



Cesium diffusion in mortars from different cements used in radioactive waste repositories

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ABSTRACT

Cement-based materials are widely used for stabilizing and conditioning radioactive waste in low- and intermediate-level repositories.

In this study, the adequacy of four different types of mortars, obtained from four different commercial cements, CEM I, II and IV (A and B), to act as barrier to ¹³⁷Cs migration was analysed. Diffusion experiments using the in-diffusion (ID) method with constant tracer concentration in the reservoirs were carried out, at increasing experimental times (150, 380 and 1500 days approximately).

In the experiments of less duration, and especially in CEM II and CEM I, two different pathways for diffusion were identified (*fast* and *slow*), leading to a double porosity system. However, the “fast” contribution to Cs diffusion, in all cases, could be neglected at larger experimental time, indicating a rearrangement of the pore structure that becomes more tight and homogeneous over time. Thus, if the experiments last enough time, only one diffusion coefficient properly describe Cs transport in these systems.

Apparent diffusion coefficients, D_a , obtained for Cs, range between $6.0 \cdot 10^{-13}$ and $1.0 \cdot 10^{-14}$ m²/s. Mortars produced with CEM IV (A and B) are the most efficient barrier for cesium transport, amongst those analysed in this study. Mortars with CEM II, which contain blast furnace slag, present the highest diffusion coefficient.

1. Introduction

Materials based on cements have many potential applications in the field of radioactive waste repositories. Concrete, mortar and cement have several uses in different repository concepts; for low and intermediate level waste the most important engineered barriers consist of cement-based materials. In high-level waste cement materials will be used for rock stabilization, limiting groundwater inflow, as well as for construction of engineered structures and for sealing of temporal or long-term service (Vieno et al., 2003). Also, cementitious materials may be used for conditioning/solidification and stabilization of the waste due to their favourable properties (Glasser et al., 1986; Atkinson and Nickerson, 1988; Atkins and Glasser, 1992; Batchelor, 2006; Ochs et al., 2016). Cements contribute both to physical and chemical containment of the radionuclides in the wastes because they can act as a barrier and because their large surface area provides high sorption capacity for radioactive species. Cementitious materials influence the chemical properties of the repository near-field, providing alkaline conditions, which favour radionuclide immobilization by sorption and low solubility. Under these conditions, radionuclide transport takes place

mainly by a diffusion process, slowed-down by sorption. Diffusion coefficients in cementitious materials are important parameters to be used in performance assessment calculations for low and intermediate level radioactive waste repositories.

Ion penetration in cement-based materials is largely controlled by their pore structure. The diffusion of ions is related to the volume of pores and their size and interconnectivity. Porosity, pore sizes and pore interconnectivity or distribution, are believed to be the main factors that affect diffusion of conservative ion through the mortars (Li et al., 2015).

Ion exchange resins used to purify coolant water in a nuclear power plant, frequently contain large amounts of ¹³⁷Cs, produced by the fission of uranium in nuclear reactors, and are typically part of low and intermediate level waste (LILW) (Ochs et al., 2016). There are few experimental data about Cs diffusion in mortars and the diffusion coefficients values show a very large variability, mainly due to the different experimental conditions. Sarott et al. (1992), performed through-diffusion experiments with hardened cement paste (HCP) and artificial pore water at pH 13.3 under oxic and anoxic conditions to study the cement carbonation; diffusion decreased with time by CaCO₃

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precipitation; in anoxic condition an average Cs effective diffusion coefficient, D_e , of $1.6 \cdot 10^{-10} \text{ m}^2/\text{s}$ was found. Skagius et al. (1999) found for structural concrete a D_e (C_s) = $2 \cdot 10^{-12} \text{ m}^2/\text{s}$; Sato et al. (2015) fitted the experimental results on concrete with D_a values of $5 \cdot 10^{-13}$ and $4 \cdot 10^{-14} \text{ m}^2/\text{s}$.

Different authors (Idemitsu et al. (1997); Sato et al. (2015), Atkinson and Nickerson (1988)) observed that for Cs diffusion, mortars and cements should be considered as “double porosity” media; their assumption was that different diffusion paths exist in the shallow (surface) or deep part of the sample (matrix). In particular, Idemitsu et al. (1997) performed diffusion experiment with Cs in water-saturated mortar and found that the measured penetration profiles of the tracer were composed of two parts: a steep slope near the surface, related to diffusion path was through fissures with a width of a few microns, and a gradual slope in the mortar interior, corresponding to the intact mortar network of submicron pores. Sato et al. (2015) studied the diffusion of ^{137}Cs , ^{154}Eu and ^{241}Am in concrete and mortar and also in this case, they needed two different D_a to fit the experimental data for the “surface” and “deep” region. The D_a values obtained by Sato et al. (2015) for Cs are: $1 \cdot 10^{-13} \text{ m}^2/\text{s}$ (“surface”) and D_a $5 \cdot 10^{-13} \text{ m}^2/\text{s}$ (“deep”). Atkinson and Nickerson (1988) also observed that for Cs diffusion, the cement showed a fast and slow diffusivity networks, and that the measured Cs profile appeared to be composed of two parts with different D_a (surface: $3.3 \cdot 10^{-14} \text{ m}^2/\text{s}$ and deep: $4 \cdot 10^{-12} \text{ m}^2/\text{s}$). Idemitsu et al. (1997) fitted the experimental results obtained by Atkinson and Nickerson (1988) also using two different D_a ($1 \cdot 10^{-12} \text{ m}^2/\text{s}$ and $1 \cdot 10^{-14} \text{ m}^2/\text{s}$).

Yuan (2009), studying chloride transport in concrete, also found that the experimental results are in agreement with the existence of different regions with their own retardation properties and with different diffusion coefficients, and concluded that the chloride diffusion coefficients are “depth dependent” because of the changes in pore structure.

The aim of this work is to obtain diffusion coefficients for Cs in mortars from different cements used for radioactive waste immobilization and to discuss the concept of “double porosity” on the bases of diffusion data obtained at different experimental times. Our hypothesis is that the porosity of the system is changing with time and tends to homogenise if enough experimental time is allowed, in contrast to the hypothesis of the existence of “shallow” and “deep” regions. Therefore, diffusion time must be considered a very important parameter for the D_a determination in these systems.

2. Materials and methods

Four commercial cements CEM I 42.5 R/SR, CEM II/A-S 42.5 N/SR, CEM IV A (V) 32.5 N and CEM IV B (V) 32.5 N, were used in this study. These cements have a low tricalcium aluminate (C3A in cement nomenclature) and alkali content, to prevent sulphate or alkali-aggregate attack (Andrade et al., 2006). General cement composition can be found in Table 1. CEM I, CEM IV A and B incorporate fly ash. Fly ash arises as a product of coal combustion: pulverised, micron-sized coal particles are combusted in air suspension where their mineral matter fuses. Fly ash is an extremely variable material and does not constitute a single material with well-defined properties (Atkins and Glasser, 1992). Blast furnace slags used for cements are usually chemically homogeneous

Table 1
Cement composition.

Cement	CEM I 42.5 R/SR	CEM II/A-S 42.5 N/SR	CEM IV A (V) 32.5 N	CEM IV B (V) 32.5 N
Clinker	95–100	83	70	58
Fly ash	–	–	29	40
Slag	–	12	–	–
Minor compounds	1	5	1	2

and constant in composition and normally glassy, to develop similar hydraulic properties than cement (Atkins and Glasser, 1992). CEM II is the only cement studied here that incorporates blast furnace slag.

A mortar is a homogeneous mixture of fixed proportions of cement, sand and water. In this work, silica sand with a size smaller than 2 mm was used to obtain mortars with a cement: sand: water relation of 1:1.75:0.45. “CEM I” samples were already prepared with 64% of CEM I and 36% of fly ash.

Mortars were prepared in PVC moulds and left to hydrate at room temperature and a relative humidity of 100%, for curing during 28 days. Mortars bulk densities determined from the ratio of the weight of the water saturated sample and its geometrical volume were very similar for the four used materials, between 2.1 and 2.2 g/cm³.

The composition of the liquid phase influences the diffusion process. To prevent strong mortar degradation during the diffusion experiment, the aqueous phase must be in equilibrium with the solid phase. Furthermore, the sample must be fully saturated to carry out the diffusion tests. To perform the experiments, synthetic cement pore water was prepared under oxic conditions using boiled Milli-Q water, and adding crushed and sieved (< 1 mm) mortars in a solid/liquid ratio of 10 g/L.

The water in contact with each solid was maintained under stirring until constant pH and conductivity were reached, approximately 30 days. Chemical composition of these four waters, filtered by 0.45 μm, is presented in Table 2. CEM II water has the highest calcium content, alkalinity and electric conductivity and lowest aluminium content. These waters were stored in dark and closed bottles until their use.

Cylindrical mortars samples, of 5 cm length and 4.5 cm radius, were sealed completely with epoxy resin and then cut in a half, leaving one face of the mortar uncovered, Fig. 1 (Left). In this way, two samples of the same mortar were obtained from each test core.

Diffusion experiments were performed using the in-diffusion (ID) method with constant tracer concentration in the reservoir. Decrease of concentration due to Cs sorption on mortars was corrected periodically spiking a small quantity of tracer. Each sample was introduced in a reservoir with 100 mL of mortar pore-water (previously equilibrated with 10 g/L of the corresponding solid). As the mortar samples were stored in a humid chamber, it was considered that two months were enough to reach sample saturation. Afterwards the tracer, ^{137}Cs (supplied by Eckert & Ziegler Isotope Products as CsCl without carrier), was added to the reservoir and the diffusion experiment started.

The ^{137}Cs initial activity, C_0 , was approximately 3100 cpm/mL. The tracer can diffuse through the uncovered mortar side and at the end of experiment (the diffusion time estimate for each set), the tracer concentration profile was obtained.

Three sets of experiments were performed for each mortar at increasing experimental times. The times selected for the different sets of experiments were: 150 days, 380 days and four years approximately.

Table 2
Chemical composition of the different mortars pore water (mmol/L).

Element	CEM I	CEM II	CEM IV A	CEM IV B
Cl ⁻	$4.78 \cdot 10^{-3}$	$2.20 \cdot 10^{-2}$	$8.46 \cdot 10^{-2}$	$1.18 \cdot 10^{-2}$
SO ₄ ²⁻	$9.16 \cdot 10^{-2}$	$6.67 \cdot 10^{-2}$	$1.08 \cdot 10^{-1}$	$1.23 \cdot 10^{-1}$
NH ₄ ⁺	$< 2.77 \cdot 10^{-2}$	$< 2.77 \cdot 10^{-2}$	$< 2.77 \cdot 10^{-2}$	$< 2.77 \cdot 10^{-2}$
Ca ²⁺	4.77	9.96	4.96	4.09
Mg ²⁺	$< 1.23 \cdot 10^{-3}$	$< 1.23 \cdot 10^{-3}$	$< 1.23 \cdot 10^{-3}$	$< 1.23 \cdot 10^{-3}$
Na ⁺	$1.00 \cdot 10^{-1}$	$3.57 \cdot 10^{-1}$	$2.52 \cdot 10^{-1}$	$1.48 \cdot 10^{-1}$
K ⁺	$4.60 \cdot 10^{-1}$	$3.07 \cdot 10^{-1}$	$7.67 \cdot 10^{-1}$	$6.39 \cdot 10^{-1}$
Al	$1.37 \cdot 10^{-1}$	$1.74 \cdot 10^{-2}$	$1.56 \cdot 10^{-1}$	$2.00 \cdot 10^{-1}$
Fe	$< 5.37 \cdot 10^{-4}$	$< 5.37 \cdot 10^{-4}$	$< 5.37 \cdot 10^{-4}$	$< 5.37 \cdot 10^{-4}$
SiO ₂	$4.66 \cdot 10^{-2}$	$2.33 \cdot 10^{-2}$	$3.16 \cdot 10^{-2}$	$4.99 \cdot 10^{-2}$
Alkalinity (meq/L)	11.82	21.49	8.86	10.51
pH	12.2	12.5	12.3	12.2
Cond. (μS/cm)	2300	3980	2750	2010

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