Solid–liquid distribution of selected concrete admixtures in hardened cement pastes

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Abstract

The distribution between hardened cement paste and cement pore water of selected concrete admixtures (BZMs), i.e., sulfonated naphthalene–formaldehyde condensate (NS), lignosulfonate (LS) and a gluconate-containing plasticiser used at the Paul Scherrer Institute for waste conditioning, was measured. Sorption data were fitted to a single-site Langmuir isotherm with affinity constants $K = (19 \pm 4)$ dm^3 g^{-1} for NS, $K = (2.1 \pm 0.6)$ dm^3 g^{-1} for LS and sorption capacities $q = (81 \pm 16)$ g kg^{-1} for NS, $q = (43 \pm 8)$ g kg^{-1} for LS. In the case of gluconate, a two-site Langmuir sorption model was necessary to fit the data satisfactorily. Sorption parameters for gluconate were $K_1 = (2 \pm 1) \times 10^6$ dm^3 mol^{-1} and $q_1 = (0.04 \pm 0.02)$ mol kg^{-1} for the stronger binding site and $K_2 = (2.6 \pm 1.1) \times 10^3$ dm^3 mol^{-1} and $q_2 = (0.7 \pm 0.3)$ mol kg^{-1} for the weaker binding site. Desorption of these BZMs from cement pastes and pore water in cement specimens prepared in the presence of the BZMs were then used to test the model. It was found that only minor parts of NS and LS could be mobilised as long as the cement composition was intact, whereas the sorption of gluconate was found to be reversible. The Langmuir model makes valuable predictions in the qualitative sense in that the pore water concentration of the BZMs is reduced by several orders of magnitude as compared to the initial concentrations. In view of the necessity for conservative predictions used in the safety analysis for disposal of radioactive waste, however, the predictions are unsatisfactory in that the measured pore water concentrations of NS and LS were considerably larger than the predicted values. This conclusion does not apply for gluconate, because its concentration in cement pore water was below the detection limit of ~50 nM.
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1. Introduction

Concrete admixtures (abbreviated as BZMs[1]) are used to improve the workability of cement, to influence physical properties, such as compressive strength, durability or setting time, and to improve mix rheology (Dodson, 1990; Ramachandran, 1995; Spiratos and Jolicoeur, 2000). In the context of the safety of cementitious repositories for low- and intermediate-level or long-lived intermediate-level radioactive waste planned in Switzerland, BZMs are of concern in the same way as other organics, such as cellulose or ion exchange resins. Sorption of radionuclides on the solid repository matrix is a key factor governing their possible later release from the repository (Hadermann, 1997). Organic substances contained in the repository may positively or negatively influence this sorption. Therefore, the role of organics needs to be addressed quantitatively in an overall performance assessment. The assessment of BZMs is complicated because of a number of special circumstances: (i) BZMs comprise a large variety of completely different chemical substances, ranging from simple carbohydrates to complex mixtures of macro-molecules; (ii) a single type of BZM is, in turn, most often composed of a variety of different compounds, the composition being in many cases ill-defined, or proprietary; (iii) it is not known which BZM will be used in the construction of cementitious radioactive waste repositories in Switzerland – the only BZMs that can be identified at the moment are those used for waste conditioning.

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[1] The abbreviation derives from the German word *Betonzusatzmittel,* no commonly used abbreviation for concrete admixtures has been found in the literature.

The pore water concentration of BZMs is a key parameter in the assessment of their role in safety analysis of a radioactive waste repository, as it directly affects the extent of possible radionuclide complexation. It is further related to the amount of BZMs bound to the surface, which may influence competitively the sorption on cement of radionuclides or other sorbing ligands. It has been shown unequivocally in the literature that BZMs, such as superplasticisers and set retarders, strongly sorb onto the surface of cement particles (Ernsberger and France, 1945; Blank et al., 1963; Rossington and Runk, 1968; Daimon and Roy, 1978; Popescu et al., 1991; Spanka and Thielen, 1995) and single mineral phases of cement (Blank et al., 1963; Rossington and Runk, 1968; Ramachandran, 1972; Costa and Massazza, 1984; Fukaya and Kato, 1986; Yilmaz and Glasser, 1991). However, these investigations were mostly done to understand the mechanism of action of BZMs and, for this reason, were mostly carried out on early stages of cement hydration. The aim of the present work is to test, whether (i) simple sorption models are suited to predict the pore water concentration of the BZMs and (ii) whether sorption mechanisms are identical for different classes of BZMs. For this purpose, sorption data for a few typical superplasticisers and set retarders on fully hydrated cement pastes were measured and fitted with one- or two-site Langmuir isotherms. Desorption of these BZMs from cement pastes and pore water analysis in cement specimens prepared in the presence of the BZMs were then used to test the predictive capacity of the sorption model. Reversibility is a prerequisite for applying Langmuir type sorption models and is therefore a good means to test the validity of the model. It is a common practice in many works concerned with BZM analysis to calculate concentrations of BZMs from measurements at a single wavelength. This may lead to biased results, because fractionation of heterogeneous BZMs may affect the spectral properties of the compounds. Possible changes in UV–Vis spectra of the BZM fractions in cement pore water have been examined in the present work, and irregularities found were included in the estimation of the overall experimental uncertainty.

2. Experimental section

2.1. Reagents and samples

Reagents of highest purity obtained from Fluka (Buchs, Switzerland) or Merck (Dietikon, Switzerland) and Milli-$Q^{\circledR}$ water were used throughout. Solutions of sulfonated naphthalene–formaldehyde condensate (abbreviated to NS) and lignosulfonate (desugarised, abbreviated to LS) were obtained from MBT (Switzerland). These solutions contain only the major components of the commercial products. So-called *PSI plasticiser* (abbreviated to PP) is added to cements used for the conditioning of radioactive waste in Switzerland. PP contains gluconate in significant amounts. The main structures of the BZMs used here are

shown in Fig. 1. Owing to the lack of knowledge of the exact composition of the BZMs used in this work, their concentrations specified here refer to the dry weight of BZM per volume of solution. Only in the case of gluconate are concentrations are given on a molar basis.

Portland cement (CPA 55 HTS, Lafarge, France) was used for preparing cement pastes. Hardened cement paste devoid of BZM (abbreviated to HCP) was the same material described by Van Loon et al. (1997). It was crushed and sieved to <70 μm. Artificial cement pore water (abbreviated to ACW-I), prepared by the procedure described in Van Loon et al. (1997), had the following composition: 114 mmol$\,$l^{-1} of Na, 180 mmol$\,$l^{-1} of K, 1.6 mmol^{-1} of Ca and a pH of 13.4. Hardened cement pastes prepared in the presence of BZM (abbreviated to BZM-HCP) were prepared according to Table 1. Portland cement was mixed in a Variac mixer (Moulinex) with half of the total water added as liquid at room temperature; remaining water was added thereafter as small-grained ice. BZM solutions were immediately added together with cement except for LS, which was added only after ∼90 min of cement hydration. The suspensions were first mixed manually and, after obtaining some degree of homogeneity, a mixer was used. Mixing speed was chosen such that the temperature did not exceed 75 °C. Aliquots of the pastes were cured in 250 cm^3 cylindrical polystyrene vessels (Semadeni, Switzerland; 65 mm diameter) after submerging the paste with ∼10 cm^3 of water. Part of this water was successively taken up by the hydration processes and therefore replaced. After an observation time of ∼30 days, the samples were stored in a glove box under controlled N$_2$ atmosphere (CO$_2$, O$_2$ < 5 ppm).

Pore water from BZM-HCP was expressed at the Institut für Bauforschung (Rheinisch-Westfälische Technische
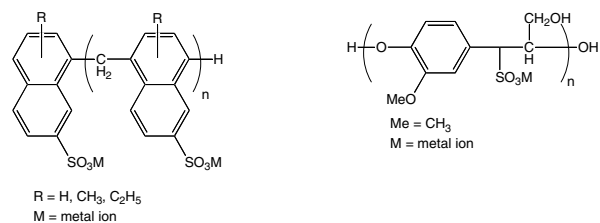
Fig. 1. Structural formulae of the BZM used in this work. The structure shown for LS is a gross simplification. Actually, LS is composed of a variety of structurally related monomers, irregularly aggregated to a macromolecule. α-ISA is a product of alkaline cellulose degradation used as a structural analogue to gluconate with weaker sorption properties.