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Degradation of mortar under advective flow: Column experiments and reactive transport modeling

Ana Trapote-Barreira [a,b,*], Jordi Cama [a,b], Josep M. Soler [a,b], Barbara Lothenbach [c]

[a] Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona 08034, Catalonia, Spain
[b] Associated Unit: Hydrogeology Group (UPC-CSIC), Catalonia, Spain
[c] Empa, Laboratory for Concrete & Construction Chemistry, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

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ABSTRACT

To study the alteration of Portland cement mortar from the El Cabril disposal facility under advective water flow conditions, and to test the applicability of the C–S–H dissolution rate law obtained in our previous study, experiments using columns filled with mortar fragments were performed. Variation of the chemical composition of the output solutions and the analyses of the mortar fragments by means of visual inspection, SEM and X-ray fluorescence (XRF), before and after the experiments, allowed interpretation of the dissolution and precipitation reactions by means of two-dimensional reactive transport calculations. The 2D model included an immobile zone (mortar grains) and a mobile zone (flowing water). The reactive transport model adequately reproduced the processes of portlandite dissolution and C–S–H dissolution and decalcification. The results proved the applicability of the previously obtained dissolution rate law of the C–S–H gel, although some uncertainties remain.

1. Introduction

The El Cabril disposal facility (Southern Spain) is a vault-type surface disposal repository for the storage of low- and intermediate-level nuclear waste. Hydrated Portland cement is one of the essential materials for this kind of construction because of its high-quality performance in many environments and well known chemical-barrier behavior. The barrier behavior is due to (i) the pH of about 13 of the pore solution which limits the solubility of many radionuclides [2,3], and (ii) the high surface area for the sorption of the radionuclides [3,4].

Since the summer of 2003 water has been collected in the water collection system of some cells at El Cabril, and the source and the inflow mechanisms of this water have been studied [5,6]. From these studies, a first reactive transport model was developed. It was concluded that the source of collected water is groundwater, and the air gap between containers and vault walls produced seasonal differences of temperature of a few degrees, causing water vapor diffusion from the walls to the concrete containers in summertime or vice versa in winter.

The existence of this flow across the concrete of the cells can provoke the alteration of concrete. The porewater of cementitious materials, which contains K, Na, Ca, Si, S, Fe and Al in solution is characterized by high pH values (≥13), and it is at equilibrium with the phases present in hydrated cement. Dilution of the porewater will perturb the local equilibrium, potentially causing dissolution of the cementitious phases and precipitation of secondary phases, which may affect flow and solute transport properties.

Studies based on leaching of cement pastes are numerous [7–12], and some of them present theoretical or multi-species reactive transport models that describe the leaching processes [13–20]. In turn, the use of reactive transport modeling to account for the cement degradation requires reliable thermodynamic and kinetic databases. Several works that deal with the thermodynamics of cement-based materials are found in the literature [21–28]. However, lack of knowledge of dissolution rate laws of the cementitious phases yields uncertain cement degradation predictions [29,30].

In this study, column experiments using ground mortar were performed to study mortar alteration by flowing water. The experimental results consisted of the measured changes in composition of the solutions flowing out of the column and observations of the solids before and after reaction. Interpretation was performed using two-dimensional reactive transport modeling (CrunchFlow) [31,32]. This approach made it possible to check the applicability of the previously obtained dissolution rate law for the C–S–H gel [1].

2. Materials and methods

2.1. Experimental methodology

2.1.1. Characterization of the mortar

Cylindrical mortar samples were provided by Enresa (Spanish radioactive waste agency), as representative of the mortar used in El Cabril walls (Table 1). The CEM I 42.5R/SR cement contains 5% of limestone

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* Corresponding author at: Jordi Girona 18-26, Barcelona, 08034, Catalonia, Spain. Tel.: +34 934006100.
E-mail address: anatrapotebarreira@gmail.com (A. Trapote-Barreira).

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Table 1
Characteristics and mix design of the El Cabril mortar samples.

Characteristics	Dimensions	11 × 10 cm
	Cured type	Moisture room
	Total porosity (%)	14.9
	Median pore diameter (μm)	0.02
	Density (g mL^{-1})	2.0
Mortar mix design	Cement I 42.5R/SR	20.00 wt.% 440.16 kg m^{-3}
	Water	13.74 wt.% 302.39 kg m^{-3}
	Sand (quartz)	54.65 wt.% 1202.75 kg m^{-3}
	Fly Ash	11.24 wt.% 247.37 kg m^{-3}
	Additive (Rheobuild 1222)	0.37 wt.% 8.14 kg m^{-3}

($CaCO_3$). Fly ash was added (64% CEM I 42.5R/SR cement and 36% fly ash). Sand and additives were added to obtain the mortar with the proportions shown in Table 1. Porosity was measured by mercury intrusion porosimetry at 28 days of hydration. The mortar was cured in a moisture room to ensure that hydration continued for as long as possible in order to reach maximum strength and durability, sufficient impermeability and reduced risk of cracking. The chemical composition of the cement and fly ash as provided by Enresa is summarized in Table 2. The clinker composition was measured by X-ray fluorescence (XRF) and the normative phase composition (Table 3) was calculated following the UNE 80304 standard [33].

The composition of the hydrate assemblage formed during the hydration of the Portland cement + fly-ash mixture was calculated based on the cement and fly ash composition (Table 2) using the GEM-Selektor software package (GEMS) [34–38] after a hydration time of 830 days (from mixing to testing). GEMS computes the equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. The chemical interactions involving pure solid phases, solid solutions, gas mixture, and aqueous electrolyte are considered simultaneously. The thermodynamic data for aqueous species, as well as for many solids, were taken from the PSI-GEMS thermodynamic database [39,40], whereas the solubility products for cement minerals were taken from the cemdata07 database [24–26] completed with the recently determined solubility products of Fe-monocarbonate, Fe-monosulfate, and Si-hydrogarnet ($C_3(F,A)S_{0.84}H_{4.32}$ in cement notation) [28,41,42]. Formation of $C_3AS_{0.41}H_{5.18}$ was excluded for its unlikely occurrence at ambient temperature [28]. A reaction degree of the fly ash of 52% after 830 days was assumed based on the investigation of [35]:

$$\%\text{fly } ash(reacted) = 10\cdot \ln(t[days]+4.5)-15 \qquad (1)$$

Table 4 lists the volume of the phases expected in the mortar based on the calculations.

Table 2
Chemical composition (wt.%) of the cement and fly ash of the El Cabril mortar, and physical characteristics of the cement. Error in XRF analysis is around 5%.

	Cement I 42.5R/SR (wt.%)	Fly Ash (wt.%)
SiO_2	21.45	55.61
Al_2O_3	2.30	30.10
Fe_2O_3	4.85	6.56
CaO	68.40	1.74
MgO	0.77	2.01
CaO free	1.78	
SO_3	1.86	
K_2O	0.34	
Na_2O	0.09	
Alkali (Na_2O equivalent)	0.31	
Cl	0.01	
Density (g/cm^3)	3.13	
Blaine Surface (g/cm^2)	3685	
D_{50} (μm)	20.20	

Table 3
Mineralogical composition of the clinker (wt.%).

Phases	Composition (wt.%)
C3S (alite)	78.7 ± 1%
C2S (belite)	2.1 ± 1%
C3A	0.0
C4AF (ferrite)	11.0 ± 0.1%
C2F	2.1 ± 0.1%

Composition in cement notation C: CaO, S: SiO_2, A: Al_2O_3, F: Fe_2O_3.

One of the mortar samples was crushed into grains of 1 to 2 mm size. The specific surface area of the mortar was determined by the BET method [43] with a Micromeritics ASAP 2000 surface area analyzer using 5-point N_2 adsorption isotherms. The samples were previously degassed for 10 h at 50 °C. The BET specific surface area was 2.88 m^2 g^{-1}. The Blaine surface was calculated from the specific surface by means of the time that a fixed volume of air needs to pass through a bed of cement. D_{50} equal 20.20 means that 50 wt.% of the sample is smaller than 20 μm.

2.1.2. Mortar column experiments

Three methacrylate (PMMA) columns of 2.6 cm in length and 2.5 cm in inner diameter were filled with ca. 25 g of mortar grains (mortar fragments with a grain size 1–2 mm; Fig. 1a). Teflon® filters (0.45 μm) were placed at the inlet and outlet of the columns to prevent particles from leaving the column. An extra filter was placed at the inlet of the column to homogenize the incoming solution. The porosity of the columns was calculated from the difference in weight between dry and water-saturated columns. This porosity does not include the internal porosity of the mortar grains which were previously saturated with water. In the saturated columns, the porosity corresponding to the water between mortar grains was 42.5 vol.%.

A peristaltic pump was used to inject Millipore MQ water from the inlet of the columns at constant flow rate, which was different in each experiment (0.014, 0.028 and 0.036 mL min^{-1}) and yielded residence times of 6.9, 3.5 and 2.7 h, respectively. The entire experimental setup (input and output solutions, peristaltic pump, columns and tubing) was enclosed in a glove box purged with N_2 (99% purity) at room temperature (23 ± 2 °C) (Fig. 1b). Input Millipore MilliQ water was purged with N_2 inside the glove box to avoid carbonation. Oxygen concentration was continuously monitored by an oxygen partial pressure detector and varied from 0.1 to 0.4% O_2, being equivalent to 2–8 ppm of CO_2 according to the CO_2 content of atmospheric air. The output solutions were collected every second day and kept inside the glove box until analyzed.

The three experiments lasted up to 3423 h until the steady state was reached. Steady state was considered to be attained when differences in the Ca and Si concentrations in output solutions were below 10% in consecutive leachate samples for at least 200 h.

Once the experiments were finished, isopropanol was circulated through the columns to remove the retained solution. Isopropanol was allowed to evaporate, and thereafter epoxy resin was pumped into the columns to fill the pore volume. After resin solidification, column slices at different lengths were produced by diamond disc cutting. The surfaces of the slices were polished avoiding contact with water to be examined optically, by SEM-EDS (scanning electron microscopy-energy dispersive spectrometry) and by XRF (X-ray fluorescence).

2.1.3. Analysis of solutions

Input and output solution pH was measured at room temperature using a Thermo Orion Ag/AgCl electrode. Calibration was made with Crison © standard buffer solutions of pH 7.00 (sodium and potassium phosphate) and pH 9.21 (borax). The reported uncertainty is ±0.05 pH units. After pH measurements, the output solutions were acidified to pH 3 to avoid any formation of calcium carbonate in the collected solutions.