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Traditional Portland cement and MgO-based cement: a promising combination?

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ABSTRACT

MgO/SiO_2 cements are materials potentially very useful for radioactive waste disposal, but knowledge about their physico-chemical properties is still lacking. In this paper we investigated the hydration kinetics of cementitious formulations prepared by mixing MgO/SiO_2 and Portland cement in different proportions and the structural properties of the hydrated phases formed in the first month of hydration. In particular, the hydration kinetics was investigated by measuring the free water index on pastes by means of differential scanning calorimetry, while the structural characterization was carried out by combining thermal (DTA), diffractometric (XRD), and spectroscopic (FTIR, ^{29}Si solid state NMR) techniques. It was found that calcium silicate hydrate (C-S-H) and magnesium silicate hydrate (M-S-H) gels mainly form as separate phases, their relative amount and structural characteristics depending on the composition of the hydrated mixture. Moreover, the composition of the mixtures strongly affects the kinetics of hydration and the pH of the aqueous phase in contact with the cementitious materials. The results here reported show that suitable mixtures of Portland cement and MgO/SiO_2 could be used to modify the properties of hydrated phases with potential application in the storage of nuclear waste in clayey disposal.

1. Introduction

Over the last decades the use of cement became crucial in radioactive waste disposal, thanks to its capability of immobilizing inorganic species arising from liquid, solid or heterogeneous matrices. Porous cementitious grouts are ideal backfills for the disposal of low- and intermediate-level waste in vaults, as they can buffer the pH of pore water over an extended period of time (Norris et al., 2014). However, chemical gradients possibly form at the interface between cement and the natural environment, which may cause significant changes in mineralogy and in the chemical conditions at the interface. In particular, neutral pH and high salt concentration in the interstitial water of clayey rocks may alter the cementitious matrix, producing carbonation, ettringite precipitation or leaching phenomena. In turn, when traditional Portland cement is used, the alkaline pH of the pore solution is responsible for the degradation of the clay and the modification of its porosity (Bartier et al., 2013; Dauzères et al., 2010; Gaboreau et al., 2011; Gaucher and Blanc, 2006; Jenni et al., 2014).

An enhancement of the compatibility between cement and clayey rocks has been observed for newly introduced low-pH cementitious binders, developed by mixing Portland cement with silica fume, fly ashes, or other pozzolanic materials that react with portlandite. However, leaching and carbonation phenomena still occur in the calcium silicate hydrate (C-S-H) binder phase formed with these formulations, resulting in a decrease in strength development. At the same time, magnesium enrichment is reported in the decalcified areas, with formation of the magnesium silicate hydrate (M-S-H) phase, a colloidal gel analogous to C-S-H (Dauzères et al., 2014, 2016; García Calvo et al., 2010; Jenni et al., 2014). Recently, a cementitious formulation based on magnesium, in the place of calcium, has been developed by taking advantage of the hydration reaction of light-burned periclase (MgO) in the presence of silica: the hydration of MgO produces brucite ($Mg(OH)_2$), which promptly reacts with SiO_2 to form M-S-H (Zhang

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et al., 2012). M-S-H also forms by hydrating $Mg(OH)_2$ in the presence of a silica source (Walling et al., 2015). The presence of brucite buffers pH to a value of about 10, which decreases to 9 when $Mg(OH)_2$ is consumed with formation of M-S-H. This pH value, much lower than that obtained by hydration of Portland cement, is more suitable for the stabilization of nuclear wastes. Therefore, Portland-based pastes containing MgO are potentially useful to enhance the compatibility of clayey rocks with the cementitious matrix in waste immobilization. In particular, for wastes coming from Magnox reactors a low pH also favours the passivation of both Mg and Al alloys (Walling et al., 2015).

In the last years, the properties of M-S-H have been investigated (Nied et al., 2016; Roosz et al., 2015; Tonelli et al., 2016), but further work is needed to fully clarify its features. In particular, in the perspective of preparing low-pH cementitious formulations for nuclear waste immobilization, it is important to investigate the hydration process and the structural properties of the hydrated phases of MgO-based formulations also containing Portland cement. Some work has been done in this field, especially addressing the possible intercalation of Mg^{2+} in C-S-H (Fernandez et al., 2008; Pytel and Malolepszy, 2000; Shrivastava et al., 1991) and the interaction between M-S-H and C-S-H (Chiang et al., 2014, 2013; Lothenbach et al., 2015).

In this paper we report a study of the hydration kinetics and the structural properties of the hydrated phases of cementitious formulations containing different amounts of MgO/SiO_2 and Portland cement. In particular, the hydration kinetics was studied by analysing the trend of free water index (FWI), measured on pastes by means of differential scanning calorimetry (DSC), as a function of the hydration time (up to 1 month). The structural characterization of the hydrated phases at different hydration times was performed on freeze-dried samples by a combination of calorimetric (DTA), diffractometric (XRD), and spectroscopic (FTIR, ^{29}Si Solid State NMR (SSNMR)) techniques. A sample containing Portland cement and SiO_2, but not MgO, was also investigated in order to better evaluate the effect of the pozzolanic reaction between silica and portlandite on the properties of the hydrated phases (Richardson, 2004; Brough et al., 1995; Haas and Nonat, 2015).

2. Experimental

2.1. Materials

CEM I Portland cement was obtained from Italcementi (Bergamo, Italy). Magnesium oxide (MgO) and fumed silica (SiO_2) were supplied by Sigma-Aldrich. The main characteristics of these raw materials are summarized in Table 1.

Table 1
Chemical composition (%) and physical properties of Portland cement, MgO and SiO_2.

	Portland cement	MgO	SiO_2
Chemical composition			
SiO_2	19.81		≥99
Al_2O_3	5.41		
Fe_2O_3	3.96		
CaO	66.60		
MgO	2.50	≥99	
SO_3	1.25		
Na_2O	0.11		
K_2O	0.17		
SrO	0.04		
Mn_2O_3	0.02		
P_2O_5	0.04		
TiO_2	0.09		
BET surface area (m^2/g)	1.5 ± 0.1	121 ± 5	395 ± 25
Mean particle size (μm)	20	44	5
Reactivity (s)		80	

2.2. Preparation of the samples

The composition of the investigated samples is reported in Table 2 together with the acronyms used throughout the paper. When both present, MgO and SiO_2 were mixed in a 1:1 molar ratio. All the pastes were prepared by manually mixing 4 g of solids with 8 g of milliQ water (purified by a Millipore Organex system, $R \geq 18$ MΩ cm), i.e. at a water-to-solid weight ratio (w/s) of 2, the minimal ratio needed to obtain a workable paste for the pure MgO/SiO_2 sample. Each paste was stored at 20 °C in a polyethylene bag to avoid air contact and prevent carbonation.

For DTA, FTIR, XRD, SEM, and ^{29}Si SSNMR measurements, lyophilized samples were prepared. To this aim, about 1 g of paste was withdrawn after defined periods from preparation (1, 3, 7 and/or 28 days, depending on the measurement) and freeze-dried (50 mTorr, 24 h) to stop the hydration reaction.

2.3. Methods

The reactivity of periclase was measured according to the citric acid reactivity test (Van der Merwe et al., 2004).

The BET surface area of the powders was measured by means of a Coulter SA 3100 analyser, using nitrogen as adsorptive gas.

pH measurements were conducted with a BASIC 20 CRISON pH-meter, according to the method previously described by Zhang et al. (2011). In a polyethylene flask 1 g of mixed solid and 10 g of distilled water were added. The container was sealed and constantly shaken in an orbital stirrer. At different time intervals, the solid particles were allowed to settle and the pH of the supernatant was measured.

Thermal analyses (DTA) were performed by means of a STD Q600 instrument (TA Instruments, New Castle, USA), operating from room temperature to 1000 °C at 10 °C/min in nitrogen flux.

Fourier transform infrared (FTIR) spectra were acquired with a BioRad FTS-40 spectrometer (Biorad, Cambridge, MA, USA), between 400 and 4000 cm^{-1}, with a resolution of 2 cm^{-1}, accumulating 32 scans. For the analysis, about 1 mg of each sample was homogenized with 100 mg of KBr and pressed to obtain a pellet.

X-ray diffractograms were recorded with a XRD Bruker New D8 Da Vinci instrument operating at 40 kV and 40 mA, with a Cu source (emitting radiation $\lambda = 1.54$ Å). Data were collected in the 5°–70° 2θ range, with an increment of 0.05°.

^{29}Si SSNMR spectra were recorded on a Varian InfinityPlus 400 spectrometer working at ^{1}H and ^{29}Si Larmor frequencies of 400.35 and 79.48 MHz, respectively. ^{29}Si Direct Excitation Magic Angle Spinning (DE–MAS) spectra were recorded under ^{1}H high power decoupling, using a 7.5 mm probehead, with a ^{29}Si 90° pulse duration of 6 μs and a spinning frequency of 5.5 kHz; approximately 8000 transients were accumulated. For all the samples (except MS100) a recycle delay of 10 s between two consecutive transients was used; for MS100 the recycle delay was 20 s. The ^{29}Si chemical

Table 2
Composition of the samples as wt% of Portland cement (C), MgO (M) and SiO_2 (S).

Sample	C (wt%)	M (wt%)	S (wt%)	w/s
C100	100	0	0	2
MS20C80	80	8	12	2
MS50C50	50	20	30	2
MS80C20	20	32	48	2
MS100	0	40	60	2
CS	62.5	0	37.5	2

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