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The potential role of the degradation products of cement superplasticizers on the mobility of radionuclides

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ABSTRACT

Superplasticizers added into cementitious materials can degrade due to hydrolytic, thermal, radiolytic and microbial effects. Short-chain organic compounds such as acetate, phthalate, oxalate, phenol, urea, etc., have been confirmed as possible degradation products of superplasticizers. This work presents a review of the degradation process of superplasticizers and a thermodynamic study on the effect that model compounds considered as proxy for their degradation products have on the solubility of several radionuclides (Ni, Eu, U). Our results indicate that the complexation capacity of the proxy superplasticizers degradation products considered (i.e. acetate, phthalate, phenol and urea) towards Ni Eu and U is almost negligible in alkaline conditions, but relatively important in the near-neutral pH range.

1. Introduction

In nuclear waste disposal facilities cementitious materials are used for construction (construction and stabilisation of galleries and tunnels shotcrete), for waste confinement and stabilisation as well as a engineering barrier (Bart et al., 2012).

Superplasticizers (SPs) are a type of organic chemical admixtures used by cement manufacturers to improve dispersion, hydration and workability properties of concrete (Taylor, 1997). During the last century, SPs formulations have been continuously evolving. In overall, four different SPs categories (Fig. 1) can be defined: (a) naphthalene-sulfonate based SPs (Tucker, 1936), (b) melamine-sulfonate based SPs (Aignesberger and Bornmann, 1975), (c) lignosulfonate based SPs (Mark, 1938), and (d) polycarboxylate ether-based SPs. (a), (b), and (c) SPs type were widely used in the past century being also named as 1st and 2nd SPs generation. (d) SPs type were described in the 90's, the so called 3rd SPs generation, being widely used in current cement formulations.

Glenium® 27 is a polycarboxylate ether-based (PCE) SPs defined as a reference material used in concrete formulations to build up different structures in the Belgian deep disposal facility for radioactive wastes (Craeye et al., 2009). In contrast to the older SPs this kind of SPs improves the dispersion of cement particles by electro-steric repulsions (Fig. 2). The chemical structure of this type of SPs is formed by a long hydrophobic chain (i.e. polyethylene glycol chain) and one or several hydrophilic groups linked through an ester bound.

Little information is available regarding the degradation of SPs in cementitious systems (Gascoyne, 2002), although the interest on this topic has recently increased because SPs are unavoidable components of some cement-based materials that will be used in the construction of a deep geological repository for radioactive waste (Wieland et al., 2014). It is well recognized that hyperalkaline conditions developed in cementitious environments can cause chemical transformations of organic substances, i.e. polymeric SPs, (degradation, aging, etc.) with the subsequent production of small organic compounds with new chemical properties (Glaus and Van Loon, 2004a; Glaus and Van Loon, 2004b; Yilmaz et al., 1993).

The influence of organic substances on the behaviour and mobility of several radionuclides is well recognized (Andersson et al., 2008, Colàs Anguita, 2014; Gaona et al., 2008; Wieland et al., 2014). The role of SPs degradation processes on radionuclide mobility through the near and far field of a radioactive waste repository is therefore a matter of concern for the assessment of the performance of radioactive waste repositories. This work aims at investigating to which extent the degradation of cement SPs may affect radionuclide migration behaviour.

2. Superplasticizers degradation: literature survey

In this section, a literature research on the degradation of SPs through hydrolysis, thermal, radiological and microbial processes is

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Glossary of terms

C_6H_5OH	Phenol
$C_2H_3O_2^-$	Acetate
$C_8H_4O_4^2$	Phthalate
H_4N_2CO	Urea
GC-MS	Gas Chromatography – Mass Spectrometry
IR	InfraRed
NMR	Nuclear magnetic resonance
OPC	Ordinary Portland Cement
PCE	Polycarboxylate ether-based
SMF	Sulfonated Melamine Formaldehyde
SN	Sulfonated naphthalene
SNF	Sulfonated Naphthalene Formaldehyde
SNFC	Sulfonated naphthalene formaldehyde condensate
SP/SPs	Superplasticizer

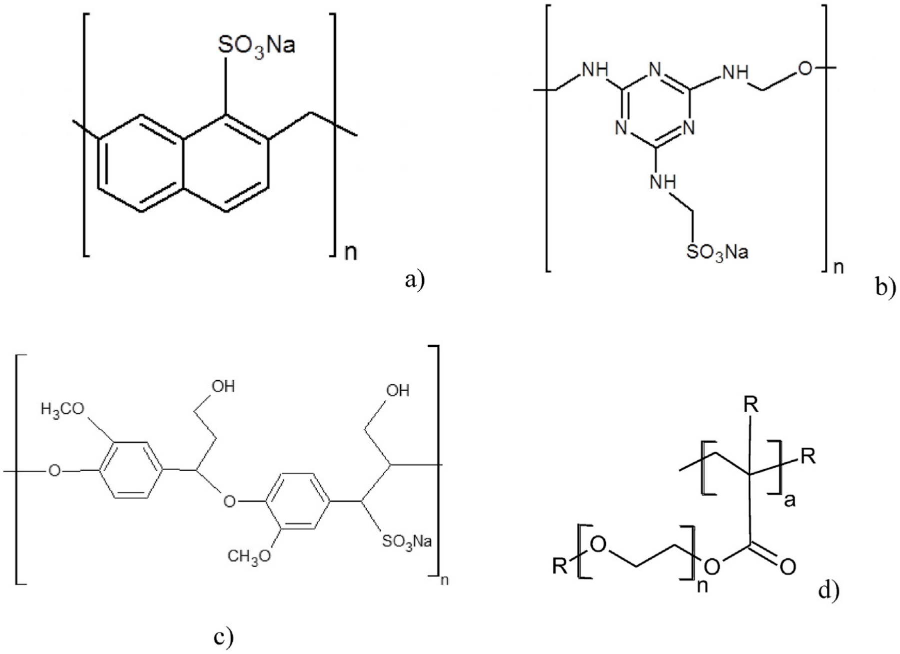

Fig. 1. a) Naphthalene sulfonate SPs type structure, b) Melamine sulfonate SPs type structure, c) lignosulfonate, and d) polycarboxylate ether-based SPs type structure.

summarised. Overall there is an important lack of SPs degradation studies (Young, 2012). To complement the literature research, available studies on degradation of main organic SPs groups' (i.e., naphthalene, melamine, etc.) have been also considered.

2.1. Hydrolytic degradation

Cementitious environments promote highly alkaline systems due to the dissolution-precipitation processes occurring within a cementitious matrix in contact with water. Overall, in ideal systems (e.g. pure water in open systems at 25 °C) four pH ranges may be defined depending on the cement degradation state: (i) fresh or degradation state I, characterized by a highly alkaline pH range (> 13) produced by the dissolution of Na and K alkalis, (ii) degradation state II, in where portlandite ($Ca(OH)_2$) dissolution controls the evolution of the system, buffering the pH around values of 12.5, (iii) degradation state III, after complete dissolution of portlandite, C-S-H gels dissolve buffering the system from pH 12.3 to 10.5 as a function of the Ca/Si ratio within the C-S-H gel, and, finally (iv) degradation state IV, where the formation of calcite within the cement matrix buffers the system pH at values < 10 (Taylor, 1997). For the current research, we only consider those studies at pH above 10.5, where SPs hydrolysis is favoured.

Yilmaz and co-workers (Yilmaz et al., 1993) studied the degradation of Sulfonated Naphthalene Formaldehyde (SNF) and Sulfonated Melamine Formaldehyde (SMF) SPs. According to their results, SNF SPs were not altered in alkaline solutions (1 M KOH) while solid precipitation was observed in SMF solutions at similar pH values. Analysis of the precipitated product confirmed the alteration of the original SMF. However, the chemical characterization of the precipitated solid was not entirely clear and thus the authors did not report conclusive SPs degradation pathways.

Naphthalene degradation based on photocatalysis was studied by Lair and co-workers (Lair et al., 2008). The authors investigated the effect of pH (from 2 to 12) on naphthalene degradation and concluded that an increase of the system pH increased the degradation rate of naphthalene. A possible explanation for this phenomenon reported by the authors is that the increase of OH^- ions in solution increase the presence of OH· radicals favouring naphthalene degradation. Intermediate degradation products were determined by GC-MS analyses; dozens of compounds were identified being 2-formylcinnamaldehyde and 1-naphtalenol the most abundant (see Appendix I).

Melamine Formaldehyde-Acrylic coatings degradation were studied by (English et al., 1983) with different analytical techniques (^{13}C NMR, IR). Under standard weathering conditions, only accounting for hydrolysis at atmospheric conditions, the degradation reaction reported by the authors was the one described in r. 1. This reaction involved the substitution of the terminal methyl by water releasing formaldehyde. No modifications of the melamine back-bone were found by the authors. Later (Gerlock et al., 1986) confirmed the same degradation pathway by using photo-enhanced hydrolysis.

$$\text{Melamine-}CH_2OCH_3 + H_2O \Leftrightarrow \text{Melamine-}CH_2OH + CH_3OH \qquad \text{(r. 1)}$$

2.2. Thermal degradation

The presence of heat generating wastes may produce temperature increases in the surrounding of the deep geological repository of high-