Effect of Soaking Time in a Solvent on Hydration Stoppage of Cement

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INTRODUCTION

In order to study the composition and microstructure of any hardening cementitious material, the ongoing hydration must be stopped [1]. At early hydration stages, the hydration stoppage is needed to suppress the further progress of hydration [2], allowing the analysis of several properties and characterization of the same sample at the same hydration age and therefore, at the same degree of hydration [3, 4]. After stopping hydration, the samples can receive additional treatments (crushing, cutting, drying, putting under vacuum) with no further progress of hydration [3]. At longer hydration times (longer than 1 month), since the progress of hydration is very slow, the hydration stoppage is performed to fulfill a requirement of several materials characterization techniques, such as thermogravimetric analysis, infrared and Raman spectroscopy, mercury intrusion porosimetry, scanning electron microscopy [1, 2], nitrogen sorption/desorption and transmission electron microscopy [3]. Even for techniques that do not specifically require hydration stoppage, such as X-ray diffraction and nuclear magnetic resonance, the process is usually done since it enables sample storage, helps to minimize carbonation due to the low relative humidity after stoppage and allows the characterization at the same degree of hydration [2].

The main goal of the hydration stoppage is the removal of water inside the pores without altering the hydration products and preserving the microstructure [2]. Commonly used hydration stoppage methods include direct drying techniques: oven drying, vacuum drying and freeze-drying [2 ,4] and solvent exchange methods: free water is replaced by an organic solvent miscible with water (first step) and the solvent is removed by evaporation (second step). Commonly used solvents are isopropanol, ethanol, methanol and acetone [4]. In case of a solvent exchange method, the main critical factor influencing on the hydration stopping efficiency is solvent soaking time, which is expressed through (Eq. 1):

$$t_E = \frac{a^2}{D} \tag{1}$$

where t_E is equilibrium time, a is the characteristic dimension and D is the diffusivity.
The process is modeled as diffusion from a sphere into a surrounding bath. If the volume of a bath is much greater than that of the sample, then the composition of the bath can be assumed to be constant (e.g., pure isopropyl alcohol) [3]. Using the diffusion equation for a sphere and a typical value of diffusivity for alcohol in cement paste ($D = 10^{-11}$ m^2/s), the time to replace the water with 99.9% isopropyl alcohol in a granule of cement paste with a radius of 1 mm would be roughly 18 hours [3]. In [5], using the same diffusion coefficient and the same thickness the time for ion diffusion starting to have effects on ion concentration throughout the specimen is calculated as less than 1 hour. The value of 15 min suggested in [4] for the same particle size.

Since there is no consensus regarding the required time for the complete stopping of hydration further research is needed. The current paper aims to investigate the influence of the soaking time in a solvent on the mineral composition and pore structure of the hydrated cement paste.

MATERIALS AND METHODS
Materials
CEM I 52.5N supplied by Nesher Cement, Israel is used for this study. Its mineral and chemical composition are presented in Table 1.

Table 1. Mineral and chemical composition of cement.

Mineral composition	wt.-%	Chemical composition	wt.-%
Alite	61.02	CaO	62.16
Belite	12.95	SiO_2	19.02
C_3A cubic	5.86	Al_2O_3	5.42
C_4AF	12.42	Fe_2O_3	3.82
Bassanite	1.87	MgO	1.31
Anhydrite	0.28	TiO_2	0.53
Portlandite	1.83	K_2O	0.37
Calcite	2.25	Na_2O	0.22
Arcanite	0.97	P_2O_5	0.4
Aphthitalite	0.55	Mn_2O_3	0.05
		SO_3	2.48
		IR	0.76
		FL	2.8
		LOI total	2.93

Preparation of samples
Cement was mixed with water in a pan mixer and then cast in molds 2.5 x 2.5 x 2.5 cm. The water to cement ratio was 0.40. After 24 hour hydration in sealed molds, samples were immersed in water for the additional 6 days. Then the cubes were crushed manually by a mortar and pestle and sieved. Particles that passed a sieve 4.75 mm and retained on a sieve 2.36 mm were immersed with isopropyl alcohol (IPA) for ¼, ½, 1 and 24 hours. Immediately after removing the samples from the solvent they were placed in a vacuum oven at 40 ° C for 3 hours.

X-ray diffraction (XRD)
The X-ray diffraction analysis was performed using a Malvern PANAlytical EMPYREAN X-ray diffractometer with the following configuration: an X-ray source was CuKα1,2 (λ= 1.5408 Å) with X-Ray generator operated at a voltage of 45 kV and a current of 40 mA; a Goniometer radius was 240 mm; the incident beam optics included 10 mm mask, 0.04 rad Soller slit along with ¼° divergence and 1° anti-scatter fixed slits; the diffracted beam optics consisted of 8 mm anti-scatter fixed slit and 0.04 rad Soller slit. The detector was PIXcel 3D detector used in 1D continuous scan mode. The scan was performed using Brag-Brentano geometry, between 10 and 70 °2θ for unhydrated cement and between 5 and 70 °2θ for hydrated cement paste. After stopping hydration, configuration was changed because of different scanning angles. Also time step, step size and total time were different between cement and cement paste. Timestep of 80.32 s along with a step size of 0.013 º2θ were used resulting in a total measurement time of 25.22 min. For cement paste, one program for all samples was applied because the same intensity and range of scanning angles were used. The quantitative analysis was performed by means of Rietveld refinement using HighScore Plus software. The analysis of the amorphous phase was performed using the external standard method. Fully crystalline alumina (α-Al_2O_3) was used as a standard.

Mercury intrusion porosimetry (MIP)

Total pore volume and pore size distribution of hardened pastes were determined using Mercury Intrusion Porosimeter Quantachrome PoreMaster-60 with a pressure up to 60000 psi (400 MPa). The following parameters were taken in calculations: Hg surface tension – 0.485 N/m, Hg contact angle - (I) 140°. Mercury volume was normalized by the sample volume. MIP dilatometer was full of the sample as much as possible for a constant sample mass, increasing the number of pieces of the sample increases its surface-to-volume ratio, which reduces boundary effects.

RESULTS

Results of X-ray diffraction and MIP are presented in Figure 1 (a, b). It can be seen that the duration of a solvent replacement has a significant influence on the phase development (Fig. 1 (a)). When the sample is immersed in a solvent for less than 30 min the reduced amount of ettringite is observed, further soaking leads to the stabilization of ettringite. After 15 min of soaking the total amount of belite is the highest and further keeping in a solvent induces its reduction. This process is accompanied by a slight increase in portlandite content. However, after 60 min of presence in a solvent belite remains stable, while portlandite is slightly decreased, which in turn is related to an increment of calcite amount. The increasing of calcite is related to the carbonation of portlandite which is consistent with results published earlier [3]. The only phase remaining stable regardless of the soaking time is alite. It worth noting that phase development is observed only at short (15 min) or prolonged (24 hours) soaking time, i.e. apart this period most of the phases are stable and stopping of hydration might be considered sufficient. An unusual increase of ettringite and decrease of belite amounts might be connected to a specific interaction with isopropyl alcohol and/or time of soaking. In case of ettringite its reduction after short soaking time seems to be induced by a partial loss of ettringite water. Concerning the reduction of belite content, there is no certain explanation except interaction with a solvent which has to be investigated in detail.
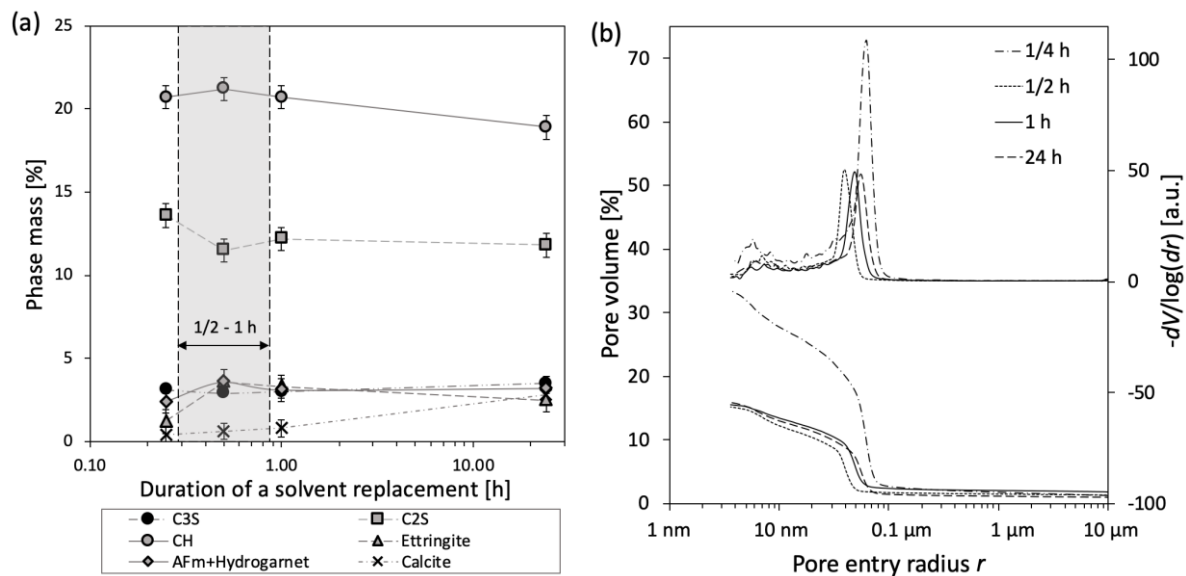

Figure 1. Influence of duration of a solvent replacement on: (a) mineral composition; (b) pore size distribution of hardened cement paste.

The total pore volume is significantly higher when cement paste is subjected to a solvent for 15 min (Fig. 1 (b)). While increasing soaking time up to 30 min reduces pore volume. Further curing has no distinguished influence on the total percolated pore volume. Irregularly high

pore volume after the short immersion in a solvent is owed to the incomplete water replacement from a pore solution and further damage of pore structure during drying stage. The paste immersed for the shortest time in a solvent had also the highest critical pore entry radius. However, after 30 min of soaking cement paste had the lowest entry radius which in turn begins to increase slightly with the increase of the duration of immersion in isopropyl alcohol. This means that longer solvent replacement may also adversely affect the pore structure of a sample.

CONCLUSIONS

In this study hydration of a hardened cement paste was stopped by a solvent replacement method. Samples were immersed in isopropyl alcohol for ¼, ½, 1 and 24 hours. By means of XRD and MIP analyses, the mineral composition of samples and its pore structure was investigated as a function of soaking time in the solvent. After 15 min of soaking, the reduced amount of ettringite and increased amount of belite were detected, whereas total pore volume was abnormally high. The increasing of soaking time to 1 h led to the stabilization of phases. Yet, pore entry radius continuously increased with soaking time after ½ hour. Further increase of solvent replacement time up to 24 hours resulted in notable carbonation of cement paste and an increase of a pore entry radius.

The optimum time of a solvent replacement might be considered as a period when the main mineral phases and total percolated pore volume preserved unchanged. Based on the obtained result this time interval is between ½ and 1 hour.

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