Role of alcohol-ethylene oxide polymers on the reduction of shrinkage of cement paste

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ABSTRACT

Concrete drying shrinkage is a major practical problem, but it can be ameliorated by means of "shrinkage-reducing agents" (SRAs). Water vapor sorption isotherms and low temperature DSC measurements suggest that alcohol-ethylene oxide polymers (AEOPs) with a better hydrophilic-lipophilic (HL-) balance are present in meso-pores in which water molecules evaporate from 75% RH to 40% RH. Short-term drying shrinkage measurements show that the better HL-balanced AEOPs reduce irreversible shrinkage, which occurs mainly from 75% RH to 40% RH during the first drying. Based on the similarity between corresponding RH regions, it is concluded that the better HL balanced AEOP in relevant meso-pores hinders agglomeration of C-S-H during the first desorption to mitigate the irreversible shrinkage and reduce the first drying shrinkage.

1. Introduction

Shrinkage reducing agents (SRAs) are admixtures, first developed in Japan [1], that are used to reduce the drying shrinkage and cracking of concrete. Shrinkage-induced cracking is unsightly and can also reduce concrete durability by various mechanisms, e.g. by allowing intrusion of chloride ions and carbon dioxide gas, which promote steel corrosion in reinforced concrete. SRAs are often used to mitigate cracking, but the mechanism of shrinkage reduction is still poorly understood.

The first generation of SRAs were moderately water-soluble non-ionic organic solutes known to reduce the surface tension of water [2]. However, it was noted that it was usually necessary to use them at aqueous concentrations well above their apparent "critical micelle concentration" (CMC) in order to obtain the maximum effect on reducing free drying shrinkage of hardened cement pastes (hcp) [3,4]. These experimental results threw doubt on the idea that SRAs work solely via a capillary tension mechanism [5]; despite intensive additional research [5–12], their mechanism remains poorly understood. Recently, we showed that SRAs reduce the unrestrained drying shrinkage of hcp mainly during the first desorption, but have little impact on further length changes during rewetting and further drying after sufficiently long process times for altering the calcium silicate hydrate (C-S-H)[1] [13]. In cases of short term drying and wetting cycles of the mortar with lower water to cement ratio, the continuous impact was confirmed to show contrary behavior [12]. The difference might be explained by a

difference of drying period for C-S-H and a difference in amount of outer C-S-H which has large impact on the irreversible shrinkage. It was also shown that portlandite crystals in hcp can be strongly modified by the use of certain SRAs [7,12,13], which seems consistent with observations that simple alcohols modify the morphology and increase the specific surface area of portlandite produced by slaking quicklime, apparently by preferential adsorption on the 001 crystal face, where alkoxide (-OR) groups can partially replace hydroxide (-OH) groups [14,15]. It is thus conceivable that certain SRAs might also modify the nanostructure of calcium silicate hydrate (C-S-H), possibly by interaction with some of its –OH groups [16]. C-S-H is a highly basic solid-solution phase of widely-varying composition, thought to be composed mainly of tobermorite-like anionic basal layers, with associated calcium cations for charge balance [17–19]. The C-S-H produced during cement or C_3S hydration is formed at a high pH from solutions slightly super-saturated with respect to portlandite. It has a very disordered structure [20,21] with many Ca-OH groups [16], which could be partly alkylated to give some Ca-OR groups.

Based on many such prior studies, a new model for the structure of the "wet" C-S-H initially formed in Portland cement hydration was recently proposed by Gartner et al. [22]. We will refer to it here as the "GMC" model. In this model, freshly-precipitated C-S-H is composed of tobermorite-like basal layers containing primarily dimeric silicate anions bonded to both sides of basal CaO sheets. The negative charge of the simplest basal sheet repeating unit, ($[Ca_2Si_2O_7]^{2-}$), is initially

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balanced by fully-hydrated calcium cations, either divalent (Ca^{2+}) or univalent ($CaOH^+$), and it is assumed that each such cation holds at least 6 oxygen atoms in their inner coordination shell. Thus, fresh wet C-S-H can be represented as a solid solution between the end members $([Ca_2Si_2O_7]^{2-}\cdot[Ca(H_2O)_6]^{2+})$ ($=C_3S_2H_6$) and $([Ca_2Si_2O_7]^{2-}\cdot2[Ca(OH)(H_2O)_5]^+)$ ($=C_4S_2H_{11}$). If γ represents the fraction of the low Ca/Si end members of this solid solution, it can readily be seen that for $\gamma = 0.4$, the composition of the solid solution becomes $C_{1.7}SH_4$. This composition is the same as that assumed by Young and Hansen [23] to account for the minimum amount of water required for complete cement hydration.

In the GMC paper [23], it is hypothesized that the organic molecules used as SRAs have a tendency to adsorb weakly onto C-S-H basal surfaces, partially shielding the silicate groups and thus inhibiting their reaction with initially hydrated charge-balancing calcium ions, while there are unsuccessful attempts to measure adsorption of non-ionic surfactants on C-S-H [24–26]. This prevents formation of calcium bridges between silicate groups brought into close proximity by capillary forces during drying. However, the roles of the different structural elements in SRA molecules are not yet well understood. In the present work, a set of 15 alcohol-ethylene oxide polymers (AEOPs) was obtained by varying the two main molecular structural elements: alcohol (alkyl group) type and poly-EO chain length. The relative effects of these changes on the hygral equilibria and drying shrinkage of hcp was then studied with the objective of determining the relationship between molecular structure and SRA performance.

2. Experimental method

2.1. Materials

We used a white cement provided by Taiheiyo Cement Corporation, the same as that used in two previous papers [27,28]. Its density was 3.05 g/cm^3, and its Blaine specific surface area was 349 m^2/kg. The chemical composition, and the mineralogical composition determined by a powder X-ray diffraction (XRD)/Rietveld method, are shown in Table 1 and Table 2, respectively.

The 15 AEOP molecules used in this work, shown in Table 3, were synthesized by Dr. Akihiro Furuta of Takemoto Oil & Fat Co. Ltd., Japan. They were derived either from water (C0(=H)) or 3 different aliphatic alcohols: ethanol (C2), butanol (C4), and 2-ethylhexanol (C8). The number of polymerized ethylene oxide (EO) units per molecule was 0 (for the simple alcohols), 2, 20, or 100. The surface tension of AEOP solutions whose concentration is equivalent to the initial mixed condition was measured using the Wilhelmy method. The results are summarized in Fig. 1.

Cement paste samples were made from white cement and de-ionized water, with 2% added AEOP by mass of cement replacing water, such that the (water + AEOP)/cement ratio was 0.55 by mass. The densities of the various AEOPs are different; therefore, the theoretical volumetric ratios of liquids to solids were different. However, a 3.46 mass% AEOP concentration solution is almost 1.0 g/cm^3, and the initial spaces between cement particles could be comparable. There is a possibility that the degree of hydration will be affected by this difference of available space for precipitation due to the presence of AEOP molecules. The experimental results will be discussed with respect to phase composition. For AEOPs with 20 or more EO groups, excessive volumes of air were entrained during standard mixing, so a vacuum mixer (Renfert Vacuum mixer twister II) was used. A 400 mL sample of cement paste was mixed for 1 min, scraped from inside the mixer, and then followed by remixing for a further 3 min. To minimize segregation, the paste was remixed manually every 30 min up to 6 h, after which it had a creamy consistency. It was then cast into a set of 3 × 13 × 300 mm slab molds, which were covered by wet paper and a poly-vinylidene-dichloride film wrap to avoid water loss from the specimens. The covered molds were stored in a thermostatic chamber at 20 ± 1 °C. The slabs were demolded after 4 days, cut into 100 mm lengths with a precision cutting machine, and then immediately stored in aluminized polymer bags for 28 days after mixing. The samples were cut using water cooling to avoid a heat impact on the samples. Due to the usage of water cooling, some of the SRA can be washed out of the sample; however, this region is only 1–2 mm from both edges, which does not have a significant impact on length change measurements. After this initial curing regime, the samples were dried for 8 weeks at 60% RH. Further details of this procedure are given in the section on long-term drying experiments.

2.2. Measurements

The phase compositions of cement paste samples were determined by XRD/Rietveld analysis. Samples sealed for 28 days, which corresponds to the beginning of drying, were submerged in acetone for 6 h, and then dried under vacuum for several minutes with an aspirator. The specimens were then stored over a saturated LiCl solution at 20 ± 2 °C for 2 weeks. The protocol for the XRD/Rietveld analysis are the same as those described in ref. [27,29]. Three samples were measured for each condition.

Thermogravimetric analyses were conducted on ~20 mg samples from the 28-day sealed samples. Dynamic TG measurements were conducted under N$_2$ gas flow from room temperature to 1000 °C, including a 7-hour holding period at 105 °C. The mass change from the end of the 7-hour 105 °C holding period up to 550 °C is referred to here as "chemically bound" water, and the mass change from room temperature to the end of the 7-hour 105 °C holding period is referred to here as "evaporable water." Evaporable water was referenced to the mass of the sample at the end of the 7-hour 105 °C holding period, and chemically bound water was referenced to the mass after heating to 550 °C. Other types of thermogravimetric analysis were conducted to show differential thermal gravimetry (DTG) for sealed samples at 28 days. A measurement was taken under N$_2$ gas flow with a 10 °C/min temperature ramp, and this method was applied to the sample at 28 days.

Water vapor sorption isotherm (WVSI) measurements were conducted by the volume method (or manometric method) using a water vapor sorption analyzer (Hydrosorb 1000, Quantachrome). The samples were ground in a ball mill, and ~20 mg samples of powder with a particle size in the range of 25–75 μm were used for the analysis. The particles were extracted using sieves with 25 μm and 75 μm openings. The parameters of the measurements were a pressure tolerance of 0.05 mm Hg and a time tolerance of 120 s. The measurement points on the adsorption and desorption branches were at $p/p_0 = 0.05$ intervals up to 0.95 and ended at 0.98 (RH = 98%). For pre-treatment, the

Table 1
Chemical composition of white cement by X-ray fluorescence elemental analysis[a].

LOI (%)	Chemical composition (mass%)											
	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	Na$_2$O	K$_2$O	Ti O$_2$	P$_2$O$_5$	MnO	Cl$^-$
2.93	22.43	4.67	0.16	65.69	0.98	2.51	0.00	0.07	0.17	0.03	0.00	0.00

[a] Conducted by Taiheiyo Cement Corporation.