Control of Drying Shrinkage of Magnesium Silicate Hydrate Gel Cements

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Abstract. Cracks were observed when the magnesium silicate hydrate gel cement (prepared by 40% MgO/ 60% silica fume) was dried. This drying cracking is believed to be caused when unbound water evaporates from the binder. The shrinkage upon forced drying to 200 °C of mortars made up from a reactive magnesium oxide, silica fume and sand was measured using dilatometry. The magnitude of the drying shrinkage was found to decrease when more sand or less water was added to the mortars and can be as low as 0.16% for a mortar containing 60 wt% sand and a water to cement ratio of 0.5, which is of a similar order of magnitude as observed in Portland cement based mortars and concretes. A simple geometrical interpretation based on packing of the particles in the mortar can explain the observed drying shrinkages and based on this analysis the drying shrinkage of the hydration products at zero added solid is estimated to be 7.3% after 7 days of curing.

Introduction

Previous work had shown that blends of a reactive magnesium oxide (MgO) and silica fume react to form a magnesium silicate hydrate gel (M-S-H) and that in contrast to claims made in the cement literature, this leads to mortar strengths not dissimilar to what can be achieved with Portland cement. Since the pH of these cements, pH~9-10, is markedly lower than that observed in blends based on Portland cement, this cement could find applications where a lower alkalinity is desirable such as in immobilisation of heavy metals for waste treatment.

Very little is known about the properties of M-S-H gel based cements and the successful application of new cements requires that judgements can be made about the durability of the products. One possible durability issue is the dimensional stability upon drying and wetting. Indeed, in early experiments it was observed that drying lead to substantial cracking. Trial experiments to overcome the cracking problem showed that adding fine sand reduced the dimensional changes upon drying sufficiently to suppress the cracking. The aim of the work reported here was therefore to characterise the drying shrinkage and to investigate how addition of fine sand modifies the dimensional stability.

Experimental Methods

Blends of a commercially available MgO (MgO, MagChem 30, M.A.F. Magnesite B.V., The Netherlands) silica fume (SF, Elkem Materials Ltd) and a milled sand were prepared. Previous work had shown that blends of 40 wt% MgO and 60 wt% silica fume react fully to produce pure M-S-H gel with an average formula of

Therefore this blend was selected for further study and a range of mortars with different sand contents and water to cement ratios (w/c) were prepared as detailed in Table 1. In all cases 1wt% sodium hexametaphosphate was added as a dispersant to improve the rheology of the pastes. Samples were cast in steel moulds (10 mm × 10 mm × 60 mm), removed from the moulds after 1 or 2 days, and then allowed to cure further in a closed box with excess water at the bottom to minimize drying of the samples.

Drying shrinkage was determined after 1 or 2 days depending on the solidity of the sample and then at 7, 14 and 28 days of curing by heating the samples rapidly (20 °C min⁻¹) to 200 °C in a dilatometer so that the length of the samples could be monitored continuously during the heating.

Table 1: Mortar Formulations (w/c : Water to Cement Ratio, SF: Silica Fume).

No.	Cement MgO/SF wt%	Sand wt%	w/c	MgO g	SF g	sand g	water g
1	100	0	0.5	40	60	0	50
2	80	20	0.5	40	60	25	50
3	60	40	0.5	40	60	67	50
4	40	60	0.5	40	60	150	50
5	100	0	0.8	40	60	0	80
6	80	20	0.8	40	60	25	80
7	60	40	0.8	40	60	67	80
9	40	60	0.8	40	60	150	80

Results

Fig.1 illustrates how the length of the samples changes during heating. Although the temperature was programmed to rise to 200 °C only, a small overshoot occurred leading to temperatures of 230 °C being reached. It is clear that the samples start shrinking around 85 °C and that the shrinkage appears to occur in 2 steps: a first one largely complete by 165 °C and a clear further one above 200 °C.

Fig.1. Examples of the Changes in Length Observed during Heating for a Mortar with 40 wt% Sand and a Water to Cement Ratio of 0.8 after 1 Day of Curing.

Fig.2. Step Shrinkage Observed during drying by Heating to 200 °C as a Function of the Volume Fraction Sand in Mortars with a Water to Cement Ratio (w/c) of 0.5 and 0.8 after 7 Days of Curing.

The total shrinkage after 7 days of curing is plotted in Fig.2 as a function of the volume fraction sand added to the mortars. In line with work on other mortars and concretes, adding sand, which itself will not shrink when the mortar is dried, reduces the drying shrinkage, and mortars with more water shrink more than mortars with less water for the same volume fraction of sand. The drying shrinkage of mortars without sand is very high, but a drying shrinkage of 0.16% as observed for the mortar with 60 wt% sand and a water to cement ratio of 0.5, is of the same order of magnitude as what is observed for cement mortars and concretes[1-3].

Discussion

The first shrinkage step can be attributed to the loss of water between the particles, whereas the second step is probably due to the M-S-H gel loosing water from within its structure. This can be deduced from the TGA on M-S-H gel, which shows that the water is lost in three steps:

The higher shrinkage for mortars with a higher water to cement ratio is in agreement with what is normally observed for cements and concretes[4] even though some authors believe the w/c ratio to be less important than often stated[5]. The observation that adding more sand reduces the shrinkage can be easily understood since the sand is not involved in the hydration reactions and will not shrink upon drying.

Fig.3. Comparison of the Experimentally Observed drying Shrinkage with the Predictions of a Simple Geometrical Model Assuming the Drying Shrinkage of the Hydration Products is 7.3%.

In terms of quantifying the shrinkage, much of the work in the literature focuses on predicting the long term drying shrinkage from early measurements, see e.g.[6, 7]. However, there are also microstructural models. The Hansen model[8] considers aggregates in concrete to act as a constraining factor to a shrinking matrix. As similar approach was used by Grassl, Wong and Buenfeld[9] in their model for the effect of aggregate size and volume fraction on shrinkage cracking. However, in such models the shrinkage only approaches zero when the volume fraction aggregate tends to 1. This does not agree with the results obtained here as the drying shrinkage tends to zero when less than half of the volume is sand. Hence, the much smaller size of the sand particles relative to the aggregates in concretes, modifies the way in which it interacts with the cement matrix.

Furthermore, plotting the shrinkage as a function of the volume fraction of all solids, v_s , rather than the volume fraction of sand, see Fig.3, causes the results for both water contents to reduce to a single trend, which shows that this is the correct normalising factor. Extrapolation of the results now shows that the shrinkage will reduce to zero when the volume fraction of solids in the paste is about 0.68.

Conclusions

The drying shrinkage of mortars made by blending MgO, silica fume, sand and water was higher when the water content was higher and/or the sand content lower, which is entirely consistent with observations for mortars based on Portland cement. Adding 60 wt% sand to a mortar with a water to cement ratio of 0.5, reduced the drying shrinkage to 0.16%, which is similar to Portland cement.

It was shown that the magnitude of the drying shrinkage depends on a characteristic minimum inter-particle distance in the paste and that therefore the shrinkage is governed by the volume fraction of solids in the paste. Moreover, the overall drying shrinkage of aged samples is limited to the shrinkage of the hydration products between the original particles. For the magnesium silicate hydrate studied here, extrapolating the results to zero solids in the paste suggests that the drying shrinkage of the hydration products amounts to 7.3% at 7 days of curing.

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