasticizers containing sulphonate groups show similarities with the corresponding reaction products formed with sulphate, in particular $AF_m$ phases ($AF_m = C_4A(F)CaSO_4H_{12}$) such as monosulphate, $C_4ACaSO_4H_{12}$ and $AF_t$ phases such as ettringite.

To overcome the high consumption of superplasticizers it is common to add the superplasticizers to the ready-mixed concrete. This has the advantage that the rapid early hydration of calcium aluminates has already taken place to some extent, including reaction of the formed calcium aluminate hydrates with sulphate in the cement. Thus, the uptake of SPs in the calcium aluminate hydrates is hindered by sulphate that has reacted to form solid monosulphate (or the more sulphate-rich mineral ettringite).

It has also been observed that superplasticizers are released during the continued cement hydration, particularly if the concrete is exposed to sulphate in elevated concentrations. This leads to a conceptual model that OMPs form if allowed to react with the calcium aluminates, but may be outcompeted by sulphate if present in sufficient concentrations. This hypothesis has been tested in a geochemical model where a thermodynamic database has been set up that consider the possibility to form OMPs that resemble the basic structures of $AF_m$ and $AF_t$ that are formed by reaction with sulphate or carbonate (only relevant for the polycarboxylate-type superplasticizers). The assumed reactions are presented in Table 7-2. An illustration to the arrangement of intercalated superplasticizers in the layered structure of calcium aluminate hydrates is shown in Figure 7-13.
Figure 7-13. Illustration to a conceptual model for intercalation of a naphthalene sulphonate type SP in the principal layers of calcium aluminate hydrate (from Flatt & Houst 2001).
Table 7-2. Hypothetical organo-mineral phases (OMP) formed by reaction between superplasticizers and calcium aluminate hydrates in the cement. OMPs are assumed to be analogous to the AFm and/or AFt minerals formed by reaction of calcium aluminates with sulphate or carbonate.

<table>
<thead>
<tr>
<th>Species acronym</th>
<th>Molar mass of functional unit (g/mol) / Reaction formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp_ns</td>
<td>220 (\text{Ca}_6\text{Al}_2(\text{Sp}_n)<em>3(\text{OH})</em>{12}:26\text{H}_2\text{O} \leftrightarrow 6 \text{Ca}^{2+} + 2 \text{Al}^{3+} - 12 \text{H}^+ + 6 \text{Sp}_m \text{s}^{-1} + 38 \text{H}_2\text{O})</td>
<td>Superplasticizer based on Naphthalene-sulphonate</td>
</tr>
<tr>
<td>Sp_pc</td>
<td>1350 (\text{Ca}_4\text{Al}_2(\text{Sp}_p)<em>2(\text{OH})</em>{12}:6\text{H}_2\text{O} \leftrightarrow 4 \text{Ca}^{2+} + 2 \text{Al}^{3+} - 12 \text{H}^+ + 2 \text{Sp}_m \text{s}^{-1} + 18 \text{H}_2\text{O})</td>
<td>Superplasticizer based on Polycarboxylate</td>
</tr>
<tr>
<td>Sp_pc_Ettringite</td>
<td>(\text{Ca}_6\text{Al}_2(\text{Sp}_p)<em>3(\text{OH})</em>{12}:26\text{H}_2\text{O} \leftrightarrow 6 \text{Ca}^{2+} + 2 \text{Al}^{3+} - 12 \text{H}^+ + 6 \text{Sp}_m \text{s}^{-1} + 38 \text{H}_2\text{O})</td>
<td>OMP Sp_ns, analogue to ettringite</td>
</tr>
<tr>
<td>Sp_ns_Monosulfoaluminate</td>
<td>(\text{Ca}_4\text{Al}_2(\text{Sp}_n)<em>2(\text{OH})</em>{12}:6\text{H}_2\text{O} \leftrightarrow 4 \text{Ca}^{2+} + 2 \text{Al}^{3+} - 12 \text{H}^+ + 2 \text{Sp}_m \text{s}^{-1} + 18 \text{H}_2\text{O})</td>
<td>OMP Sp_ns, analogue to monosulphate</td>
</tr>
<tr>
<td>Sp_pc_Monosulfoaluminate</td>
<td>(\text{Ca}_6\text{Al}_2(\text{Sp}_p)<em>3(\text{OH})</em>{12}:26\text{H}_2\text{O} \leftrightarrow 6 \text{Ca}^{2+} + 2 \text{Al}^{3+} - 12 \text{H}^+ + 6 \text{Sp}_m \text{s}^{-1} + 38 \text{H}_2\text{O})</td>
<td>OMP Sp_pc, analogue to ettringite</td>
</tr>
<tr>
<td>Sp_pc_Monocarboaluminate</td>
<td>(\text{Ca}_4\text{Al}_2\text{O}_3(\text{Sp}_p)<em>2(\text{OH})</em>{12}:21\text{H}_2\text{O} \leftrightarrow 8 \text{Ca}^{2+} + 4 \text{Al}^{3+} - 26 \text{H}^+ + 2 \text{Sp}_p \text{c}^{-1} + 35 \text{H}_2\text{O})</td>
<td>OMP Sp_pc, analogue to monocarboaluminate</td>
</tr>
</tbody>
</table>

8 Sp denotes superplasticizer
 _ns is a functions unit group in naphthalene-sulphonate
 _pc is a functions unit group in polycarboxylate
 _Ettringite refers to an OMP with a structure analogous to ettringite
 _Monosulfoaluminate refers to an OMP with a structure analogous to monosulphoaluminate
 _Hemicarboaluminate refers to an OMP with a structure analogous to hemicarboaluminate
 _Monocarboaluminate refers to an OMP with a structure analogous to monocarboaluminate

9 It has been assumed that the polycarboxylate superplasticizer contains a small amount of sulphonate groups originating from a naphtalene sulphonate copolymer
7.3.2 Combined intercalation and surface complexation – mixing with Olkiluoto Brackish SO4 groundwater

Model Phreeqc calculations are presented in this sub-section for the combined reactions of first PNS and then PCE superplasticizers with groundwater. The superplasticizers are assumed to have formed OMPs with calcium aluminate hydrates (with similar structures to ettringite) and surface complexes. The calculations add 270 mM superplasticizer to a concrete porewater and the porewater is then re-equilibrated with the added superplasticizer and an assembly of cement minerals (portlandite, CSH-gel, ettringite etc) and surface complexation sites. The system is then reacted with groundwater (Olkiluoto Brackish_SO4 groundwater OL-KR6_135_8) in 100 sequential steps where the porewater is exchanged in each step. In each step the system is equilibrated with the cement minerals, OMPs and with the surface complexation sites.

The 270 mM concentration of superplasticizer was selected to be generally representative of PNS superplasticizer concentrations in concretes and grouts (equivalent to 59 kg/m³). The higher molar mass of the repeat unit in the PC superplasticizer considered (Table 7-2) results in a higher mass concentration than typically used (360 kg/m³ vs 6 kg/m³). However, the modelling is used to show the main trends rather than exact values. The DOC concentrations in the porewater are estimated in Section 8.2.

7.3.2.1 Intercalation and surface complexation – Naphthalene sulphonate SP

The results presented in Figure 7-14 show an intricate interaction between the different cement components, the Sp_ns and the groundwater. The first event is an early depletion of monocarboaluminate after ~13 porewater exchange steps, followed by ingrowth of thaumasite. During this transition the concentration of dissolved Sp_ns increases reaching a plateau value of about $5.1 \times 10^{-3}$ mol/kg w. During this phase the model predicts the presence of an OMP (Sp_ns_Ettringite). For as long as the OMP exists in the system, the amount of adsorbed Sp_ns remains constant, which is in line with expectation of sorption saturation. Once the OMP becomes depleted after ~60 porewater exchange steps, the adsorbed Sp_ns is gradually replaced by adsorbed sulphate. This is also accompanied by a gradually decreasing concentration of dissolved superplasticizer.

The distribution of Sp_ns between its dissolved, adsorbed and intercalated forms is shown in Figure 7-15 together with the total amount of Sp_ns in the system for the different porewater exchange steps.
**Figure 7-14.** Model results for the combined formation of intercalated (OMPs) minerals between Sp_ns and calcium aluminate hydrates and competitive sorption of Sp_ns by surface complexation. The results show the gradual progression of 100 porewater exchange cycles with groundwater. Equilibration between groundwater, cement minerals, OMPs and surface complexes takes place in each reaction step.

**Figure 7-15.** Model results showing the distribution of Sp_ns between dissolved, adsorbed and intercalated forms during 100 porewater exchange cycles with groundwater. The total amount of Sp_ns in the system is also shown.
7.3.2.2 Intercalation and surface complexation – Polycarboxylate SP

The results presented in Figure 7-16 show an intricate interaction between the different cement components, the PCE superplasticizer (Sp_pc) and the groundwater. The first event is an early depletion of Sp_pc_monocarboaluminate after ~23 porewater exchange steps. Then SP_pc_Ettringite is replaced by Sp_pc_Monosulphate-Fe during a period of ~3 reaction steps, followed by a rapid ingrowth of thaumasite which marks the end of OMPs in the system. During this transition the concentration of dissolved Sp_pc is slightly increased reaching a maximum value of about $1.2 \times 10^{-2}$ mol/kg w. For as long as the OMPs exists in the system, the amount of adsorbed Sp_pc remains invariant, which is in line with expectation of sorption saturation. Once the OMP becomes depleted after ~27 porewater exchange steps, the adsorbed Sp_pc is gradually replaced by adsorbed sulphate. This is also accompanied by a gradually decreasing concentration of Sp in dissolved form.

The distribution of Sp_pc between dissolved, adsorbed and intercalated form is show in Figure 7-17 together with the total amount of Sp_pc in the system for the different porewater exchange steps.

![Figure 7-16. Model results for the combined formation of intercalated (OMPs) minerals between Sp_pc and calcium aluminate hydrates and competitive sorption of Sp_pc by surface complexation. The results show the gradual progression of 100 porewater exchange cycles with groundwater. Equilibration between groundwater, cement minerals, OMPs and surface complexes takes place in each reaction step.](image-url)
Figure 7-17. Model results showing the distribution of Sp_ns between dissolved, adsorbed and intercalated forms during 100 porewater exchange cycles with groundwater. The total amount of Sp_ns in the system is also shown.
8 ANALYSIS OF THE INFORMATION

In this chapter, relevant cement and concrete recipes are used to estimate concentrations of DOC and sulphonates from superplasticizers in the initial cement porewater, and following porewater exchange. Information is also gathered to provide background concentrations of DOC and sulphate in Olkiluoto groundwater. The estimated concentrations and the information from the literature review are then used to answer the questions posed in Section 1.5.

8.1 Background information and assumptions

8.1.1 Assumptions relating to the superplasticizer structures

Table 8-1 Assumptions relating to the superplasticizer structures. PCE vary extensively in terms of the frequency and length of polyethylene ether groups. Here, we assume that each PEG side chain has 23 units (MW 1000), and there is a 1:3 ratio between reacted and unreacted carboxylic acid groups in a metacrylate backbone. The PEG groups represent 74% of the mass of the structure.

Table 8-1. Assumptions relating to the superplasticizer structures

<table>
<thead>
<tr>
<th></th>
<th>PNS</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMM of the repeat unit</td>
<td>220</td>
<td>85</td>
</tr>
<tr>
<td>%C by mass</td>
<td>60</td>
<td>56</td>
</tr>
<tr>
<td>% SP in commercial product</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>g commercial product/mol SP repeat unit</td>
<td>440</td>
<td>243</td>
</tr>
</tbody>
</table>

8.1.2 Assumptions relating to degradation

Alkaline hydrolysis of PCE superplasticizers is not expected to be hindered when PCE are bound to cement particles, as the carboxylate ester groups are not expected to interact directly with the particles. Therefore, it is assumed that the carboxylate ester groups in the PCE can undergo hydrolysis releasing PEG from the polymer backbone relatively quickly, i.e. in the operational or resaturation phase of the repository. PEG is assumed to remain in solution, rather than sorb. The degradation of PEG is expected to be a biodegradation process, and so will be sensitive to the pH conditions in the cement. Equally, biodegradation of the smaller molecules of both PNS and PCE superplasticizer products (Table 4-1) that remain preferentially in the porewater during cement hydration will be dependent on biologically-viable conditions.
The polymeric polycarboxylate backbone and the PNS polymer are expected to remain bound to the cement to a large extent and biodegradation of the bound polymers is expected to be negligible. Slow desorption will release these polymers from the cement, but even at this point chain scission reactions are required prior to biodegradation, and this is likely to be a very slow process if it happens at all. Following chain scission, the monomers, dimers and oligomers are considered to be biodegradable. Once biodegradation becomes viable, for example in the groundwater surrounding the cement, the biodegradation of the smaller units is expected to be faster than larger units. Therefore, the molecules produced during biodegradation of the larger molecules will have relatively short residence times due to their faster rate of degradation than formation.

8.1.3 Cements and concretes considered

The cementitious materials considered here are Posiva’s rock bolt mortar (low pH) and ternary and binary low pH concretes, and SKB’s B200 concrete mix for the dome plug and rock bolt grout. All of these are intended for use in spent fuel repositories. Posiva currently intends to use Pantarhit LK (FM) naphthalene sulphonate superplasticizer, while SKB intends to use the PCE superplasticizer Glenium 51. The components of these cementitious materials are given in Table 8-2 and Table 8-3.

Table 8-2. Components of some of Posiva’s potential concretes and mortar

<table>
<thead>
<tr>
<th>Component</th>
<th>Ternary concrete mix (Holt et al. 2014)</th>
<th>Binary concrete mix (Holt et al. 2014)</th>
<th>Rock bolt mortar (low pH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 42,5 MH/SR/LA (kg/m³)</td>
<td>105</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>CEM I 42,5 N – SR 3 (kg/m³)</td>
<td></td>
<td>402</td>
<td></td>
</tr>
<tr>
<td>Silica (kg/m³)</td>
<td>91</td>
<td>80</td>
<td>553 including water in the silica slurry</td>
</tr>
<tr>
<td>Fly ash (kg/m³)</td>
<td>84</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Quartz (kg/m³) filler</td>
<td>114</td>
<td>256</td>
<td>1186</td>
</tr>
<tr>
<td>Local aggregate (kg/m³)</td>
<td>1840</td>
<td>1805</td>
<td></td>
</tr>
<tr>
<td>Effective water content (kg/m³)</td>
<td>126</td>
<td>125</td>
<td>29+ water from silica slurry</td>
</tr>
<tr>
<td>Water/binder–ratio (-)</td>
<td>0.45</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Pantarhit LK (FM) superplasticizer</td>
<td>4.5 – 7.5 % by binder content (13 – 21 kg/m³)</td>
<td>4.5 – 7.5 % by binder content (9 – 15 kg/m³)</td>
<td>22 kg/m³</td>
</tr>
</tbody>
</table>
Table 8-3. Components of some of SKB’s cementitious materials for their spent fuel repository

<table>
<thead>
<tr>
<th>Component</th>
<th>B200 concrete mix for dome plug (Grahm and Malm 2014)</th>
<th>Rock bolt support grout (Hallbeck 2010)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 42.5 (Cementa) (kg/m³)</td>
<td>120</td>
<td>340</td>
</tr>
<tr>
<td>Silica* (kg/m³)</td>
<td>80</td>
<td>227</td>
</tr>
<tr>
<td>Water (kg/m³)</td>
<td>165</td>
<td>267</td>
</tr>
<tr>
<td>Limestone filler Limus 25 (kg/m³)</td>
<td>369</td>
<td></td>
</tr>
<tr>
<td>Sand 0-8 mm (kg/m³)</td>
<td>1037</td>
<td></td>
</tr>
<tr>
<td>Gravel 8-16 mm (kg/m³)</td>
<td>558</td>
<td></td>
</tr>
<tr>
<td>Quartz filler</td>
<td>1324</td>
<td></td>
</tr>
<tr>
<td>Glenium 51 PCE superplasticizer (kg/m³)</td>
<td>6.4</td>
<td>4</td>
</tr>
</tbody>
</table>

*Dispersed – assumed to be 50% water

8.1.4 Groundwater

After repository closure, saline groundwater will resaturate the repository and enter the pores of the concrete. The influx of water will enhance outward transport of the dissolved superplasticizer components, by diffusion and/or advection. Advection is likely to be more important for shotcrete and grout in this time period than for the plugs.

The groundwater at Olkiluoto has been investigated by Pedersen et al. (2008). The DOC concentration between 4-742 m depth has been found to be between 1.8 and 39 mg/L (0.15 – 3.3 mM), and to show no correlation with depth. There was a correlation between DOC and total cell counts, as expected. Sulphur cycling was most active at a depth of 300 m, ~100 m above the depth of the spent fuel repository. The microbial population was also abundant at this depth. The sulphate concentration of the water at 400-450 m depth ranged from very low concentrations up to ~200 mg L⁻¹, or about 2 mM. The water at the depth of the L/ILW repository and at depths that may flow into the spent fuel repository during the resaturation phase has higher maximum sulphate concentrations (~5 mM).

8.2 Estimated concentrations of DOC and sulphate

8.2.1 DOC in the porewater

The organic compounds in the porewater of the cementitious materials will initially include:

- Cement grinding agents (e.g. Yamamoto et al. 2008, Wieland et al. 2014)
- Solution phase superplasticizers
- Smaller molecular components of the superplasticizer product
Cement grinding agents are used at around 50 - 200 g per tonne cement. Wieland et al. (2014) determined DOC concentrations of ~15 mM in OPC and ~8 mM in low pH cement porewater arising from grinding agents. This is a useful baseline for consideration of the additional organic carbon from the superplasticizers.

Table 8-4 shows the stepwise estimation of DOC concentrations in the initial porewater arising from superplasticizer products used in the cements and concretes described in Table 8-2 and Table 8-3. The chemical components of the superplasticizers are as described in Table 8-1. It is assumed that 90 % of the organic matter of the PCE superplasticizer and 98 % of the PNS sorbs during cement hydration, following the results of Wieland et al. (2014) for a low pH cement (ESDRED). Recalculating the fresh cement DOC values in Yamamoto et al. (2008) suggests that ~96% of the PCE TOC and ~98.5% of the PNS TOC sorbed, which is in reasonable agreement with Wieland et al. (2014). The initial DOC porewater concentrations from the superplasticizer products (Table 8-4) are found to be fairly similar for the two different superplasticizers in low pH cement and concrete, and to those determined in Wieland et al. (2014). For PCE superplasticizers, the initial DOC porewater concentration may be much higher than this because of the hydrolysis reactions that could release PEG into solution. PEG comprises 74% of the PCE superplasticizer considered in this analysis. The DOC concentrations in the initial porewater if all PEG is released are given in brackets.

The initial DOC concentration will decrease due to advection and diffusion of the superplasticizer components that are in the solution phase. Section 7.1 showed that the amount of the initial DOC released via diffusion from even large structures such as the plug will decrease by an order of magnitude over the first 50 years.

After the initial porewater has been replaced or the DOC diffused out, a lower concentration of superplasticizer is expected in the porewater due to leaching. In Table 8-4, it is estimated that 0.1% of the amount of superplasticizer remaining in the cement desorbs. The same value is used for both PCE and PNS, since the greater amount of PNS leached than PCE in Yamamoto et al. (2008) was thought to reflect the greater amount used to make the cement. Therefore, it is assumed that the leachability is similar. 0.1% was selected as about 80 mg of the PNS superplasticizer used in Yamamoto et al. (2008) remained in the porewater of the fresh grout, while about 310 mg PNS was present in the solution phase at L/S 10 in the powder leach tests. The PNS results suggest that ~230 mg of the PNS leached into L/S 10, or 23 mg/L. If the porewater is 20% of the volume of the cement, this relates to the release of 4.6 mg of PNS per porewater exchange, or ~0.1% of the PNS in the concrete.

The estimated longer term DOC concentrations are similar to the background concentrations in the groundwater. For PCE, early hydrolytic release of the PEG side chains into the initial cement porewater would lead to lower longer term DOC concentrations.

---

10 5.5 g dm⁻³ PNS or 2.14 g dm⁻³ PCE in the grout paste. Fresh grout leached with L/S = 4; 20 mg dm⁻³ of PNS and PCE in solution, i.e. 80 mg dm⁻³ grout paste.
Table 8-4. Stepwise evaluation of the DOC and sulphate concentrations in the initial and longer term porewater of selected Posiva and SKB low pH concretes and grouts. The amount remaining in the initial porewater is based on sorption to ESDRED low pH cement in Wieland et al. (2014)

<table>
<thead>
<tr>
<th></th>
<th>Posiva’s rock bolt mortar (low pH)</th>
<th>SKB’s rock bolt support grout</th>
<th>Posiva’s Ternary concrete</th>
<th>Posiva’s Binary concrete</th>
<th>SKB’s B200 concrete mix for dome plug</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP</td>
<td>Pantarhit LK (FM)</td>
<td>Glenium 51</td>
<td>Pantarhit LK (FM)</td>
<td>Pantarhit LK (FM)</td>
<td>Glenium 51</td>
</tr>
<tr>
<td>Assumed porosity</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Assumed density</td>
<td>2200</td>
<td>2200</td>
<td>2400</td>
<td>2400</td>
<td>2350</td>
</tr>
<tr>
<td>(kg/m³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SP in cement (kg/m³)</td>
<td>22</td>
<td>4</td>
<td>21</td>
<td>15</td>
<td>6.4</td>
</tr>
<tr>
<td>% SP in SP product</td>
<td>40</td>
<td>35</td>
<td>40</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>SP concentration - all SP in the porewater (g/L)</td>
<td>44</td>
<td>7</td>
<td>84</td>
<td>60</td>
<td>22.4</td>
</tr>
<tr>
<td>DOC concentration - all SP in the porewater (g/L)</td>
<td>26.4</td>
<td>3.9</td>
<td>50.4</td>
<td>36</td>
<td>12.3</td>
</tr>
<tr>
<td>Sulphonate if all SP is in the porewater (g/L)</td>
<td>15.8</td>
<td>0.0</td>
<td>30.2</td>
<td>21.6</td>
<td>0.0</td>
</tr>
<tr>
<td>Assumed initial SP sorption (%)</td>
<td>98</td>
<td>90</td>
<td>98</td>
<td>98</td>
<td>90</td>
</tr>
<tr>
<td>DOC in porewater from SP (g/L) initial</td>
<td>0.53</td>
<td>0.39 (or 3.0 considering PEG release)</td>
<td>1.01</td>
<td>0.72</td>
<td>1.23 (or 9.3 considering PEG release)</td>
</tr>
<tr>
<td>DOC in porewater from SP (mM) initial</td>
<td>44</td>
<td>32 (250 considering PEG release)</td>
<td>84</td>
<td>60</td>
<td>103 (780 considering PEG release)</td>
</tr>
<tr>
<td>Sulphonate in porewater (mM) initial</td>
<td>3.96</td>
<td>0</td>
<td>7.56</td>
<td>5.4</td>
<td>0</td>
</tr>
<tr>
<td>DOC in porewater from SP (mM) longer term</td>
<td>2.16</td>
<td>0.29 (0.075 considering PEG release)</td>
<td>4.12</td>
<td>2.94</td>
<td>0.92 (0.24 considering PEG release)</td>
</tr>
<tr>
<td>Sulphonate in porewater (mM) longer term</td>
<td>0.19</td>
<td>0.00</td>
<td>0.37</td>
<td>0.26</td>
<td>0.00</td>
</tr>
</tbody>
</table>
8.2.2 Sulphate added via PNS

The amounts of sulphate and sulphonate in Posiva’s low pH cement recipes are shown in Table 8-5. The calculations assume that Pantarhit LK (FM) contains the active ingredient at a concentration of 40%, and 36% of the PNS is sulphonate. The maximum amount of sulphate in the cement is assumed to be 3%, based on Cementa’s CEM I 42,5 SR3 MH//LA cement. The superplasticizers comprise a larger proportion of the sulphur species in the concretes than the rock bolt mortar.

Table 8-4 suggests that with 2% of the PNS remaining in the initial porewater of the Posiva rock bolt mortar and concretes, the sulphonate concentration would be between 4-8 mM. Wieland et al (2014) measured total S concentration in cement porewaters, and they were about 3 mM higher for cements prepared with PNS than with PCE after 1310 days, which is quite consistent with the values in Table 8-4. OPC prepared with PCE also had a higher porewater sulphate concentration after 1310 days than OPC prepared without superplasticizer. The difference here was about 1 mM; an equivalent comparison was not carried out for the low alkali and low pH cements. Therefore, competition for binding sites may also increase the porewater sulphate concentration, even when the superplasticizer does not contain sulphonate groups.

Table 8-5. Sulphate and sulphonate in Posiva’s concrete and rock bolt mortar

<table>
<thead>
<tr>
<th></th>
<th>Ternary concrete mix (Holt et al. 2014)</th>
<th>Binary concrete mix (Holt et al. 2014)</th>
<th>Rock bolt mortar (low pH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 42,5 MH/SR/LA (kg/m³)</td>
<td>105</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>CEM I 42,5 N – SR 3 (kg/m³)</td>
<td></td>
<td></td>
<td>402</td>
</tr>
<tr>
<td>Maximum sulphate from cement (kg/m³)</td>
<td>3.2</td>
<td>3.6</td>
<td>12</td>
</tr>
<tr>
<td>Pantarhit LK (FM) superplasticizer (kg/m³)</td>
<td>13 – 21</td>
<td>9 – 15</td>
<td>22</td>
</tr>
<tr>
<td>Maximum sulphonate from Pantarhit LK (FM) (kg/m³)</td>
<td>3.0</td>
<td>2.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

8.2.3 Superplasticizer release processes

Superplasticizer release processes have been explored using a conceptual model in Chapter 7. The model demonstrates that there are variations in the dissolved superplasticizer concentration as the porewater exchanges with the brackish groundwater over time. An increase is observed in the transition period between the depletion of monocarboaluminate and ingrowth of thaumasite, as the monocarboaluminate is assigned sorption capacity in the model and thaumasite is not. However, the increase is not very significant in terms of the large uncertainties in estimating the porewater concentration. A rapid decrease in the superplasticizer concentration in the porewater occurs once the superplasticizer-ettringite, or superplasticizer-iron monosulfate, phase...
has disappeared from the system. Although the amount of organic mineral phase dictates the length of the higher porewater concentration, the amount of adsorbed superplasticizer controls the long term release of lower concentrations of superplasticizer.

### 8.3 Analysis

The questions relating to the risks of using superplasticizers (Section 1.5 answered below.

- Do the organics leach out of the cement paste or not?

A significant amount of superplasticizer material remains in the cement porewater during cement hydration. This and PEG released from hydrolysis of the PCE sidechains lead to high initial DOC porewater concentrations. Experimental data suggest that the initial porewater contains the highest concentrations of organic carbon from the superplasticizer. The long term leaching of the superplasticizer that binds to the cement during hydration is much more limited and is expected to occur slowly.

- How much organic material leaches and when?

The organic carbon concentration in the initial cement and concrete porewaters is expected to be 30 – 100 mM DOC for both PCE and PNS superplasticizers. However, relatively rapid hydrolysis of the PCE sidechains in the context of a repository could lead to a higher DOC concentration, of about 250 – 800 mM. All of these DOC concentrations are in excess of the background DOC concentration in the groundwater.

The high DOC concentrations from superplasticizers will persist for a period that depends on the outward transport of the dissolved species and/or the rate of exchange of the cement porewater. This can vary considerably, but will be slowest during diffusion-controlled transport from the largest structures with low porosity, such as the plugs. Calculations show that the amount released from the plugs will decrease by an order of magnitude over 50 years, therefore the high DOC concentrations will be released from the concrete early in the post resaturation phase, if not before.

After the loss of this material, the porewater concentration will be controlled by any superplasticizer intercalated in organic mineral phases. A very small proportion of the superplasticizer may be in this fraction, especially for PCE and PNS that are added to ready-mixed concrete. The superplasticizers will exchange out of the organic mineral phases due to sulphate ions present in the brackish groundwater. As PCE superplasticizers are less strongly associated with these phases, the proportion desorbed in each porewater exchange is higher, and the phases are depleted after fewer porewater exchanges, compared to PNS. Once the organic mineral phases have been depleted, the surface complexation equilibrium between the adsorbed and solution phase superplasticizer and sulphate concentrations will be the controlling factor.
After the initial porewater DOC has been removed from the pore volume, the DOC concentrations from superplasticizers will similar to those from natural DOC in the groundwater. These concentrations will decrease slowly over time.

- What kind of organic degradation products are formed?

Experiments have identified the presence of smaller molecular units in solution, either from the reagents remaining in the superplasticizer products or from degradation. As the smaller units sorb to a lesser extent than the polymeric backbones of the superplasticizers, the initial porewater concentration is dominated by these. Alkaline hydrolysis of the carboxylate ether groups in PCE superplasticizers could lead to the release of high concentrations of PEG. Under biologically-viable conditions, PEG will be biodegraded, producing smaller PEG units.

Scission of the polymeric backbones of the superplasticizers is expected to be a very slow process. This needs to occur before subsequent degradation processes can occur. Biodegradation appears to be important for degradation of oligomers, dimers and smaller species and is expected to lead to the formation of the species shown in Table 4-1. The concentration of these species depends on their residence time in the system with respect to formation and degradation. Biodegradation is unlikely in OPC and is likely to be highly restricted in low pH cement porewater, which still has an initial pH of 11. Therefore, biodegradation is expected to occur to a large extent outside the concrete or cement pores.

- Do the organics leached affect radionuclide solubility or sorption?

It is clear that superplasticizers can affect radionuclide solubility, and may have an effect that is comparable to strong complexing agents such as EDTA and citrate (see Section 5.2). The majority of experiments investigating the influence of superplasticizers on radionuclide sorption have focussed on cement. The general picture is that radionuclide sorption is reduced when superplasticizers and radionuclides are mixed with HCP, i.e. when the solution-phase concentration of the superplasticizer is much higher than expected in an actual cement porewater. However, when the results have been extrapolated to conditions in a real cement, an effect is thought to be unlikely. It is not, however, always clear that the extrapolation applied is valid.

In a spent fuel repository, cement is not used as a sorption matrix to limit radionuclide transport. Therefore, the effect of the superplasticizers on radionuclide sorption is most relevant once they have been transported out of the cement pores, where they may influence radionuclide sorption to rock or bentonite. Andersson et al. (2008) reported a possible influence of PCE on Eu(III) sorption to granite at a DOC concentration of 1.7 mM. However, the effect of the experimental regime on the results was not fully understood and so the results are not entirely conclusive. The estimated DOC concentrations in the cement porewater from PCE in the longer term, assuming no hydrolytic release of PEG, were 0.3 - 1 mM (Table 8-4), thus the effect may be expected to be limited, especially at a time and location where the superplasticizers would be expected to come into contact with radionuclides.
• Do the superplasticizers sorb to other components of the repository?

Bentonite has been seen to have a high sorption capacity for superplasticizers. Bentonite is used extensively in spent fuel repositories as a backfill and so is likely to reduce the superplasticizer concentrations in the water.

• Do the superplasticizers affect cement mineralogy, strength and/or degradation?

The main influences of superplasticizers on cement are positive, resulting in lower porosity and greater strength (e.g. El-Didamony et al. 2013). Uptake of superplasticizers into hydrating cement phases can, however, lead to their incorporation into organic minerals phases. This is particularly relevant for PNS, due to the sulphonate groups. As this process has negative effects on the ability of the superplasticizer to carry out its function, it is not clear that extensive organo-mineral phase formation is likely in the optimised grout and concrete recipes. Wieland et al. (2014) showed that PCE and PNS superplasticizers did not affect the kind and amount of hydration products formed after 28 days of hydration, within the sensitivity of XRD, and Lothenbach et al (2007) showed a similar result for PCE superplasticizer. These studies suggest that the use of superplasticizers does not affect the physical properties of cement.

Furthermore, superplasticizers have not been seen to have a significant effect on cement porewater chemistry, suggesting that they will not accelerate cement degradation significantly.

• Could the organic material stimulate microbial activity, particularly sulphate-reduction to sulphide?

Both types of superplasticizer may stimulate microbial activity in the post-closure period of the repository. They contribute a significant amount of DOC to the initial cement porewater, and this DOC is expected to be dominated by smaller, biodegradable units. PEG released by the abiotic alkaline hydrolysis of PCE superplasticizers is also likely to be of a length that has been seen to be biodegraded. Therefore, the early flux of DOC from the use of superplasticizers is likely to consist of biodegradable material. The factor limiting its biodegradation is the pH of the cement porewater, thus microbial stimulation may be most likely once it has been transported out of the cement pores.

Hallbeck (2010) suggested that monomers of cement additives will be degraded within 100 years of closure. This early period has relatively favourable conditions for biodegradation from being open during the operational phase and the influx of groundwater during re-saturation. In any case, this initial flux of DOC is expected to stimulate microbial activity in the early period, which is of little concern for the repository.

In the longer term, the superplasticizers will continue to make a lesser but significant contribution to the DOC concentration. The PC backbone of the PCE superplasticizer and the PNS polymer are expected to be relatively stable and both their release from the cement particles and chain scission are expected to be slow. If bacteria are present that
release polymerase enzymes, degradation could be accelerated. Chain scission will therefore control the rate of microbial stimulation in the long term.

The named biodegradation products of PNS include pyruvate, while lactate and acetate are possible or even probable degradation products. Since these can be used by sulphate reducing bacteria, there is a risk that they stimulate sulphate reduction. Table 8-6 shows the number of moles of sulphide that would be produced per mole of DOC from the PNS superplasticizer, the PC backbone and PEG-23 (MW 1010), assuming that all of the carbon atoms can be involved in sulphate reduction. The PEG leads to the highest theoretical concentration of initial sulphide production and this is the most degradable molecule considered. However, it is difficult to interpret this theoretical sulphide production further, given that degradation is most likely after the DOC has left the cement pores, and that the sulphide will react with other species such as Fe(II).

**Table 8-6. Theoretical amount of sulphate that can be reduced during the respiration of the superplasticizers (SP) and PEG in the initial cement porewater. The reduction of sulphate to sulphide involves an 8 electron transfer**

<table>
<thead>
<tr>
<th></th>
<th>Average oxidation state of C</th>
<th>Moles of electrons transferred during oxidation of 1 mole of DOC to CO₂</th>
<th>Moles of sulphate reduced to sulphide per mole DOC oxidised</th>
<th>Maximum initial DOC concentration from SP (mM) (from Table 8-4)</th>
<th>Maximum initial sulphide production (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNS</td>
<td>-1.1</td>
<td>5.1</td>
<td>0.64</td>
<td>84</td>
<td>54</td>
</tr>
<tr>
<td>PC (after hydrolysis of ester group)</td>
<td>-0.5</td>
<td>4.5</td>
<td>0.56</td>
<td>103</td>
<td>58</td>
</tr>
<tr>
<td>PEG-23</td>
<td>-1</td>
<td>5.0</td>
<td>0.63</td>
<td>780</td>
<td>490</td>
</tr>
</tbody>
</table>

- Could the sulphonate content of PNS and PMS increase sulphate in the system, and thus enhance cement degradation and sulphide production?

The use of PNS increases the initial sulphate concentration of the cement by a few mM, which is a significant increase. The use of PCE increases the initial cement porewater sulphate concentration by about 1 mM. This sulphate, together with the DOC from the superplasticizer products could stimulate additional sulphate reduction, and this is most likely to occur once the material had migrated out of the cement to more favourable conditions. In the longer term, the sulphonate concentration in the porewater is estimated to be about 10% of the maximum sulphate concentrations in the groundwater at this depth (2 mM).
9 RISK-BENEFIT SCORECARDS

The risk-benefit scorecards for the different types of superplasticizer are given in this chapter, based on the analysis given in Chapter 8. OPC concrete has not been included in the scorecards as a suitable recipe was not available. The rationale for the selecting the values assigned are as follows:

- The concentrations of superplasticizer used were based on the recipes given in Table 8-2 and Table 8-3 for the low pH silica fume grouts and concretes.
- The initial porewater concentrations are based on Table 8-4.
- The leachability of both superplasticizers bound to cement has been seen to be very low in experiments, and the greater leaching of PNS than PCE in Yamamoto et al. (2008) reflected the greater amount used to make the cement. Therefore, it is assumed that the leachability is similar.
- As the same leachability is applied to the different systems (see above), the amount leached per porewater exchange is considered to be proportional to the concentration used.
- PCE superplasticizers release biodegradable PEG polymers as a result of alkaline hydrolysis. The degradation potential of the PEG is particularly high, as biodegradation of PEG of the expected size (23 repeat units) has been observed in a number of environments. However, the degradation of both PNS and the PC backbone of PCE is restricted by the need for chain scission reactions prior to the documented biodegradation pathways of oligomers, dimers and smaller molecules.
- Superplasticizers have been seen to affect the solubility of different radionuclides to different extents, and so the same value was assigned to the two superplasticizers here. The value is quite high, as both PNS and PCE were seen to have a similar effect on Eu(III) as EDTA and citrate in Dario et al. (2004).
- The effect of superplasticizers on radionuclide sorption is difficult to define, partly due to experimental challenges, the need to extrapolate data and because it depends on the solid phase and the radionuclide as well as the superplasticizer. In a spent fuel repository, the effect on radionuclide sorption to granite may be the most important consideration.
- The influence on microbial growth is greatest in the early period, as the smaller more biodegradable molecules preferentially remain in solution during cement hydration. PEG release also is expected in this early period. Microbial stimulation after this initial “pulse” is expected to be much lower due to the slow degradation of the superplasticizer polymeric backbones.
- There is no evidence that the superplasticizers increase the rate of cement degradation. Conversely, the additional density and low porosity made possible by the use of a superplasticizer is expected to improve the performance of the cement.
### Table 9-1. Scorecards for PNS and PCE superplasticizers in low pH silica fume concrete and low pH silica fume grout.

<table>
<thead>
<tr>
<th>1= low</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5= high</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration used</td>
<td>Pantarhit LK (FM) low pH silica fume concrete</td>
<td>Pantarhit LK (FM) low pH silica fume grout</td>
<td>Glenium 51 low pH silica fume concrete</td>
<td>Glenium 51 low pH silica fume grout</td>
</tr>
<tr>
<td>Initial porewater concentration</td>
<td>2</td>
<td>1</td>
<td>2 (PEG 5)</td>
<td>1 (PEG 4)</td>
</tr>
<tr>
<td>Leachability</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Amount leached per porewater exchange</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Degradation potential</td>
<td>2</td>
<td>2</td>
<td>2 (PEG 5)</td>
<td>2 (PEG 5)</td>
</tr>
<tr>
<td>Influence on radionuclide solubility</td>
<td>4</td>
<td>4</td>
<td>4 (PEG 1)</td>
<td>4 (PEG 1)</td>
</tr>
<tr>
<td>Influence on radionuclide sorption</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Influence on microbial growth</td>
<td>3 (early period) 2 (longer term)</td>
<td>3 (early period) 2 (longer term)</td>
<td>5 (early period) 2 (longer term)</td>
<td>5 (early period) 2 (longer term)</td>
</tr>
<tr>
<td>Negative influence on cement degradation</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The scorecards highlight that the advantages of using a PCE superplasticizer lie in the low initial concentration needed, thus the lower amount of organic carbon introduced to the system. PCE also consists of around 75% PEG by mass, and the relatively early release of this into the porewater following alkaline hydrolysis is expected to reduce the later release of DOC further. This means that a much smaller amount of organic carbon will be present in the cement after the first few porewater exchanges, compared to when PNS is used.
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