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Impact of drying on pore structures in ettringite-rich cements

I. Galan [a,*], H. Beltagui [b], M. García-Maté [c], F.P. Glasser [a], M.S. Imbabi [b]

[a] *Department of Chemistry, Meston Building, University of Aberdeen, Aberdeen AB24 3UE, United Kingdom*
[b] *School of Engineering, Fraser Noble Building, University of Aberdeen, Aberdeen AB24 3UE, United Kingdom*
[c] *Departamento de Química Inorgánica, Cristalografía y Mineralogía, Universidad de Málaga, 29071 Málaga, Spain*

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ABSTRACT

Drying techniques affect the properties of cement pastes to varying extents. The effect of different drying techniques on calcium sulfoaluminate-based (C$A) cements and their constituent phases is reported for a range of simulated and commercial C$A pastes which are benchmarked against an OPC paste. The recommended methodologies used to dry samples were identified from the literature and include D-drying and solvent exchange. These methods were used in conjunction with mercury intrusion porosimetry (MIP) and X-ray powder diffraction (XRPD) measurements to assess the changes in pore structure and the damage to crystalline phases, respectively. D-drying and isopropanol exchange are the most satisfactory and least damaging methods for drying C$A based pastes.

1. Introduction

An important factor influencing the durability of cement systems is *permeability*. Cement pastes are porous across a wide range of length scales and pore networks often have interconnections which collectively define permeability. However, permeability is difficult to measure directly and it is common to focus instead on pore measurements. The pore structure greatly influences the permeability as well as other properties such as compressive strength and ionic diffusion. Image analysis, BET gas adsorption, mercury intrusion porosimetry (MIP) and scattering techniques (tomographic X-ray, neutron) have been utilised to map the pore structure.

Many commonly used methods to determine pore structures require samples to be dried to empty the pores with concomitant danger of irreversible alteration of porosity and pore interconnectivity. The use of MIP to measure the porosity of hydrated cement pastes has been much debated in the literature. MIP has high sensitivity in the right pore size range for cement pastes but, besides being a potentially intrusive and damaging method, it does not necessarily measure the actual pore sizes but instead measures an intruded volume when a given pore entry size is exceeded [1]. Moreover, isolated pores cannot be accessed by mercury. However, these limitations can also be an advantage if the requirement is to obtain information relating to permeability: the pore entry size will give information about the accessibility to the connected pore network.

Non-destructive techniques requiring no special specimen preparation are available, such as X-ray computed tomography (CT) and neutron scattering. However, these methods are still being developed: data are difficult to obtain and interpret unequivocally. It is also likely that most commercial CT instruments do not have sufficient resolution to map pores smaller than a few microns. While progress has been made in interpreting the data [2–5] very little information relating to permeability has thus far been achieved.

Previous studies on the influence of drying methods on the pore structure focus mainly on hydrated OPC pastes, and much conflict is found. There is however general agreement that oven drying at high temperatures (105 °C) is the most damaging method as it expels structural water from C–S–H [6] and it also has a strong impact on ettringite which above approximately 70 °C dissolves and leads to monosulfoaluminate formation [7]. A number of less damaging methods are described in the literature; oven drying (at various temperatures <100 °C), desiccant drying over either silica gel or calcium chloride, D-drying, vacuum drying, solvent replacement and freeze-drying. While a number of studies [8,9] suggest that freeze-drying is the best method to preserve the microstructure, others assert that this method causes irreversible change of the pore structure [10,11] and also results in severe cracking [12].

Collier et al. [12] suggest that acetone quenching, in which water is displaced, thereby stopping hydration reactions but without dissolving significant quantities of cement components, was the better method. According to Konecny and Naqvi [13] solvent replacement best preserves the coarser pore structure, although freeze drying best preserves pores with radius smaller than 5 nm. Zhang and Scherer [14] recommend using isopropanol exchange followed by ambient drying as being the least destructive to the microstructure while also preserving the pore structure of the cement. Snoeck et al. [15] checked the influence of different drying techniques on the water sorption properties

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[*] Corresponding author. Tel. +44 1224274733.
E-mail address: isabelgalan@abdn.ac.uk (I. Galan).

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of Portland cement pastes concluding that isopropanol exchange followed by vacuum drying was the least damaging method. Feldman and Beaudoin [16] and Beaudoin and Tamtsia [17] compared methanol and isopropanol exchange, finding less damage when using isopropanol. It is probable that methanol interacts chemically with cement paste forming artefact solids such as methoxides [18–20].

Calcium sulfo-aluminate (C\$A) cements are receiving increasing attention since their manufacture produces less CO_2 than ordinary Portland cement (OPC) [21–24] and also due to their special properties which cannot be achieved with Portland cement, such as very high early strength. These binders may have quite variable compositions, but the clinkers normally contain more than 30 wt.% of ye'elimite, also known as Klein's compound or tetracalcium trialuminate sulfate ($C_4A_3\$$) [25] and, when mixed with calcium sulfate and hydrated, form much AFt (ettringite). Cements with large amounts of ye'elimite may have special applications such as achieving high strength development at early-ages [26,27] and as matrices for radioactive waste encapsulation [28,29]. Whatever the application, durability in the cement service environment is important and it is likely that durability is related to a number of factors, including pore structure and permeability.

Not much has been reported about drying damage to C\$A based pastes. Typically, the clinker is blended with 6–15% gypsum prior to hydration: AFm, ettringite and aluminium hydroxide are major constituents of hardened C\$A pastes. Zhang and Glasser [30] showed that ettringite (AFt) and monosulfate (AFm) phases in cement pastes are particularly sensitive to the drying method used. Both contain much molecular water and can lose crystallinity easily upon heating and/or drying. Not surprisingly, ettringite-rich cement pastes tend to be more sensitive than OPC pastes to the drying method used. While OPC pastes can also undergo drying damage, the problem becomes potentially more severe in the case of C\$A cements which contain high amounts of both AFm and AFt.

The stability of ettringite in terms of temperature and water vapour pressure has been reported [31]. Formation and decomposition of ettringite have been shown to be reversible with hysteresis. The initial decomposition product, a so-called meta-ettringite, has low crystallinity to XRD and a variable water content of 10–13 molecules per formula unit [32]. AFm can exist in different hydration states but the series based on C_4AH_{13} and including SO_4-AFm almost always predominates. Stability of AFm phases as a function of relative humidity (and thus drying technique) has also been reported [33].

The present paper reports new data and the impact of different drying methods in ettringite-based matrices.

2. Experimental procedure

2.1. Materials

The experimental work was carried out on hardened cement paste samples, all of which were cured for a minimum of 120 days at ambient and as such can be considered to be ‘mature pastes’. The range of samples used for the study included (i) hydrated ye'elimite mixed with gypsum, (ii) laboratory synthesized C\$A cement, (iii) commercial Chinese C\$A cement and (iv) an OPC sample which was used as a benchmark. Apart from these multiphase clinkers, phase pure ettringite (AFt) was also synthesized.

The compositions of the reactant systems are shown in Table 1. ‘Laboratory synthesized’ is defined as made in temperature controlled furnaces using laboratory-grade reactant chemicals. The specimens intended for measurement were cast in 25 × 25 mm cylinders and cured.

Ye'elimite and C\$A samples require higher water/binder ratios to completely hydrate and form hydration products with high water content such as ettringite. Specific values for each set of samples are explained in the following sections.

Table 1
Sample information.

Sample ID	Cement composition	Water/binder ratio
YE-1	Laboratory synthesized ye'elimite with 33% added gypsum	0.64
YE-2	Laboratory synthesized ye'elimite with 9% added gypsum	0.85
Lab-C\$A	Laboratory synthesized C\$A cement with 9% added gypsum	0.70
Com-C\$A	Commercial Chinese C\$A cement	0.70
OPC	CEM I 52.5R	0.32

Note: percentages of gypsum are expressed per sample (YE-1 contains 67% ye'elimite and 33% gypsum).

2.1.1. Ettringite

Phase-pure ettringite ($C_6A\$_3H_{32}$) was prepared according to the method reported by Balonis and Glasser [34]. Ettringite was made by mixing two solutions: the first solution from 6.65 g $Al_2(SO_4)_3 \cdot 18H_2O$ added to 100 ml ultrapure water and the second, by dispersing 4.44 g $Ca(OH)_2$ in 250 ml of ultrapure water. The two solutions were mixed under nitrogen and then diluted to 500 ml with additional reagent water to which 0.5 ml of 1 M NaOH had been added. The mixture was sealed in a high density polyethylene (HDPE) bottle and stirred vigorously on a 60 °C hot plate for 48 h. The purity was checked using XRD. The filtered precipitate was then dried using the range of methods described subsequently.

Water content calculation in ettringite samples

After drying, the residual water contents of AFt samples were calculated according to Eq. (1) from Zhang and Glasser [30]:

$$n_{AFt} = (1248.6 - 31.7 \times 18)(W - W_i)/18W_i \qquad (1)$$

where n_{AFt} is the number of water molecules left in AFt after drying (using the different methods explained in Section 2.2), W_i is the weight after ignition at 1050 °C for ~45 min and W is the weight before ignition. The results obtained are shown in Table 2.

2.1.2. Laboratory samples

Ye'elimite was synthesized by mixing stoichiometric amounts of previously dried $CaCO_3$, Al_2O_3 and $CaSO_4$ and heating the mix at 1250 °C for a total of 45 min with intermediate grinding every 15 min. Purity was confirmed by XRD and weight loss measurements to ensure that SO_3 was retained.

The ye'elimite was mixed with laboratory grade gypsum before adding water to form a paste. Table 1 shows the two gypsum/binder and water/binder ratios chosen. The “water” in the water/binder ratio does not include water contained in gypsum. The first mix (YE-1) had gypsum/binder 0.33 and water/binder 0.64; these values being similar to the theoretical amounts needed for the formation of ettringite (gypsum/ye'elimite 0.56 and water/ye'elimite ~ 1). The composition of the second mix (YE-2), with gypsum/binder 0.09 and water/binder 0.85, was chosen to form a physical mixture of AFm and AFt (see Fig. 5 pattern before drying for details: the AFm formed was sulfate-AFm: $C_4A\$H_{12}$).

Table 2
Water content of dried AFt. These samples were unsuitable for MIP.

Drying method	Drying time	H_2O content	Damage (based on XRD)
Saturated solution of $CaCl_2$	~2 months	31.8	No
D-dried	15 h	31.5	No
Oven dried at 40 °C	20 h	29.2	No
Oven dried at 60 °C	6 h	16.6	Yes
Oven dried at 60 °C	24 h	12.7	Yes
Oven dried at 105 °C	72 h	12.1	Yes