



# Characterization and degradation of a polyaryl ether based superplasticizer for use in concrete barriers in deep geological repositories

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## ABSTRACT

Superplasticizers are important additives used in concrete barriers in geological waste repositories. Superplasticizers have been a major concern in the long-term assessments of safe geological disposal for radioactive waste since superplasticizers and their degradation products can act as complexing ligands and thereby increase the mobility of radionuclides. In this work a new type of superplasticizer, based on a polyaryl ether polymer, has been characterized. It was found that the superplasticizer combines the structural features of polycarboxylate ether based superplasticizers and sulfonated naphthalene-formaldehyde based superplasticizers and that it contains organophosphate charged groups. A novel method for evaluating the rate of degradation of the superplasticizer under alkaline conditions was elaborated and the degradation products and rate constant of the process was determined. The results demonstrate that degradation occurs rapidly compared to the typical lifetime of a repository.

## 1. Introduction

Cementitious materials are used as one of the engineered barriers in geological repositories for radioactive waste. Superplasticizers (SPs) are of great importance for the building industry as the most commonly used organic cement admixture. Addition of SPs improves the workability of concrete, reduces the amount of mixing water, modifies mixture rheology and induces retardation of setting (Hanehara and Yamada, 1999; Winnefeld et al., 2007; Guan et al., 2010; Yamada et al., 2006). The presence of superplasticizers also improves the mechanical properties of the concrete (Aitcin and Neville, 2003; Peiwei et al., 2001; Plank et al., 2010). The former generations of SPs include modified lignosulfonates (Mark, 1938; Yousuf et al., 1995), sulfonated naphthalene-formaldehyde condensates (SNF) (Tucker, 1936; Redin et al., 1999) and sulfonated melamine-formaldehyde condensates (Aignesberger and Bornmann, 1975; Grabiec, 1999) (Fig. 1, a, b and c). The modern generation is represented by polycarboxylate ether based compounds (PCE) (Plank et al., 2008; Ochs et al., 2016) (Fig. 1, d). Recently a new type of SPs, called polyaryl ether based SPs (PAE), was introduced combining the structural features of SNF and PCE SPs (Strobl, 2015). The exact composition of this admixture is proprietary information, but according to the open access sources provided by the manufacturer (BASF AG, Switzerland), it contains both aromatic rings (like in SNF) and long side chains connected to the backbone (like in

PCE) (Strobl, 2015).

Superplasticizers can have several possible impacts on the long-term safe disposal of radioactive waste (Wieland et al., 2014; Keith-Roach Miranda, 2008; Glaus et al., 2004). Over time the superplasticizers will leach out into the geological repository and the surrounding environment. Superplasticizers and their degradation products can act as complexing ligands and thereby increase the mobility of radionuclides. Therefore superplasticizers have been a major concern in the long-term assessments of safe geological disposal for radioactive waste (Wieland et al., 2014). The effect of all superplasticizers is based on their adsorption to the positively charged cement particles, mostly to ettringite and monosulfate, via ionic groups (e.g. sulfonate or carboxylate) which also renders an excess of negative charge that induces an electrostatic repulsion between the particles resulting in better dispersion of the latter ones (Uchikawa et al., 1997; Plank and Hirsch, 2007; Zingg et al., 2008; Ferrari et al., 2010). The improved properties of ether based SPs as concrete additives originate from their structures. Besides the charged groups they contain long side chains. The side chains are represented by methoxy polyethylene glycol (PEG) in PCE SPs (Plank et al., 2008; Wang et al., 2016), and according to our findings in this work, similar side chains are present in PAE SPs. After the adsorption, the side chains cause steric hindrance, which in turn facilitates the dispersion of the cement particles (Fig. 2) (Uchikawa et al., 1997). According to the information provided by the manufacturer, the

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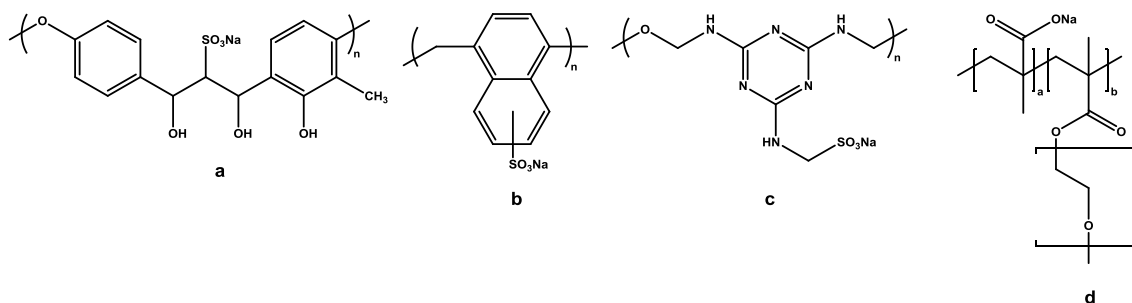


Fig. 1. Monomeric units of lignosulfonate SPs (a), sulfonated naphthalene-formaldehyde SPs (b), sulfonated melamine-formaldehyde SPs (c) and polycarboxylate ether based SPs.

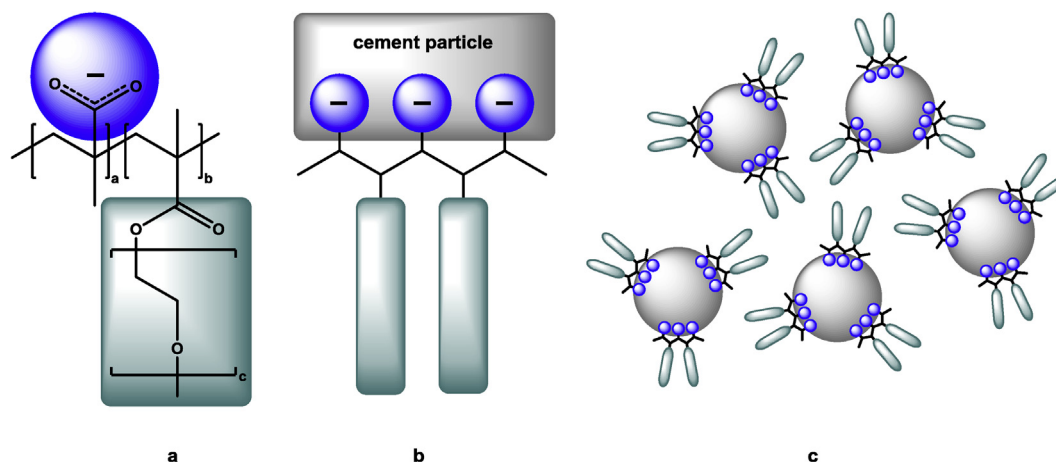


Fig. 2. Action of PCE SP: composition of PCE SP (a, the carboxylate group is highlighted with dark blue and the side chain is highlighted with light blue), adsorption of PCE SP on the cement particle (b), dispersion of cement particles with the adsorbed PCE SP molecules due to steric and electrostatic reasons (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

performance of PAE SPs is even better than PCE SPs (Strobl, 2015). However, to the best of our knowledge, the structure of PAE SPs has not yet been described in open sources.

Despite the fact that PCE SPs were invented relatively recently (Cerulli et al., 1994) and PAE even more recently, they have wide prospective. Cements with PCE SPs are proposed to be used for construction of engineered concrete barriers for nuclear waste repositories in Finland, Switzerland and Japan (Wieland et al., 2014; Andersson et al., 2008). It is also under consideration to use the PAE SP for construction of engineered concrete barriers in a Swedish final repository for short-lived radioactive waste (SFR). However, in order to use organic admixtures for the barrier material of nuclear waste repositories, the properties of the substances should be thoroughly studied. In particular, the ability of ether based SP to affect the mobility of radionuclides in the repository is important since they can either form coordination compounds with cationic radionuclides or interact with the cement particles resulting in increased or decreased uptake of radionuclides by surface complex formation or competition for the surface adsorption sites, respectively (Lövgren, 2005). That is why the properties of PCE SPs, such as their influence on mobilisation of radionuclides (Wieland et al., 2014; Glaus et al., 2004), complexation ability (Greenfield et al., 1998; Jansen et al., 2012), and interaction with the cement matrix (Winnefeld et al., 2007; Sun et al., 2014; Wieland et al., 2006) have been widely studied. However, to the best of our knowledge these properties of PAE based SP have not yet been reported.

The data on PCE SPs' properties reported in different sources display some degree of inconsistency. Thus, the complexation ability of superplasticisers is a matter of debate. Some authors claim that the formation of complexes of PCE SP with  $K^+$  and  $Ca^{2+}$  either do not occur or that such a process is not important for the formation of concrete

(Winnefeld et al., 2007; Lothenbach et al., 2007), while some authors have an opposite opinion (Jansen et al., 2012; Ferrari et al., 2012). Such variability may be caused by two reasons. Firstly, the structure and chemistry of PCE SPs can vary significantly between different products (Winnefeld et al., 2007; Zingg et al., 2008; Yamada et al., 2000), that is why the data correct for one PCE SP can be erroneous for another one. For instance, for the series of PCE SPs with known structures, Winnefeld et al. (Winnefeld et al., 2007) reported the liquid phase residue from 14% to 63% by mass depending on the structure of the polymer after 60 min of adsorption on cement particles. Secondly, both PCE SP and PAE SP could undergo degradation in cement media, and reactivity, sorption behaviour and other properties of the degradation products could differ from those of the initial material. Concrete is a porous material which contains highly alkaline solution (cement pore water, pH 11.5–13.7) (Lothenbach and Winnefeld, 2006; Berner, 1988) in the pores even at moderate humidity regardless of the presence of “free” water in the system (Espinosa and Franke, 2006). Such fluid can cause alkaline hydrolysis of SP, however even for PCE neither the degradation kinetics nor the structures of the degradation products were systematically investigated. There are some available data, but they cover only the leaching of PEG from the concrete made with PCE SPs (Lagerblad, 2006; Herterich et al., 2004; Guérandell et al., 2011). Also it is not clear if the studied PEG originates from the hydrolysis of ester groups of SP or if it was present in the SP as an impurity or unreacted starting material. In turn, the degradation of PAE polymers has not yet been studied.

In the present paper, two main topics are covered. The PAE SP MasterEase 3500 (BASF AG, Switzerland) has been characterized using various physicochemical methods (ICP-OES, UV, FTIR and NMR spectroscopies, TOC analyses and SEC). The kinetics of the degradation and resulting detachment of phosphate groups in the aforementioned SP in

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