Cement and Concrete Research 58 (2014) 76–88

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

On the physico-chemical evolution of low-pH and CEM I cement pastes interacting with Callovo-Oxfordian pore water under its in situ CO_2 partial pressure

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ARTICLE INFO

Article history:
Received 27 April 2011
Accepted 9 January 2014

Keywords:
Microstructure (B)
Carbonation (C)
Cement paste (D)
Durability (C)
Degradation (C)

ABSTRACT

Within the framework of geological repositories for radioactive waste, structural concretes must be adapted to the underground chemical conditions. CEM I cement-based materials are characterised by high pH that may produce an alkaline plume in the near-field of the repository. In order to avoid this problem, low-pH cements have been designed. This study compares the physico-chemical behaviour of a low-pH material with a CEM I cement paste, both being subjected to leaching by an aqueous solution. An original experimental setup was designed to reproduce the underground conditions using a specific CO_2 regulation device. Under these conditions, the low-pH material was strongly degraded, which results in coarser porosity, whereas thickness degradation of the CEM I cement paste is limited by the precipitation of a magnesium-calcite crust over the surface, which reduces the exchange of soluble species. This paper also presents a new approach for microstructure characterisation based on high-resolution X-ray microtomography.

1. Introduction

In France, the current option developed by the French National Radioactive Waste Management Agency (*Agence nationale pour la gestion des déchets radioactifs* — Andra) for the geological disposal of intermediate long-lived waste includes several cementitious materials that are used in contact with clayey rocks dated from the Callovo-Oxfordian (COX) (mudstone from Bure, France) and bentonite [1]. Due to its neutral pH, the natural interstitial water in the mudstone will generate modifications in the cementitious materials, because it contains high concentrations of sulfate, carbonate, chloride and magnesium. Furthermore, under in-situ conditions, the development of an alkaline plume (typical pH of Portland cement pore water = 13.2–13.5) is accompanied by calcium, sodium, potassium and hydroxyl diffusion originating from the concrete degradation. Diffusion of these solutes alters the confining properties of the clayey materials by mineralogical transformations and related porosity changes [2–4]. For the purpose of limiting the perturbations caused by the concrete structures, new cementitious binders, called low-pH and comprising Portland cement, silica fume and fly ashes, were designed [5–7]. The objective was to create a new concrete formulation with the main following constraints: (i) pore solution pH lower than 11 to limit the alkaline attack of the clayey environment; (ii) low hydration heat; (iii) moderate shrinkage, and (iv) high mechanical strength. The influence of the natural water of (COX) mudstone on CEM I cement paste was studied through experimentation and modelling [8] and underlined the main following chemical degradation processes: leaching, carbonation and sulfate attack. The impact of that degradation proved to be spatially limited and quickly inhibited. A large quantity of studies explores the chemical durability of cementitious materials: in sulfated water [9–13], in carbonated pure water [14] or in multi-ionic water [9,10,13,15–21]. A very interesting study was carried out by Garcia-Calvo et al. [22], comparing the physico-chemical behaviour of two different concretes: a low pH and a CEM I exposed to a solution in equilibrium with granitic rock. The results obtained by this author are compared with the present study in an extended discussion section. In order

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http://dx.doi.org/10.1016/j.cemconres.2014.01.010

Table 1
Compositions of cements (Lafarge data).

	Chemical phase analysis [g/100 g]			Components and composition [mass]	
	Val DZ	Le Teil		Val DZ	Le Teil
CaO	64.6	66.8	C3S	68	66.5
SiO_2	20.7	22.2	C2S	17	16.8
Al_2O_3	3.2	2.9	C3A	0.9	<5
Fe_2O_3	4.6	2.6	C4AF	14	8.1
CaO (free)	1.8	0.0	Clinker	97	97
MgO	0.6	0.9	Gypsum	4	2.7
K_2O	0.6	0.2	Filler	3	3
Na_2O	0.1	0.2			
CO_2	1.1	1.3			
SO_3	2.8	2.2			

to understand the long-term evolution of concrete in situ, this study aims at comparing the short-term influence of the pore water from COX mudstone on two cement pastes made from Portland and low-pH cements, respectively. The practical objective is to know if the low-pH material may be used as a structural material in the geological repository. After a brief presentation of both materials, solutions and experimental devices, this paper will mainly focus on the experimental results obtained by multi-technical characterisations. A key original contribution of the present approach is the experimental device specially developed for imposing high CO_2 partial pressure observed in situ in the clayey rock. A thorough discussion is carried out to compare results from this study and literature data.

2. Materials and methods

2.1. The cementitious materials

The cements used for the elaboration of pure CEM I and low-pH cement pastes were two sulfate-resisting Portland cements (SRPC) from the Lafarge Corporation (Val d'Azergues (Val DZ) and Le Teil, respectively). The former cement was very poor in C_3A and rich in C_4AF, while the latter was chosen for its very low alkaline content. Their bulk chemical compositions and mineralogies were provided by Lafarge (Table 1). The data were obtained by Bogue modified calculation coupled with Rietveld analysis.

The low-pH cement was prepared with a water-to-binder ratio (w/b ratio) of 0.4, and cured in a sealed bag for eleven months in order not only to avoid carbonation and desiccation, but also to preserve the pore solution. The binder consisted of 37% CEM I cement, 30% fly ashes and 33% silica fume (mass percentages with respect to cement weight) [6]. 1% superplasticiser (*CHRYSO Fluid Optima 175*) was added to the mixture during preparation. The CEM I cement pastes were made with a water/cement (w/c) ratio of 0.4, and samples were cured in a solution equilibrated with portlandite for five years. The difference of curing time in the CEM I and the low pH cement pastes can have a possible impact on the reactive mechanisms. This point will be examined in the discussion according to the experimental results. The decision to use cement paste with five years of curing was due to our desire to compare the new results obtained with older studies using this material in the laboratory (in carbonated and/or sulfated waters). Cylinders measuring 80 mm in diameter were prepared for both materials. Half-discs measuring 15 mm in thickness were used for degradation experiments. Lateral surfaces of the sample were protected with a bi-composed epoxy resin (Resoltech 3030) in order to generate one-dimensional degradation. The uncovered surface exposed to the aggressive solution during the experiment measured about 0.5 dm^2.

The initial mineralogical compositions of both materials were inferred rom cement paste analyses by X-ray diffraction (XRD) (Fig. 1) and nuclear magnetic resonance (NMR) (Fig. 2). CaO/SiO_2 ratios of C–S–H were estimated through punctual SEM-EDX microanalysis ($N \approx 100$ points for both studied cement pastes). The CEM I cement paste consisted of portlandite, ettringite, C–S–H (with a high CaO/SiO_2 ratio, 1.5–1.8), brownmillerite (C_4AF) and belite (C_2S) (Figs. 1a, 2a). The low-pH cement paste included two hydrates, ettringite and C–S–H (with a low CaO/SiO_2 ratio), as well as several residual anhydrous phases, such as mullite (from fly ashes), quartz (from fly ashes and silica fume), and C_2S (Figs. 1b, 2b). The material also contained aggregates of silica fume which could be divided into two types. The first type was hydrated and calcium-enriched: it could correspond to silica gel with calcium, or to C–S–H with a low CaO/SiO_2 ratio. The CaO/SiO_2 ratio, measured by EDS, ranged from 0.5 to 0.8 (Fig. 3). The second type corresponded to unhydrated silica fume aggregates which were characterised by a chemical shift of −108 ppm in the ^{29}Si NMR experiments, as shown in Fig. 2b. The low-pH cement paste also contained small amounts of ettringite, as well as mullite brought by fly ashes.

^{29}Si NMR is the optimal tool to analyse C–S–H structure [23–26]. The two ^{29}Si NMR spectra obtained from both cement pastes enhanced very different C–S–H structures (Fig. 2). The Q^1-type Si tetrahedron is of the end-chain type, whereas the Q^2-type Si tetrahedron is of the middle-chain type. A high Q^1/Q^2 ratio means that the C–S–H structure is characterised by short chains of Si tetrahedra. These jennite-like structures having a high CaO/SiO_2 ratio were found in the CEM I cement paste (Fig. 2a). Conversely, a low Q^1/Q^2 ratio means than the C–S–H structure is characterised by long chains. Such a low Q^1/Q^2 ratio was observed for the low-pH cement paste (Fig. 2b). The measured water porosities of the Portland and low-pH cement pastes were 34% and

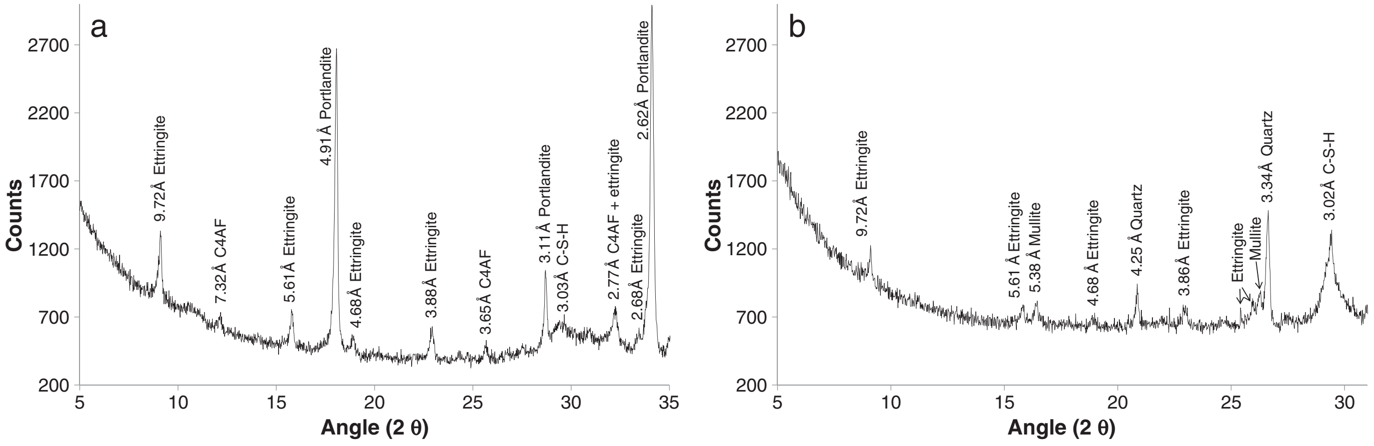

Fig. 1. X-Ray pattern of a) a CEM I and b) a low-pH cement paste (Cu K-α, λ = 1.5405 Å).