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*CAPITALIZING ON SELF-DESICCATION FOR AUTOGENOUS DISTRIBUTION OF CHEMICAL ADMIXTURES

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Abstract

For many concretes and mortars, self-desiccation results in the creation of empty capillary porosity within the cement paste microstructure, accompanied by a decrease in achieved hydration, an increase in internal stresses, and an increased propensity for early age cracking. One solution to this problem for low water-to-cement ratio concretes where external curing is ineffective has been the development of internal curing. In internal curing, water reservoirs, typically being either fine lightweight aggregates with a high moisture content or superabsorbent polymer particles, are distributed uniformly throughout the concrete microstructure and undergo desiccation themselves, while maintaining saturated conditions within the hydrating cement paste. Since these reservoirs typically contain pores that are much larger than those in the hydrating cement paste, the internal stresses are significantly reduced and early age cracking can be avoided. To date, these internal reservoirs have been filled with water only. Here, it is proposed to fill them with solutions of chemical admixtures such as shrinkage-reducing admixtures or corrosion inhibitors. Two possible advantages of the autogenous distribution of chemical admixtures over delivery by conventional addition to the mixing water are the mitigation or avoidance of possible detrimental interactions between chemical admixtures or detrimental influences of the admixture on fresh concrete properties and a potentially more efficient delivery of admixtures that are partially absorbed by the cement during hydration and in the resulting hydration products. Preliminary results for the FLAIR (Fine Lightweight Aggregates as Internal Reservoirs) system are presented for the case of a shrinkage-reducing admixture. It is envisioned that the FLAIR technology will have the greatest applicability to chemical admixtures that effect the properties of the hardened concrete (as opposed to the fresh concrete), such as shrinkage-reducing admixtures, corrosion inhibitors, and admixtures employed to mitigate alkali-silica reactions.

1. Introduction and objective

The effects of self-desiccation on concrete performance can be either beneficial or detrimental. For example, the reduced internal relative humidity produced during self-desiccation can be beneficial for concrete floors, where higher internal relative

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humidities can contribute to problems with mildew, mold, and other detrimental chemical reactions with carpeting and other flooring materials [1]. For intermediate water-to-binder ratio (w/b) concretes (e.g., 0.4 to 0.45), sealed curing and self-desiccation may actually result in an earlier depercolation of the capillary pores, as hydration will not occur in the larger pores emptied during self-desiccation, being instead concentrated in the water-filled smaller pores and pore entryways [2]. This should lead to lower transport coefficients and greater durability. Conversely, for high-performance concretes with lower w/b, self-desiccation often leads to repercolation of the capillary pores at later ages [2], (early age) cracking [3], and poor durability. To avoid self-desiccation within the hydrating cement paste component of mortar or concrete, internal curing, utilizing either water-filled fine lightweight aggregates (LWA) or superabsorbent polymers (SAP), has been proposed [4-6], and a methodology for mixture proportioning for internal curing presented recently [7]. In this case, the initially water-filled LWA or SAP particles sacrificially self-desiccate while the hydrating cement paste, with its smaller pore diameters, remains saturated. The objective of this study is to investigate the extension of internal curing to the autogenous distribution of solutions of chemical admixtures, as opposed to simply water. In this preliminary study, results for utilizing fine LWA to distribute a shrinkage-reducing admixture (SRA) into a high-performance mortar will be presented. The proposed technology has been given the acronym FLAIR (Fine Lightweight Aggregates as Internal Reservoirs).

2. Experimental

Three mortar mixtures were prepared: 1) a control low w/b mixture with neither SRA nor fine LWA, 2) a mixture with fine LWA prewetted with a 10 % by mass fraction solution of the SRA (FLAIR delivery), and 3) a mixture with fine LWA prewetted with only water while the same quantity of SRA as in the previous mixture was now added directly to the mixing water (conventional delivery). The LWA used in this study was an expanded shale, passing through a #8 sieve, but retained on a #16. It had a saturated surface dry specific gravity of 1.67 and a water absorption of 20 % per unit dry mass LWA. The prewetted LWA was prepared by first oven drying, cooling to room temperature, and then mixing in a sealed plastic container with the appropriate volume of either water or the SRA solution. The prewetted LWA in the sealed container was then placed in a chamber maintained at 23 ^{o}C for a minimum of 24 h. The details for the prepared mortar mixture proportions are provided in Table 1. Cement and Concrete Reference Laboratory (CCRL) proficiency cement sample 152 [8] was used for all three mixtures. The mortars were prepared in an epicyclic mixer, with the water and chemical admixtures being placed in the mixing bowl first. Then, the cement was added and mixing performed on low speed for 30 s. All of the sands were added during 30 s of further mixing on low speed, followed by 30 s of mixing on medium speed. After a rest of 90 s, final mixing on medium speed for 1 min was performed. Mixtures 2 and 3 were prepared with the prewetted LWA replacing an equal volume of the S15 coarse sand.

The air content of the fresh mortar was determined according to ASTM C185 [9], and the following specimens were prepared: 50 mm cubes for compressive strength testing, 25 mm diameter by 400 mm corrugated tubes for evaluation of autogenous deformation [10], and 25 mm by 25 mm by 285 mm prisms for measurement of drying shrinkage. All specimens were placed in an environmental chamber maintained at 23 ^{o}C. The capped corrugated tubes were removed periodically and their length determined using a digital dilatometer [10]. The cube and prism molds were first sealed in two plastic bags and then placed in the environmental chamber. After 1 d of curing, the cube and prism specimens were demolded and placed in a new set of double plastic bags. After 3 d of sealed curing, the prisms to be used in the evaluation of drying shrinkage were removed from their plastic bags and placed in a 23 ^{o}C, 50 % relative humidity environment. Both their mass and length were periodically recorded.

Table 1 – Mortar mixture proportions used in study.

Material	Mixture 1 CONTROL	Mixture 2 FLAIR	Mixture 3 CONVENTIONAL
w_O/c^A	0.30	0.30	0.30
Cement	1250 g	1250 g	1250 g
Water	365.4	365.4	359.01
Water-reducing admixture	16.0	16.0	16.0
Shrinkage-reducing admixture (SRA)	---	---	6.39
F95 (fine) sand	593.75	593.75	593.75
Graded sand (C778)	451.25	451.25	451.25
20-30 sand (C778)	451.25	451.25	451.25
S15 (coarse) sand	878.75	279.65	279.65
Prewetted fine LWA containing:	---	383.33	383.33
Water for LWA	---	---	63.89
10% SRA solution for LWA	---	63.89	----

$^A w_O/c$ calculated assuming 60 % water content for the water-reducing admixture and considering any SRA added to the mixing water as replacing an equal mass of water.

For each of the three mortar mixtures, three cubes were prepared for each compressive strength evaluation (after 7 d, 28 d, and 91 d of sealed curing), four prisms were prepared for the measurement of drying shrinkage, and two tubes were prepared for the measurement of autogenous deformation. After the cubes were broken at the appropriate age, small portions of one per set were retained and ground to a powder with a mortar and pestle, for the subsequent measurement of degree of hydration by loss-on-ignition (LOI) techniques, correcting for the LOIs of the original cement powder and the sands present in each mixture. Based on a propagation of error analysis, the estimated uncertainty in the calculated degree of hydration was 0.01, assuming a coverage factor of 2 [11].

3. Results and Discussion

3.1 Fresh Mix Properties

The measured air contents of the three mixtures are provided in Table 2, along with their achieved degrees of hydration and compressive strengths. The control mixture exhibits the lowest air content as it was an extremely dry mixture that was somewhat difficult to mix and mold. In comparing the other two mixtures, it is observed that the mixture in which the SRA was added via the prewetted LWA has a significantly higher air content than the mixture where the SRA was added by conventional means. This specific SRA is known to have air detraining properties and the experimental results indicate that FLAIR delivery does have the potential to eliminate or reduce this potentially detrimental side effect of the SRA, when compared to conventional delivery via the mixing water. This example illustrates one potential advantage of FLAIR delivery of chemical admixtures versus conventional delivery in the mixing water, namely the mitigation or avoidance of potentially detrimental interactions between multiple admixtures or detrimental side effects of the admixture in the fresh concrete.

Table 2- Measured physical properties of mortar mixtures. Numbers in parentheses for air contents indicate the standard deviation between two or three batches of fresh mortar, for compressive strengths indicate the measured coefficient of variation for three specimens, and for degree of hydration indicate the estimated uncertainty, as specified above.

Physical Property	Mixture 1 CONTROL	Mixture 2 FLAIR	Mixture 3 CONVENTIONAL
Air content	3.4 % (0.6 %)	8.3 % (0.4 %)	5.1 % (0.4 %)
7 d compressive strength (MPa)	38.8 (2.8 %)	36.5 (4.6 %)	40.4 (6.0 %)
28 d comp. strength (MPa)	42.1 (6.7 %)	41.0 (3.7 %)	41.0 (4.5 %)
91 d comp. strength (MPa)	43.7 (4.5 %)	42.6 (9.9 %)	42.7 (11.4 %)
7 d degree of hydration	0.53 (0.01)	0.57 (0.01)	0.59 (0.01)
28 d degree of hydration	0.57 (0.01)	0.66 (0.01)	0.66 (0.01)
91 d degree of hydration	0.59 (0.01)	0.68 (0.01)	0.68 (0.01)

3.2 Degree of Hydration and Strength Development

Table 2 also provides the measured values of compressive strength and degree of hydration at ages of 7 d, 28 d, and 91 d for the three mortars. Degrees of hydration in the mixtures with the prewetted LWA (#2 and #3) were greater than that in mixture 1 at all ages, due to the extra water provided by the internal curing, in agreement with previous observations [12]. The compressive strengths of the three mixtures are nominally identical within the measured variation of the testing. The expected compressive strength reduction due to the increased air contents of mortar mixtures 2 and 3 are basically offset by the beneficial effects of their increased degrees of hydration. These results indicate that the FLAIR delivery of the SRA is equivalent to delivery by conventional means in terms of achieved hydration and strength.

3.3 Autogenous Deformation and Drying Shrinkage

The measured autogenous deformation curves for the three mortar mixtures are provided in Figure 1. Previously, it has been demonstrated that the addition of either water-filled fine LWAs or an SRA results in substantial decreases in the measured autogenous shrinkage at ages beyond 1 d [3]. Thus, it is no surprise that including both in the same mixture, whether via FLAIR or conventional delivery of the SRA, results in a substantial reduction in the measured autogenous deformation. The two delivery mechanisms provide equivalent reductions in autogenous shrinkage, suggesting that the extra internal curing water and the presence of the SRA are functioning similarly with respect to autogenous deformation, regardless of how they are introduced into the mortar mixtures.

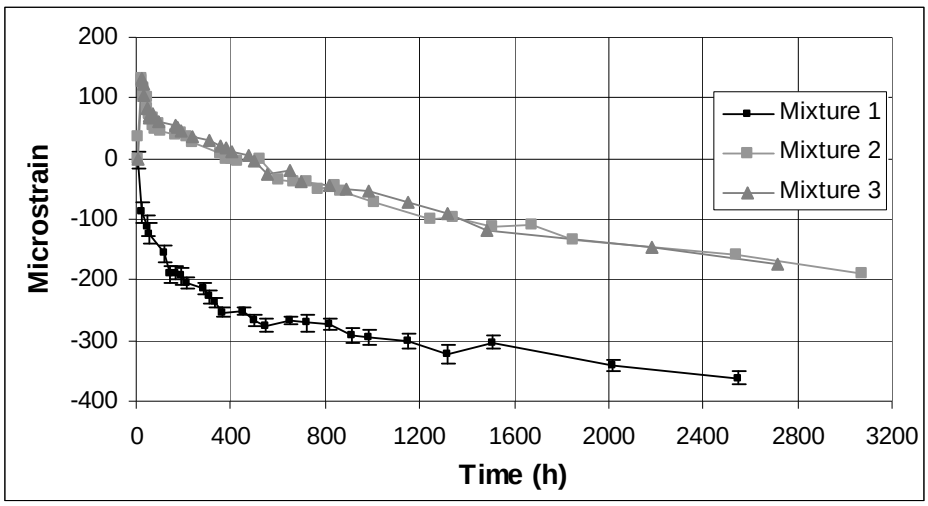

Figure 1- Measured (average of two samples) autogenous deformations vs. time for the three mortar mixtures. Error bars on lower curve indicate range of values for the two mixture 1 specimens.

The curves for drying shrinkage microstrain vs. time are provided in Figure 2. For both mixtures with internal curing and SRA, less drying shrinkage is observed, despite their higher overall water content and greater mass loss during drying. As shown in Figure 3, for each of the three mortar mixtures, a nearly linear relationship was observed between measured mass losses and measured drying shrinkage microstrains. For the two mixtures with internal curing and SRA, the slope of the drying shrinkage microstrain vs. mass loss curve is less at early ages (< 7 d), as indicated in Table 3. The SRA reduces the surface tension of the pore solution [13, 14], leading to a reduced saturation level and reduced strain within the three-dimensional microstructure when exposed to a constant (reduced) relative humidity drying environment. Because there is a greater quantity of total water in mixtures 2 and 3 relative to mixture 1, they do

exhibit a greater mass loss during drying but with less accompanying shrinkage. In terms of the early (< 7 d) and later (> 7 d) age shrinkage, as indicated in Table 3 and Figure 2, mixture 2 with FLAIR delivery exhibits slightly more shrinkage at early ages, but less subsequent shrinkage at later ages when compared to mixture 3 with conventional delivery of the SRA. This would be expected as the SRA would be released (drawn out) from the prewetted fine LWA during the first few days of hydration under sealed conditions. As some of the SRA may be absorbed by the cement hydration products, delaying its introduction into the hydrating cement paste system may potentially improve its efficiency at later ages. This is the second potential benefit of FLAIR vs. conventional delivery of chemical admixtures. Because the FLAIR-delivered admixtures are not initially distributed throughout the cement paste component of the fresh concrete, it is envisioned that the FLAIR technology will be most readily applicable to admixtures that influence the properties of the hardened concrete, such as SRAs, corrosion inhibitors, and admixtures employed to mitigate alkali-silica reactions. Further research is needed to evaluate the FLAIR technology in such systems.

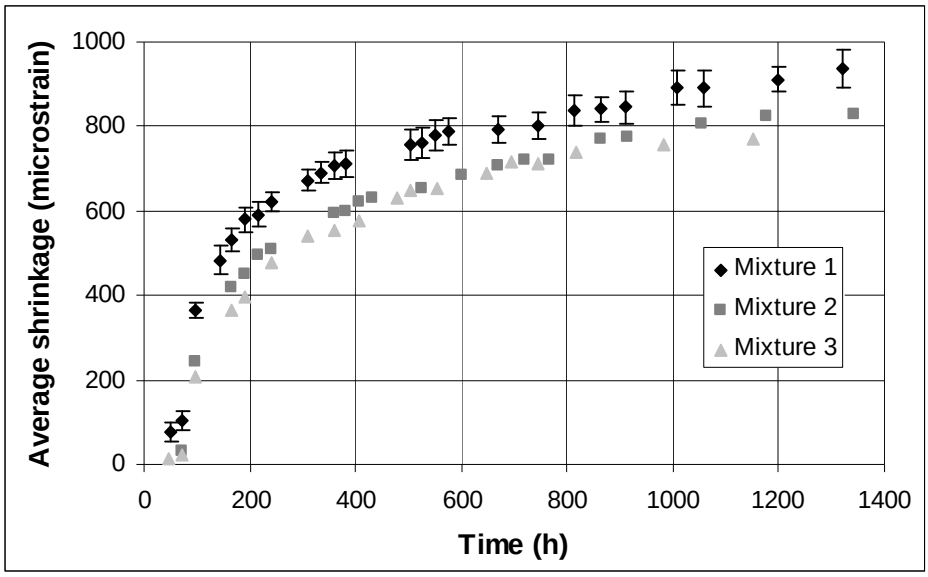

Figure 2- Measured drying shrinkage microstrain vs. time (average of four samples) for the three mortar mixtures. Error bars on upper curve indicate ± one standard deviation for the four mixture 1 specimens.

Table 3- Computed slopes of drying shrinkage microstrain vs. mass loss curves for the three mortar mixtures. Slopes are in units of microstrain per percent mass loss.

	Mixture 1 CONTROL	Mixture 2 FLAIR	Mixture 3 CONVENTIONAL
Slope (3 d to 7 d)	516.	306.	267.
R^2 (3 d to 7 d)	0.997	0.996	0.987
Slope (7 d to 50 d)	330.	280.	331.
R^2 (7 d to 50 d)	0.987	0.996	0.982

4. Conclusions

The FLAIR concept of utilizing prewetted fine lightweight aggregates for the autogenous distribution of chemical admixtures in mortars and concretes has been presented and demonstrated. Potential benefits of FLAIR include the mitigation or avoidance of potentially detrimental influences of the admixture in the fresh concrete and a possibly increased efficiency of the admixture performance at later ages if it is partially absorbed during cement hydration. Further research is needed to determine the applicability of FLAIR to other admixtures such as corrosion-inhibiting admixtures and admixtures for mitigating alkali-silica reaction, and the practicality of utilizing the technology at ready-mix plants and pre-casting facilities.

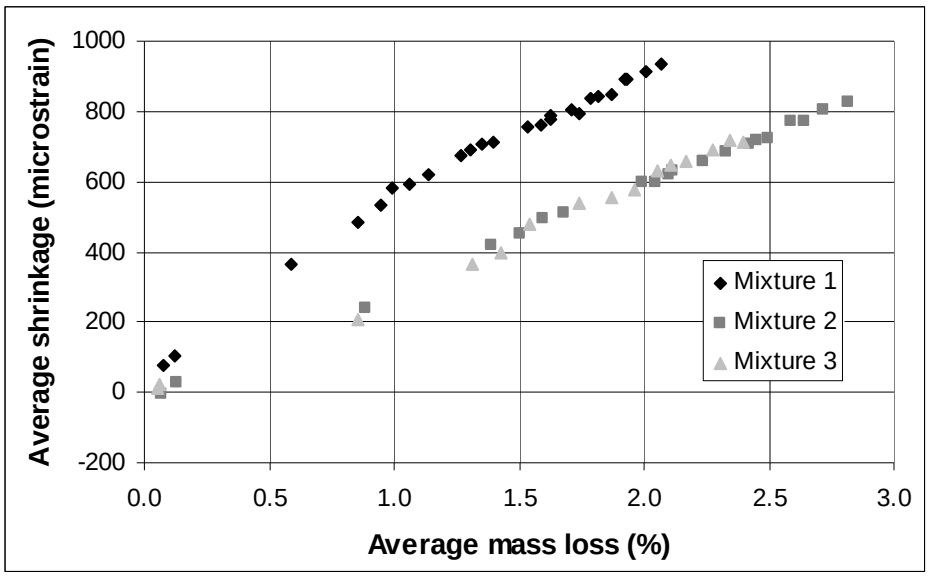

Figure 3- Measured drying shrinkage microstrain vs. measured mass loss (average of four samples) for the three mortar mixtures.

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† Certain commercial products are identified in this paper to specify the materials used. In no case does such identification imply endorsement by the National Institute of Standards and Technology, nor does it indicate that the products are necessarily the best available for the purpose.

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