

ASSESSING EARLY AGE PROPERTIES OF CEMENTITIOUS SYSTEMS BY WATER- ISOPROPANOL REPLACEMENT

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Abstract:

In order to measure properties of cementitious materials at the very early age, the hydration of the cement need to be stopped. This is a delicate task in all cases of demanding precise degree of hydration of the samples or the need to avoid gradients for certain properties induced during sample manipulation.

In this study, a new method to assess early properties by water-solvent replacement is proposed. Isopropanol (C₃H₈O) has been used to replace a part of mixing water of binder paste, limiting the maximum degree of hydration it can achieve.

Calorimetry and TGA results confirmed that cement paste samples hydrated with water-isopropanol released lower hydration heat and produced less hydration products. The microstructure of the samples has been investigated by SEM and no influence has been observed on the macrospores above 1 μm. The mechanical strengths of the mortar containing isopropanol reduced as the isopropanol content increased. A set of curves has been obtained to identify the appropriate combination of water- isopropanol replacement rate and hydration duration for a specific hydration degree.

The study proved that the isopropanol-water replacement method could effectively delay and repress the hydration process of cement so as to access the early hydration state of cementitious material. It has however to be noted that this method has limits with respect to direct moisture-transport related studies.

Introduction

In order to study the properties of cementitious material at the very early age, the hydration reactions of cement should be stopped at desired hydration degree. Capillary water in the fresh cementitious sample should be partially removed while the weak microstructure of the sample should be maintained. Drying and water-solvent exchange are the most used techniques for this purpose. Drying can remove water efficiently but will induce inevitable alternation on the microstructure [1] [2], while the water-solvent exchange can better preserve the pore structure [1] [3] [4] [5].

Other than common techniques, this study proposes a water-solvent replacement already for the mixing of the binder paste. In our method the solvent replaces a certain volume of mixing water while the volume ratio of solid and liquid remains unaltered; the reduction of water available for cement hydration effectively reduces the degree of hydration the system can achieve. Isopropanol is chosen as the inert solvent to replace water due to its weak impacts on the microstructure [6].

Description of experiments

The cement used in this study is CEM-I 32.5 from Heidelberg Cement. Paste samples have been produced at a solid to liquid volume ratio of $v_{\text{solid}}/v_{\text{liquid}}=0.8$ and hydrated with water or 5-15 vol.-% aqueous solution of isopropanol. The influence of the isopropanol on the kinetics and the degree of cement hydration has been studied by Calorimetry and TGA, respectively. The microstructure of the samples has been investigated in the SEM using BSE. Degree of hydration was estimated through different analysis: (i) comparing heat release and Portlandite content of hydrated samples to the respective theoretical maxima derived from thermodynamic modelling [7] [8]; (ii) image analysis of SEM results, i.e. content of unhydrated cement and (iii) scaling compressive and tensile strengths of mortar (prisms 4x4x16cm³) paste comprising paste with $v_{\text{solid}}/v_{\text{liquid}}=0.8$ and 58 vol.% CEN sand 0-2mm.

Result and analysis

- Hydration kinetics and degree of hydration

Figure 1 presents the heat released by the samples hydrated with water and aqueous solutions of isopropanol, measured by isothermal heat flow calorimetry. Overall, samples containing isopropanol release less heat than the reference sample indicating reduced hydration with increasing isopropanol content (reduced heat flow in Figure 1a and total heat in Figure 1b). Figure 1a shows that the appearance of the characteristic maximum of heatflow is delayed with increasing content of isopropanol, indicating a

slowdown of hydration reactions. From the results of isothermal heat flow calorimetry one can take that the hydration reactions of the cement have been delayed and repressed due to the presence of isopropanol.

Figure 2 illustrates TGA results for samples containing up to 15 vol.-% of isopropanol, hydrated for 24 hours. TGA raw data were normalised to residual weight of unhydrated cement at 1000°C. This returns both physically and chemically bound water of the hydrated samples and allows correction for carbonates either already present in the unhydrated cement or coming from carbonation during manipulation. From the derivative weight loss peak at about 450°C Portlandite content was obtained and corrected in case of carbonation during sample manipulation (peak at about 700°C for CaCO₃). Overall, total bound water of the samples decreases and Portlandite decreases with increasing isopropanol content. Again, this indicates a reduced degree of hydration due to the presence of isopropanol.

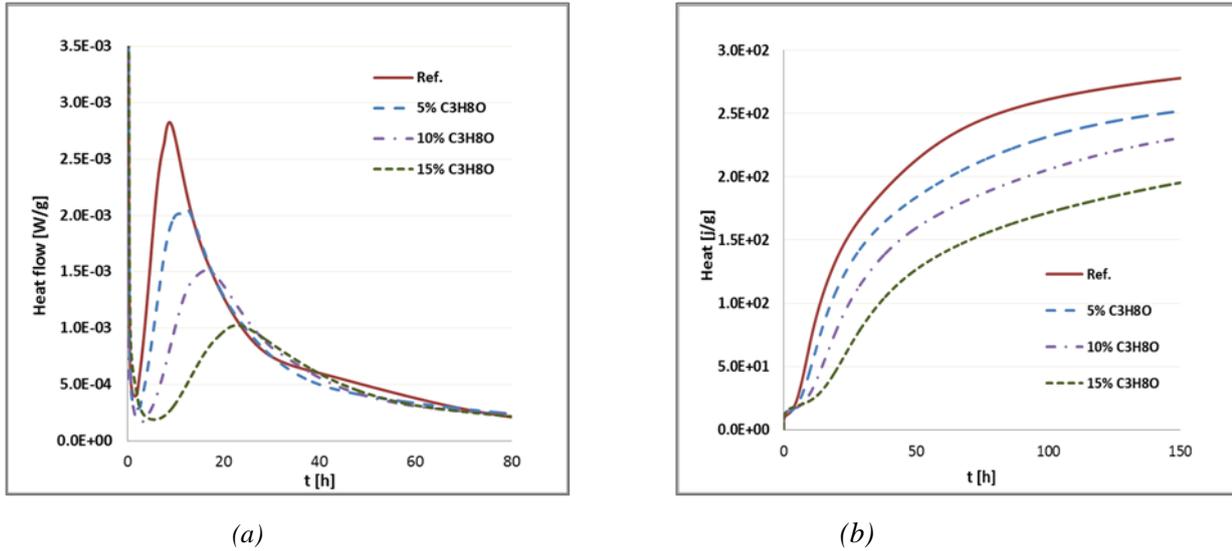


Figure 1. Normalized heat flow (a) and total heat (b) released during hydration of the paste samples hydrated with mixed solutions containing 0% to 15% of isopropanol (with liquid/cement volume ratio of 0.4).

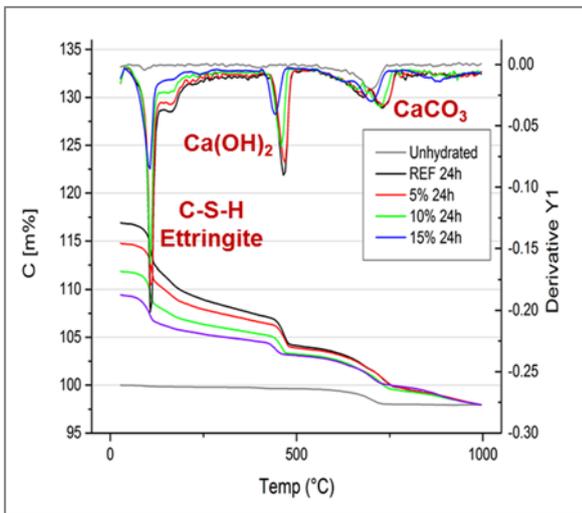


Figure 2 Influence of isopropanol on the hydration product (24h), measured by TGA.

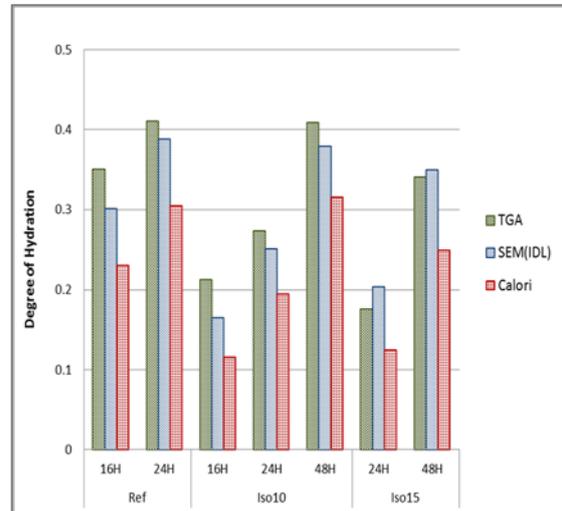


Figure 3 Comparison of the hydration degree estimated by TGA, SEM and Calorimetry

The hydration degrees quantified through calorimetry, TGA and SEM are shown in the Figure 3. It contains data on samples hydrated up to 48 hours. Despite some variation one can deduce that the water-isopropanol replacement can effectively delay and repress the hydration reactions.

- Microstructure

The microstructure of the samples has been studied using the Backscattered electron (BSE) imaging. Figure 4 illustrates the microstructure of three groups of samples with similar hydration degree of 13%, 22%

and 30%, respectively. Each group contains two samples with different mix and different hydration time. The three groups of images illustrate well the evolution of the microstructure: the presence of amorphous hydration products in the beginning, the appearance and the development of the shell surrounding the anhydrous cement grain, the filling of the pores by the outer product [9]. The images within a group are showing similar microstructure, even though the mixture and the hydration time of the samples are different.

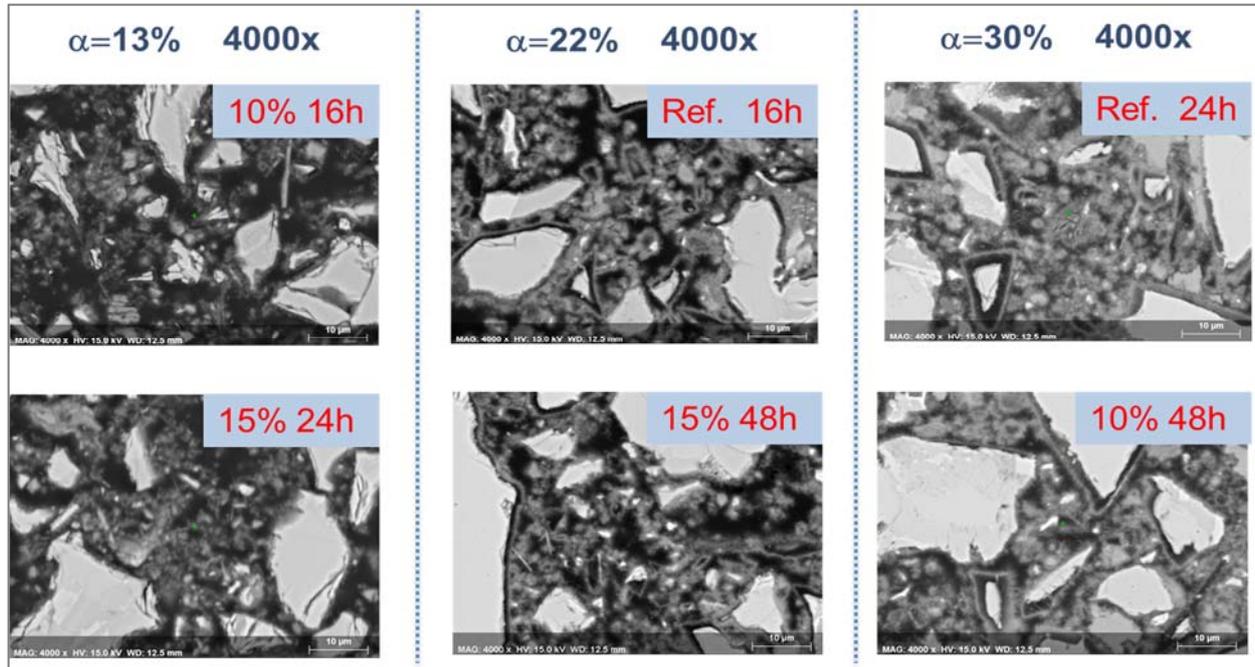


Figure 4 Evolution of microstructure of the samples hydrated with isopropanol, at different hydration state. Images obtained by BSE. The hydration degree for the three groups is respectively 13%, 22% and 30%.

- Mechanical properties

The compressive strength and tensile strength of mortars was measured at 105 days and 287 days. Both tensile and compressive strengths reduced. Relative strength reduction (Figure 5) was used to scale degree of hydration achieved after 105 days and 287 days of hydration respectively (Figure 6), based on the hypothesis that the hydration degree is about 90% or 95% respectively.

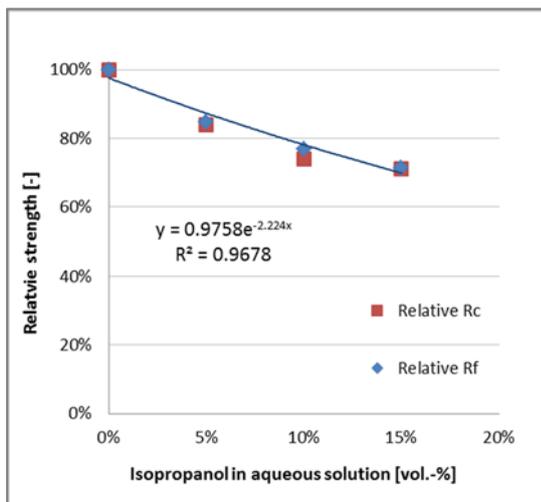


Figure 5 Relative strengths (compressive and tensile) of the samples hydrated with isopropanol, at 105 days

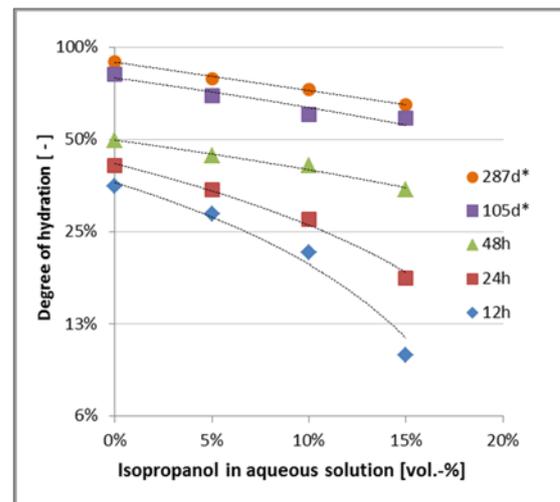


Figure 6 Curves set for hydration degree estimation based on TGA results and compressive strength test.

Discussion & Conclusions

Figure 6 shows a set of curves of hydration degree as a function of hydration time and isopropanol content, deduced from the experimental data. Results of three independent methods let us conclude that the hydration reactions of the cement have been delayed and repressed due to the presence of isopropanol. This comes certainly from the reduced volume of water but also from its much reduced activity, considering complete miscibility and azeotropic properties of isopropanol aqueous solutions. The latter may be responsible for the disproportional reduction (about factor 2) of the final degree of hydration. Moreover, reduced water activity should impact on hydration kinetics. In regard to the further constriction of the pore solution with on-going cement hydration, water activity should increasingly reduce and hydration reactions slowed down. This bears the advantage for targeting low degree of hydration using high isopropanol content that very early changes in the degree of hydration will become marginal and samples can be obtained.

It has however to be noted, that due to the lower surface tension of isopropanol, capillary as well as disjoining pressure in the cementitious matrix will be altered, that for example may affect moisture-transport [10] or drying shrinkage [11]. This requires samples to be carefully dried to remove isopropanol and resaturated with water before for example measuring drying shrinkage.

This study proposed an alternative method to precisely stop cement hydration at desired and/or low degree of hydration. While the idea is based on common water-solvent exchange, the alternative consists of hydrating cement with aqueous solution of isopropanol (i) at defined isopropanol content for (ii) a defined time. With the results at hand one can identify the appropriate combination of water- isopropanol replacement and hydration time in order to obtain the samples at target degree of hydration.

This allows assessing material properties at low and/or desired degree of hydration with less time limitation during sample manipulation, keeping a better preserved and homogenous microstructure.

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