Cement and Concrete Research 84 (2016) 76–84

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

Assessment of early age properties of cementitious system through isopropanol–water replacement in the mixing water

X. Wang [a,b,*], A.B. Eberhardt [a], E. Gallucci [a], K. Scrivener [b]

[a] Sika Technology AG, Switzerland
[b] Laboratory of Construction Materials, Ecole Polytechnique Fédérale de Lausanne, Switzerland

ARTICLE INFO

Article history:
Received 29 September 2015
Accepted 15 February 2016
Available online 1 April 2016

Keywords:
Hydration (A)
Isopropanol–water replacement (C)
Thermal analysis (B)
Microstructure (B)
Mechanical properties (C)

ABSTRACT

In this study, a new method to assess early properties of cementitious materials by water-solvent replacement is investigated. Isopropanol was used to replace a part of mixing water of binder paste, limiting the maximum degree of hydration it can achieve. Results of four independent methods (calorimetry, thermo-gravimetric analysis, back-scattered electron imaging and mechanical strength) confirmed that the hydration reactions of the cement have been effectively delayed and suppressed due to the presence of isopropanol. A set of curves is obtained to identify the appropriate combination of i) the extent of water–isopropanol replacement and ii) time for achieving the targeted degree of hydration. This allows assessing material properties at low and/or desired degree of hydration with less time limitation during sample manipulation, achieving a better preserved and homogeneous microstructure. It has however to be noted that this method has limits with respect to direct moisture-transport related studies.

1. Introduction

In order to study the mechanical and physico-chemical properties of cementitious materials at very early age, samples with relatively low degrees of hydration are desirably obtained. However, considering the fast kinetics of the early chemical reactions and sample geometry, stopping the on-going hydration process is a delicate task and often produces sample comprising gradients of properties induced by gradients in the degree of hydration. This is especially true and critical for specimens which need time to be equilibrated at specific conditions prior to measurement (e.g. relative humidity for drying shrinkage). Consequently whatever the method used to stop the hydration one has to decide between two alternatives: either strongly limiting sample thickness to enable fast and homogeneous removal of water from the core of the sample with limited gradients of properties but with sample geometry being insufficient for mechanical testing of bulk properties. Or if sample sizes have to match geometry requirements for mechanical tests, gradients of bulk properties from the surface of the sample into the core would have to be accounted for (details in what follows). Therefore, a desirable approach for stopping cement hydration allows stopping the chemical reaction at a defined state and/or allows sample manipulation at minimum progress and does not produce gradients of properties.

Two common water removal techniques are widely used: drying and solvent exchange. However, both methods contain shortcomings with respect to the targets defined previously. Drying techniques include oven drying, vacuum drying and freeze drying etc. Oven drying involves sample brought into moisture equilibrium at temperatures between 60 °C and 105 °C at atmospheric pressure. Oven drying can remove effectively evaporable water (usually within 24 h), but it also damages the microstructure since it removes structural water as well from the hydrated cement paste (hcp) and alters the pore structure [1–4]. Microwave drying has been used for accelerated curing, but the rapid thermal expansion of the pore liquid could cause damage [5,6]. Vacuum drying is very slow therefore it cannot effectively stop early hydration at desired time [7]. Furthermore, this technique can induce stresses and micro cracks in the solid phase in hcp [2], and it removes significantly less water than oven drying at 105 °C [8]. Freeze drying [9] will also damage the pores of hcp producing cracks and alterations to the microstructure similar to oven drying [2].

In solvent exchange methods [1,10] water is replaced by organic liquids, such as acetone [11], ethanol, ether, methanol [12], and isopropanol [9,13,14]. The organic liquid could be adsorbed onto the surface of solid phase (for example hydrating C_3S) and cannot be completely removed without affecting the microstructure, since solvents can react with $Ca(OH)_2$ leading to aldol condensation [1,15]. Evidence was found [10] that there is a reaction between the solvents (particularly methanol) and cement paste during thermal analysis, but no indication of a reaction at room temperature. Knapen [12] reported on several solvents that replacement (including ethanol, ether and methanol) could result in a formation of carbonate-like phase due to an interaction upon heating during posterior analysis such as thermo-gravimetric analysis (TGA). According to Collier [11], the pores are better preserved when using acetone replacement comparing with other drying techniques.

---

[*] Corresponding author.
E-mail address: xiaomeng.wang@outlook.com (X. Wang).

http://dx.doi.org/10.1016/j.cemconres.2016.02.009

Table 1
Composition of the cement tested.

Component	Content [wt.%]	Component	Content [wt.%]
Alite	61.6	Periclase	0.3
Belite	12.8	Gypsum	0.4
Aluminate	10.0	Bassanite	2.0
Ferrite	6.7	Anhydrite	1.5
Lime	0.2	Calcite	4.4

Among all organic liquids used for solvent exchange, isopropanol seems to have less impact on the composition or microstructure. Konecny and Naqvi reported that isopropanol replacement best preserved the finest pores comparing to drying techniques [9]. Feldman and Beaudoin [14] found that methanol and isopropanol applied least stress to the microstructure of hcp. Feldman [13] also found that there was no interaction between isopropanol and hydrated cement while the methanol penetrates the C—S—H. Bach [16] found that the isopropanol exchange has less influence on the stability of ettringite comparing to the freeze drying. Zhang and Scherer [17] concluded that isopropanol exchange followed by ambient drying is the best known water removal method for preserving the microstructure with minimal effect on the composition of cement.

However, as indicated previously the application of solvent exchange to stop hydration is limited for small specimens of several millimetres to one centimetre. For larger specimen such as samples with standard dimension for conventional mechanical test, more time is needed for the solvent to penetrate from the surface to the core of specimen, which is undesirable at the very early age where hydration reactions are advancing rapidly. Furthermore, hydration reactions in the core of specimen will be stopped much later than those at the surface, resulting in a gradient of hydration state from the surface to the core of specimen.

In what follows a new technique is introduced that can be used to stop precisely cement hydration, in particular also at low degree of hydration. Moreover this approach also allows the production of large samples comprising no gradients of properties. Furthermore, hydration can be stopped or at least reduced to an extent that enables manipulation of large samples with immature and homogeneous degree of hydration, required for complete investigation of early age properties of cementitious materials.

Other than common water removal techniques to stop cement hydration reactions at early age, this study proposes a water exchange already at the stage of mixing, in particular, a defined amount of water is replaced by an equivalent volume of inert solvent before the mixing with the solid components (cement and/or sand) [18]. Isopropanol was chosen as the inert solvent to replace water due to its weak impact on the microstructure as mentioned above. Cement is then hydrated with the water–isopropanol aqueous solution. In this alternative system, less water is available for cement hydration and the quantity of available water determines the degree of hydration the cementitious system can achieve.

2. Description of experiments

Considering that the reactions and/or kinetics of the cement hydration in the aqueous solution of the organic solvent may be changed and that water available for cement hydration may differ from its molar ratio in the aqueous solution of the solvent, the methodology had to be refined towards evaluating time to achieve complete hydration as well as scaling water replacement and achievable degree of hydration.

Table 3
Density of the water–isopropanol mixture (in 100 ml aqueous solution).

Replacement ratio (by volume)	Unit	2.5%	5.0%	7.5%	10.0%	12.5%	15.0%
Volume of water	[ml]	97.5	95.0	92.5	90.0	87.5	85.0
Weight of mixture	[g]	99.2	98.8	98.4	98.0	97.7	97.4
Weight of isopropanol	[g]	1.7	3.8	5.9	8.0	10.2	12.4
Density of the mixture	[g/ml]	0.992	0.988	0.984	0.980	0.977	0.974

To do so, cement paste samples hydrated with mixed water–isopropanol aqueous solutions of various contents of isopropanol were produced. The influences of the isopropanol on the hydration kinetics of cement and on the hydration products were studied by isothermal heat conduction calorimetry and thermo-gravimetric analysis (TGA), respectively. The microstructure of the hcp samples hydrated with isopropanol was investigated by scanning electron microscopy (SEM) using back-scattered electrons (BSE). Mortar samples hydrated with water–isopropanol solution were prepared for mechanical properties measurement. Restrained ring tests for drying shrinkage were performed as well to study the combined influence of isopropanol on mechanical and transport properties of tested material.

2.1. Materials

The cement used in this study is the CEM-I 32.5 from Heidelberg Cement. The composition of the cement was determined by X-ray diffraction analysis (XRD), as shown in Table 1.

The principal properties of isopropanol are listed in Table 2 and compared to that of water. The density of aqueous solutions of isopropanol decreases slightly with increasing isopropanol content, as shown in Table 3.

2.2. Calorimetry, TGA and SEM on hydrated paste samples

Aqueous solutions with water–isopropanol replacement rate of 5%, 10% and 15% were prepared. Four groups of cement pastes were produced by mixing the cement with water and the three water–isopropanol solutions, keeping a liquid/cement weight ratio of 0.4. Fresh pastes were mixed at a speed of 1600 rpm for 2 min.

The heat released during the hydration of different pastes was measured by isothermal calorimetry (TAM Air), starting immediately after the mixing and up to 7 days. Approximately 10 g of fresh paste sample was used for each measurement.

Cylindrical paste samples (with the diameter of 27 mm and the height of 110 cm) hydrated with water and the aqueous solutions containing 5%, 10% and 15% of isopropanol were produced. After 12 h, 16 h, 24 h and 48 h of hydration, part of the samples were ground into powder for TGA while other samples were cut into slices with a thickness of 5–10 mm and transferred into isopropanol to remove residual water (common solvent exchange on reasonable sample geometry). After a vacuum drying for the removal of isopropanol, these specimens were

Table 2
Principal properties of isopropanol, from [17].

	Formula	Molecular occupational area	Density (20 °C)	Boiling point	Diffusion coefficient in water	Surface tension	Vapour pressure
		$[nm^2]$	$[g/cm^3]$	[°C]	$[cm^2/s]$	[mN/m]	[kPa]
Water	H_2O	11.4	0.9982	100	–	71.99	3.17
Isopropanol	$(CH_3)_2CHOH$	27.2	0.7855	82	2.02×10^5	20.93	6.02