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Hydration of mineral shrinkage-compensating admixture for concrete: An experimental and numerical study

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The use of shrinkage-compensating admixture in concrete has been proven to be an effective way to mitigate the shrinkage of concrete. The hydration of a shrinkage-compensating admixture in cement paste and concrete is investigated in this paper with numerical simulation and experimental study. An ettringite-based mineral shrinkage-compensating admixture (MSA) is developed taking use of industrial by-products. The MSA is designed with special considerations to the stoichiometry of ettringite formation, i.e. it should provide stable sources of sulfate and alumina which are necessary for the ettringite formation. Experimental results prove that the new MSA can successfully compensate the autogenous shrinkage of concrete.

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1. Introduction

Shrinkage of concrete deserves special consideration when a concrete structure is designed, which may cause cracking if the concrete is restrained by internal steel bars or connected structural elements. The use of shrinkage-compensating admixture in concrete has been proven to be an effective way to mitigate the shrinkage of concrete. The negative volume change (shrinkage) of concrete is counteracted with some reactions that have swelling potentials via which the shrinkage is compensated. The start of research about shrinkage-compensating admixture dates back to about 60 years ago when Lossier [10] used a mixture of Portland cement, an expanding agent, and a stabilizer to make a concrete with controlled expansion. The expanding admixture is made by burning a mixture of gypsum, bauxite and chalk to form calcium sulfate and calcium aluminate (mainly C₅A₃). These compounds react with water to form ettringite [12]. The formation of ettringite as the major source of expansion is commonly used in modern concrete to compensate the shrinkage. The work on shrinkage-compensating admixture is continued by Lafuma [9] and Klein and Troxell [8], the latter being the foundation of the shrinkage-compensating cement widely used in practice.

Besides the use of expansion potential generated by the ettringite formation, another important type of shrinkage-compensating admixture takes use of the hydroxide formation, e.g. Ca(OH)₂ (portlandite) and Mg(OH)₂, from the hydration of quicklime and periclase, respectively. The use of quicklime as the expanding agent is mostly employed in Japan [11], and periclase has been employed in dam constructions as the expanding agent in China for decades [5].

This study is aimed to study the hydration of a shrinkage-compensating admixture with numerical simulation and experimental study. An ettringite-based mineral shrinkage-compensating admixture (MSA) is developed taking use of industrial by-products, i.e. fly ash and slag. The MSA is designed with special considerations to the stoichiometry of ettringite formation, i.e. it should provide stable sources of sulfate and alumina which are necessary for the ettringite formation. The fly ash and slag are rich in alumina compared to the clinker and react remarkably slower than the aluminates in clinker, which provides alumina for the formation of ettringite in the late stage of the hardening process. A three-dimensional computer model (CEMHYD3D) is used to simulate the hydration process of cement containing this shrinkage-compensating admixture. The admixture is tested for its influence on the length change and compressive strength of mortar made with the MSA. Experimental results prove that the new MSA can successfully compensate the autogenous shrinkage of concrete. The relative amount of ettringite in cement pastes containing various amounts of this admixture is analyzed with X-ray diffraction (XRD) analysis. Microstructural changes of cement containing this MSA are simulated with the three-dimensional computer model.
2. Experimental

2.1. Materials

The oxide compositions and properties of materials used for developing the MSA are listed in Table 1. A ground granulated blastfurnace slag (GGBS) provided by Orcem BV, fly ash by Euroment BV, and one type of premixed anhydrite by Rethmann group and an analytically pure anhydrite are used in the experiments. Five recipes for the MSA are designed from these ingredients, in which the Rethmann group and an analytically pure anhydrite are used in the experiments. Practical suggestions for industrial applications are presented based on the experimental results.

CEMHYD3D. Factors such as the replacement level, calcium sulfate form, and w/b ratio of the paste on the performance of MSA are investigated. Practical suggestions for industrial applications are presented based on the experimental results.

2.2. Sample preparation and test results

The mortar is made with a Hobart force mixer. Two groups of mortar samples are mixed with a two step procedure for about 15 s. The cement containing MSA is mixed with a two step procedure for about 15 s. The chemical shrinkage measurement follows the methods by Van Eijk [14] at 23 ± 1°C. Paste samples for the XRD analysis are cured in saturated lime water at 23 ± 1°C till the test ages. The hardened paste is submerged into isopropyl alcohol to stop the hydration for 30 min, and is wet ground in ethanol to a fineness passing through the 150 μm sieve. The slurry is filtered and washed with ethanol and further with diethyl ether. The dry sample is loaded into a metallic sample holder, avoiding preferred orientation of crystals and assuring that there is a smooth surface. The scan with the PANalytical X’Pert PRO X-ray Diffractometer starts from 2θ = 5° to stop the hydration for 30 min, and is wet ground in ethanol to a fineness passing through the 150 μm sieve. The slurry is filtered and washed with ethanol and further with diethyl ether. The dry sample is loaded into a metallic sample holder, avoiding preferred orientation of crystals and assuring that there is a smooth surface.
2, 7 and 28 days (Fig. 3). All the samples have a comparable compressive strength. The compressive strength tests of Hori and Morioka[7]. The results of the chemical shrinkage measurements are used to determine the time conversion factor during the computer modeling of cement paste with CEM-HYD3D, presented in Section 3.2.

2.5. Chemical shrinkage measurements

The results of the chemical shrinkage measurements are plotted in Fig. 4. Three recipes are tested, including the neat Portland cement paste, pastes containing 10% and 20% MSA1, respectively. The measurements for the latter two groups stopped at 11 and 21 days, respectively, due to the break of the bottles caused by the paste expansion. The chemical shrinkage increases rapidly during the first 7 days, and slows down afterward. All three recipes show comparable chemical shrinkage, which is expected. On the one hand, the addition of MSA into cement reduces the chemical shrinkage because the fly ash and GGBS in MSA hydrate at a slower rate than the clinker. On the other hand, the MSA contains anhydrite calcium sulfate, which will react to form ettringite. The formation of ettringite involves more water than the hydration of clinker, which results in larger chemical shrinkage because more water is compressed[2]. These two effects of replacing Portland cement with MSA on the chemical shrinkage counteract with each other.

The increase of ettringite is mainly caused by the increased dosages of MSA in the paste. The decrease of portlandite can be affiliated with two factors: (1) the dilution effect of MSA in cement, i.e. less calcium silicates in cement with more MSA, and (2) the pozzolanic reaction of fly ash and GGBS, which consume portlandite as well.

3. Investigation of various factors on the performance of MSA

The effects of various factors on the performance of the MSA are experimentally investigated, including the calcium sulfate type, composition of the MSA and the water/binder ratio.

3.1. Calcium sulfate

The effect of calcium sulfate type is firstly investigated. In all the measurements, the MSA1 is used, which is made with a pre-mixed anhydrite. The pre-mixed anhydrite is a mixture of anhydrite and accelerator, which is able to promote the hydration rate of anhydrite. The MSA2 is made with analytically pure anhydrite. Length change of mortar samples containing 10% MSA1 or MSA2 in the binder is tested (Fig. 6). The trends of the length changes are similar for samples containing the two MSA, but the magnitude for MSA2 is obviously higher than that for MSA1, for both the peak and the steady state values.

A possible explanation could be that the pre-mixed anhydrite hydrates much faster than the pure anhydrite, thus most of the expansion potentials occur during the first 24 h, which is typically observed for dihydrate gypsum in cement. However, during this stage the mortar is relatively plastic, for which expansion can hardly be generated. The measurement starts from 24 h after the mixing and the volume change of the first 24 h is not monitored.

A conclusion can be drawn that pure anhydrite is more suitable for MSA than the premixed anhydrite. It results in higher and more
stable expansion compared to those made with premixed anhydrite as the magnitude of expansion with MSA2 is obviously higher than that with MSA1, for both the peak and the steady state values. Pure anhydrite is thus always used in the following recipes for producing MSA, designated as MSA2, MSA3, MSA4 and MSA5.

3.2. Composition of MSA

The effect of composition of MSA is investigated by changing the mass fractions of different ingredients in the MSA. The compositions of MSA2, MSA3, MSA4 and MSA5 are listed in Table 2. Note that in all these three MSA, the pure anhydrite is used, instead of the premixed anhydrite. In MSA3, the mass fraction ratio of fly ash to GGBS is changed, from 0.28 to 1.11, while the fraction of anhydrite is kept constant. In MSA4, the fraction of anhydrite is lowered to 20% and the ratio of fly ash to GGBS is raised to 3.0. In MSA5, the same fraction of anhydrite as that in MSA2 is used, but the fly ash and GGBS is replaced by CEM I 32.5R. All the mortar samples contain 10% of these MSAs in the binder.

The length changes of samples containing the different types of MSA are plotted in Fig. 7. It can be seen all the samples show similar trends of length change except those with only anhydrite, which show no clear peaks. The use of MSA2 has the highest efficiency for shrinkage compensation. Increasing the ratio of fly ash to GGBS is not favorable for compensating the autogenous shrinkage (see the lines MSA2 and MSA3). Lowering the fraction of anhydrite in the MSA is also detrimental for the shrinkage-compensating capacity (see line MSA4). Using pure anhydrite in concrete appears to be able to compensate the autogenous already, although the magnitude of expansion is lower than the MSA2 with fly ash and GGBS.

3.3. Effect of water/binder ratio

The effect of water/binder ratio on the autogenous length change of mortar samples is investigated. Mortar samples with water/binder ratios of 0.4 and 0.5 are prepared, with neat Portland cement, or 10% of the Portland cement being replaced by MSA2. The measured length changes are plotted in Fig. 8.

The w/b ratio has an obvious influence on the shrinkage-compensating capacity of the MSA. The magnitude of expansion is greatly reduced if the w/b ratio shifts from 0.5 to 0.4. These drastic effects could be explained with two factors. On the one hand, the state of water in the pores strongly affects the autogenous shrinkage of the mortar samples. Self-desiccation takes place when the w/b ratio is low, which aggravates the autogenous shrinkage. On the other hand, the formation of ettringite involves large amount of water. Hence, the availability of water for the formation of ettringite is essential, which controls the expansion potential. The effects of w/b ratios on the autogenous length change of samples without MSA is much less prominent, most likely associated with the strength development of the sample. The strength of mortar samples with w/b ratio of 0.4 is higher than those of 0.5. Hence, the expansion is smaller because higher strength is associated with lower autogenous shrinkage [7].

Based on the experimental results, it can be concluded that the w/b ratio is critical for the shrinkage-compensating capacity of the MSA. High w/b ratios are preferred.

3.4. Curing conditions

Prism samples without sealing are prepared and cured in a dry environment (23 ± 1 °C, 60 ± 5% RH). The surface of the prism is open to the dry air. The length changes of these samples are plotted in Fig. 9. It can be seen that when the samples are cured in the dry environment, their length changes are not significantly influenced by the MSA. The drying shrinkage varies slightly with the dosages of MSA. Thus, special care should be taken when curing concrete made with MSA. Moist or at least sealed curing should be implemented, especially during the early ages.

The shrinkage of the prisms containing MSA is greater than that of the Portland cement when cured in a dry environment. The ettringite formation has a high water demand. Thirty-two moles
of water is needed for every mole of ettringite formed. Hence, if the cement contains more aluminum and sulfate, more ettringite is formed, which aggravates the self-desiccation effect and consequently increases the drying shrinkage.

If the prisms are cured in a sealed environment, no water loss from the mortar occurs. Hence, the hydration of cement can proceed to a relatively high degree, considering the w/b used in the experiments (0.5). The expansion effect yielded by the ettringite formation can thus counteract the effect of the self-desiccation. As a net result, expansion of prisms is observed and the autogenous shrinkage is counteracted.

4. Numerical simulation of the hydration of MSA

4.1. Principle of CEMHYD3D

CEMHYD3D is one of the most advanced and well-known models for cement hydration [13]. It has at least three major advantages: (a) it uses fundamental knowledge about hydration reactions and hydration products in the hydrating pastes; (b) the algorithm employed in the model is very flexible. New types of reactions and hydration products can be added into the computer model by extending or modifying corresponding modules (e.g. modules of dissolution and reaction) without changing the others; (c) the system is represented by a digitized microstructure; hence, microstructural characteristics are easily evaluated [14].

CEMHYD3D is a digitized computer model that uses voxels to represent the phases in the hardening paste/concrete. Each voxel is assigned to a phase that is susceptible to move and to transform into another phase. A procedure consisting of dissolution, diffusion, reaction, and precipitation processes is followed to simulate the gradual growth of grains and disappearance of reactants. Results of the simulation such as hydration degree, phase distribution, porosity and phase connectivity are used to predict the performance of the hardened cement pastes. Good accordance between the model predictions and experimental results has been found [1,14].

The simulation starts with a microstructure representing the fresh paste and proceeds by using the cellular automation and random walk algorithms to simulate the reactions of cement. The starting microstructure is reconstructed from the information of the cement powder such as the distribution of clinker phases (via scanning electron microscopic images) and particle size distribution. Hydration of the starting microstructure is simulated in an iterative process consisting of discrete cycles. Reactions obeying a series of rules take place if the diffusing species collide with other solid/diffusing species. The possibility of the chemical reaction depends on the nature of the two species colliding. The diffusing voxels are converted into hydration products preserving the volume stoichiometry.

The microstructure is updated after each hydration cycle. Properties related to the hydration process such as the hydration degree, amount of combined water, heat development and chemical shrinkage are calculated.

4.2. Simulation

The hydration of cements with various amounts of MSA is simulated by with CEMHYD3D. The model is used to simulate the hydration degrees of phases (clinker, MSA) and the microstructure of the hardened paste.

First, the results of the chemical shrinkage tests are used to determine the time conversion factor “B” which relates hydration cycles to real time. The time/cycle conversion factor is an essential parameter in modeling the cement hydration process [1]. It is proven in experiments that there is a linear relationship between the hydration degree of cement and the chemical shrinkage of its hydration [6]. The chemical shrinkage is measured in experiments...
as a function of hydrating time, and the hydration degree is simulated as a function of the hydration cycles. Hence, a linear regression analysis can be used to determine "B" which gives the best linear relation between the measurements and the hydration degree. The results of the analysis for neat Portland cement are shown in Fig. 10. The fitted value of the time conversion factor ($B = 4.0 \times 10^{-3} \text{ h/cycles}^2$) is in line with the values found for a wide range of other cements ($B = 3.8 \times 10^{-3} \text{ h/cycles}^2$) [3]. It is further used in the following simulations for other cements containing different amounts of MSA.

The extrapolated chemical shrinkage for the complete hydration of Portland cement is 6.3 mL per 100 g cement, which is in good agreement with the measurements by Czernin [4], and the prediction by Geiker and Knudsen [6].

The simulated hydration degree of Portland cement without MSA is plotted in Fig. 11, together with the calculated hydration degree from the measurements. In the calculation, the chemical shrinkage of Portland cement hydration is taken to be 6.3 mL per 100 g cement based on the discussion above. It can be seen that the hydration degree of Portland cement in the paste is well predicted.

The hydration of cements with various amounts of MSA is simulated with the computer model. MSA1 is taken as an example. It is shown in the results that all cements containing various amounts of MSA1 show similar reaction degrees in all the recipes (Fig. 12a).

However, the major components in MSA, viz. anhydrite, fly ash, and GGBS, react in significantly different rates. Anhydrite reacts much faster than the other two components. A detailed comparison about the reaction degree of anhydrite shows that in all the recipes anhydrite reacts in an almost identical rate (not included in figures). After 24 h, about 90% of anhydrite has reacted, and after 80 h all the anhydrite has reacted. The reaction degrees of fly ash and GGBS are low. After 28 days, their reaction degrees are between 0.3 and 0.35, varying with different dosages of MSA.

The volume fraction of ettringite in the pastes is plotted in Fig. 13 in pastes with different dosages of MSA1. In the simulation it is assumed that no external volume change of the paste occurs. It can be seen that with increasing dosages of MSA in the pastes, the volume fraction of ettringite increases as well, in line with the results of the XRD analysis (Fig. 5). If 5% MSA1 replacement is used, most of the ettringite is formed during the first 10 h already, while for 20% MSA, the amount of ettringite keeps increasing to about 100 h, and reaches an approximately constant fraction after that.

4.3. Relation between length change and dosage of MSA

If the length change of mortar samples containing various amounts of MSA is plotted as a function of the MSA dosage in cement (Fig. 14), it can be seen that there is a threshold value for the dosage of MSA to compensate the autogenous shrinkage, between 5% and 10%, below which no shrinkage-compensating effect is generated at all.

For samples containing more than 10% MSA and at later ages (60 d and 120 d), there is an approximately linear relation between the dosage and length change. Hence, the magnitude of the expa-
tion can be easily controlled by adjusting the dosage. This is very important in practice because in construction industry different requirements are frequently encountered. Hence, a robust method to predict the expansion is useful.

5. Conclusions

An ettringite-based mineral shrinkage-compensating admixture is developed, which takes use of industrial by-products. It is shown that 10% of this MSA can already successfully compensate the autogenous shrinkage of mortar samples. Higher dosages result in larger expansions. There is a linear relationship between the free expansion of mortar samples and the dosage of MSA in cement for dosages above 5% of MSA in cement. Hence, the dosage used in practice can be flexibly adjusted according to different expansion requirements. Effects of various factors on the performance of the MSA are investigated. The expansion of mortar is slightly influenced by the proportioning of its ingredients, but strongly influenced by the w/b ratio in concrete and the curing conditions. The drying shrinkage of concrete containing this MSA is comparable to normal concrete.

The increasing dosage of MSA in cement is accompanied by a reduction in the compressive strength of the samples in the free expansion state. The compressive strength is comparable for 5% and 10% replacement levels by this MSA to that with Portland cement, but the compressive strength for 15% and 20% of replacement levels is obviously reduced. Therefore, dosages between 5% and 10% MSA are preferred, which can compensate the autogenous shrinkage and avoid loss of strength.

The hydration of cement pastes containing various amounts of MSA is simulated with CEMHYD3D. Cement pastes containing higher dosages of MSA have a bigger fraction of ettringite crystals, which is confirmed with XRD analysis.

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