

Microscopic assessment into causes for early age strength gain with various amine-based admixtures in concrete

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INTRODUCTION

Chemical strength enhancers have been extensively used by cement and concrete producers to boost the strength development of their products. Some classes of strength enhancers can also prevent agglomeration of the fine cement particles during grinding, working as grinding aids. Examples of such chemicals are the tertiary alkanol amines, such as triethanol amine (TEA), diethanol isopropanol amine (DEIPA), ethanol di-isopropanol amine (EDIPA) and tri-isopropanol amine (TIPA).

BACKGROUND STUDIES OF ADMIXTURES IN PASTE AND MORTARS

Recent work on a newly developed early age strength enhancement technology (ethanol diglycine or EDG) has shown important improvements in strength performance at 24 hours when added to the mixing water of EN-196 mortars prepared with 23 different cements (commercially available or laboratory ground using commercial clinkers). The active strength enhancer used in the mortars ranged between 0.005% and 0.02% of the cement weight. It was shown that 19 of the 23 OPCs tested (83% of the cements) showed up to 21% higher 1 day strength than the reference mortar without additives, indicating a robust response of the technology across different cement chemistries. Various cement paste and mortar based studies already undertaken to explain these enhanced performances showed distinct changes in the cement paste pore size distribution, the amount of ettringite, and the calcium hydroxide (CH) amount, distribution, form and crystal size, without significant relative changes to the amounts of the various cement phases being detected [1,2].

TESTING OF CONCRETE SAMPLES WITH ADMIXTURES

To ascertain if these observations in the paste and mortar are also reproduced in concrete, the primary material in which this admixture would be employed, concrete laboratory samples were produced with a selection of differing amine-based admixtures dosed at 200 ppm in a uniform 0.56 w/cm 256 kg/m³ cement content mix containing homogeneous aggregate types. The selection of 'clean' aggregates of appropriate composition (coarse granite and quartz sand) was important in minimizing the misidentification of the calcium hydroxide component in the cement paste. Compressive strength test results on the concretes shown in Table 1 confirmed the anticipated early age strength enhancements. At 1, 3 and 28 days age sub-samples of the concrete were removed and further hydration was interrupted by immersion in isopropanol for 24 hours. These sub samples were then impregnated with araldite resins and prepared as fluorescent resin-impregnated thin sections and polished

surfaces for investigation by optical and scanning electron with energy dispersive X-ray analysis (SEM-EDX) microscopy respectively.

Table 1: Performance and strength of concrete mixes (std. dev. in parentheses).

Additive	Slump (mm)	Air%	1 day (MPa)	3 days (MPa)	28 days (MPa)
Blank	70	4.6%	15.9 (0.5)	28.3 (0.6)	38.0 (3.0)
EDG	57	4.4%	17.9 (0.3)	27.4 (0.7)	38.6 (1.0)
DEIPA	70	4.3%	17.4 (0.0)	27.6 (0.0)	39.0 (1.4)

Great care was taken in preparing these early age concrete samples (1 and 3 days) as the aggregates were obviously extremely hard, and the surrounding hydrated cement paste fraction was, at this stage, still extremely porous and friable where it was not fully and uniformly impregnated with an araldite resin.

OPTICAL MICROSCOPY

The optical microscopic examinations of fluorescent resin impregnated thin sections confirmed the EDG samples were more homogeneous with a lower total CH volume and crystal size than seen in the blank sample. This difference was most pronounced in CH development at the interfacial transition zone (ITZ) on aggregate particles (Figure 1).

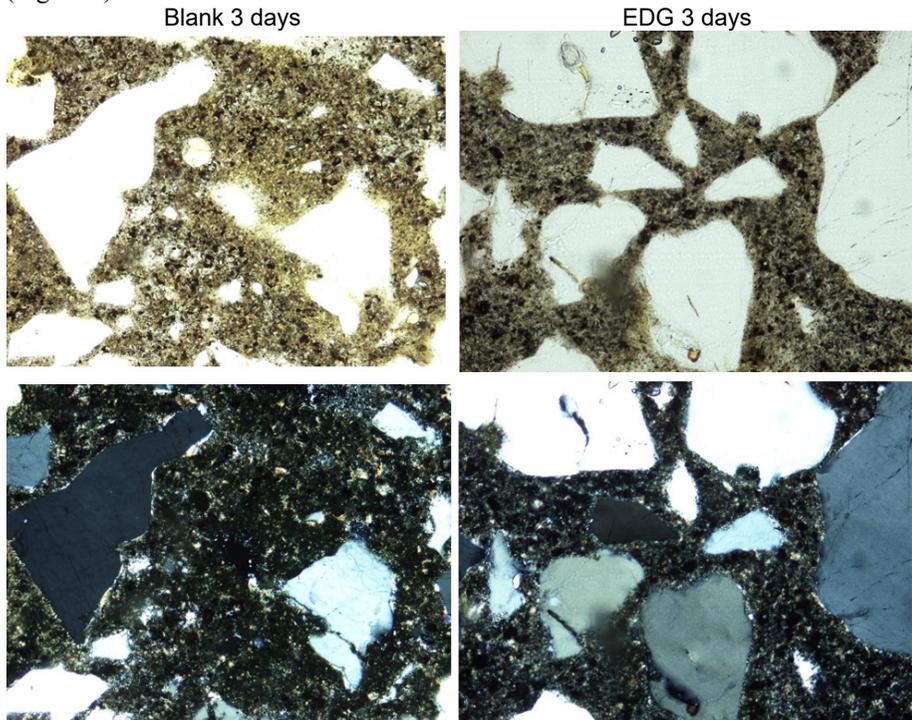


Figure 1: Comparison of blank (left) and EDG additive concrete (right). Image widths 1.25mm, taken in plane polarized (top row) and crossed polarized (bottom row) light modes.

The observed differences in paste homogeneity, calcium hydroxide amount, size and location, while still present, were not as pronounced with the other admixtures when compared to the blank sample. However, due to the nature of polarizing optical light microscopy it was not easy to quantify these differences (extinction, birefringence et cetera).

SEM-EDX STUDIES

With this issue in mind the remainder of the investigation was undertaken using polished samples examined under the SEM-EDX microscope. For each sample, 10 areas were selected at constant settings (BSE mode, Mag x200, 20Kv, WD 11mm, Spot size 40 nm) to include a substantial component of cement paste and some aggregate particle edges. These 10 gray scale backscatter images were then segmented as shown in Figure 2 to highlight the main constituents. Due to the scale at which these samples were being examined, some loss of accuracy in terms of paste capillary porosity was suspected. However, the microstructural characteristics discussed above, most obviously the differences in CH formation at the ITZ, were still clearly evident.

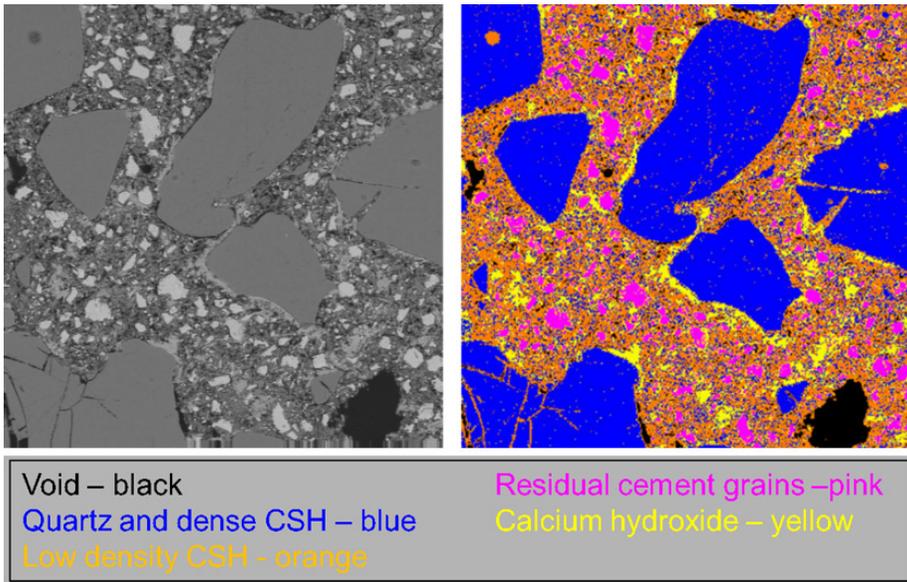


Figure 2: BSE gray scale image (left) and equivalent segmented images (right). Magnification x200, image width 620 microns.

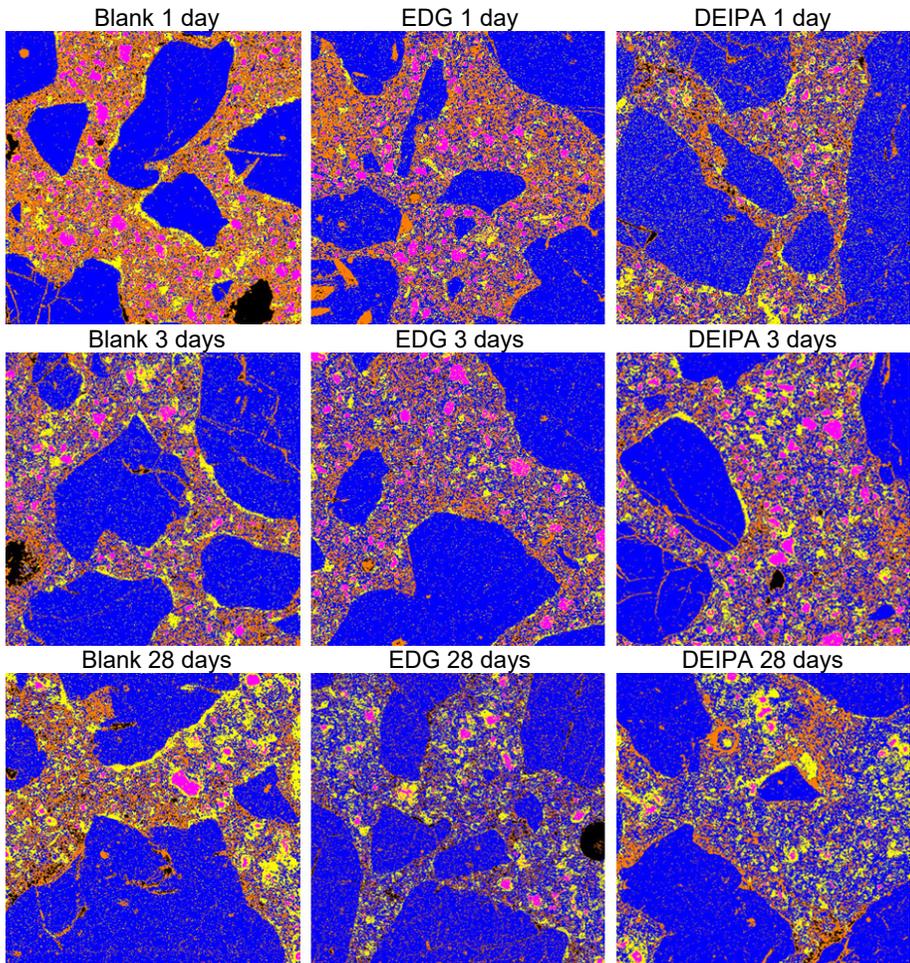


Figure 3: Compositional maps based of polished surface backscatter gray level (BSE) segmentation. These show a reduced amount and size of calcium hydroxide crystals and a noticeable reduction in the amounts developing on the aggregate to cement paste ITZ. Calcium hydroxide component being shown in yellow. Image widths 620 microns.

These compositional maps (Figure 3) also show a clearly more homogenous and denser cement paste in the EDG (and to a lesser degree the DEIPA additive) samples when compared to the blank sample. These images also show differences in the development of these various cement paste densities with time. The amounts of the various constituents were also quantified for 10 segmentation maps from each sample and the results of these are summarized in Table 2. This segmentation data clearly shows that the amount of residual cement grains decreases with increased time (as expected), and also shows lower amounts in the EDG and DEIPA samples at 1 day as

compared to the blank. The total amounts of CH are also lower in all EDG samples as compared to the blank. However, any clear relationship between the amount of CH formation and the amount of aggregate (ITZ formation) is somewhat limited as a result of the increasing amount of denser CSH being incorporated by segmentation into the aggregate category within the older samples.

Table 2: Calculated percentage of various constituents with voids and microcracks removed (standard deviation of values from 10 areas are shown in the parenthesis).

days	Constituent	Blank%	EDG%	DEIPA%
1	Cement grains	6.6 (1.0)	6.1 (1.4)	5.2 (2.3)
	Quartz and dense CSH	55.5 (7.0)	60.0 (6.9)	59.8 (10.3)
	CH (Portlandite)	13.1 (1.9)	10.0 (0.8)	11.9 (2.5)
	Porous CSH	24.7 (4.7)	24.0 (3.7)	23.1 (5.9)
3	Cement grains	4.2 (1.5)	3.8 (1.5)	5.0 (0.7)
	Quartz and dense CSH	63.0 (5.5)	66.2 (7.5)	63.7 (3.2)
	CH (Portlandite)	13.8 (1.4)	11.4 (2.5)	14.3 (1.2)
	Porous CSH	19.1 (3.4)	18.0 (2.6)	17.1 (1.9)
28	Cement grains	2.2 (0.3)	2.6 (0.6)	1.2 (0.5)
	Quartz and dense CSH	64.3 (2.9)	67.6 (2.8)	72.0 (6.7)
	CH (Portlandite)	15.5 (1.6)	15.0 (1.3)	13.2 (2.4)
	Porous CSH	18.1 (2.2)	14.8 (2.0)	13.7 (2.8)

In order to try and further quantify what was visually evident by the qualitative optical and SEM examination, the same BSE gray scale segmentation maps (10 maps for each sample) were converted into binary images, now only highlighting the CH component (Figure 4). These images were then cleaned up by removing the finer detected (removing the noise) material before measuring all the remaining calcium hydroxide above an area of 25 microns.

This data shown in Table 3 shows a clear and consistent differences in the amounts and size of the CH crystal present. However, further work is still required in order to establish a method of quantify the extent of the coarse sized CH crystal growth on the aggregate edges (ITZ). Some caution should be taken on these findings due to the relative low levels of magnification being employed, especially in regard to amounts of residual small cement clinker grains and cement paste capillary porosity; however, they do still help explain some of the potential reasons for the clear differences in strength development.

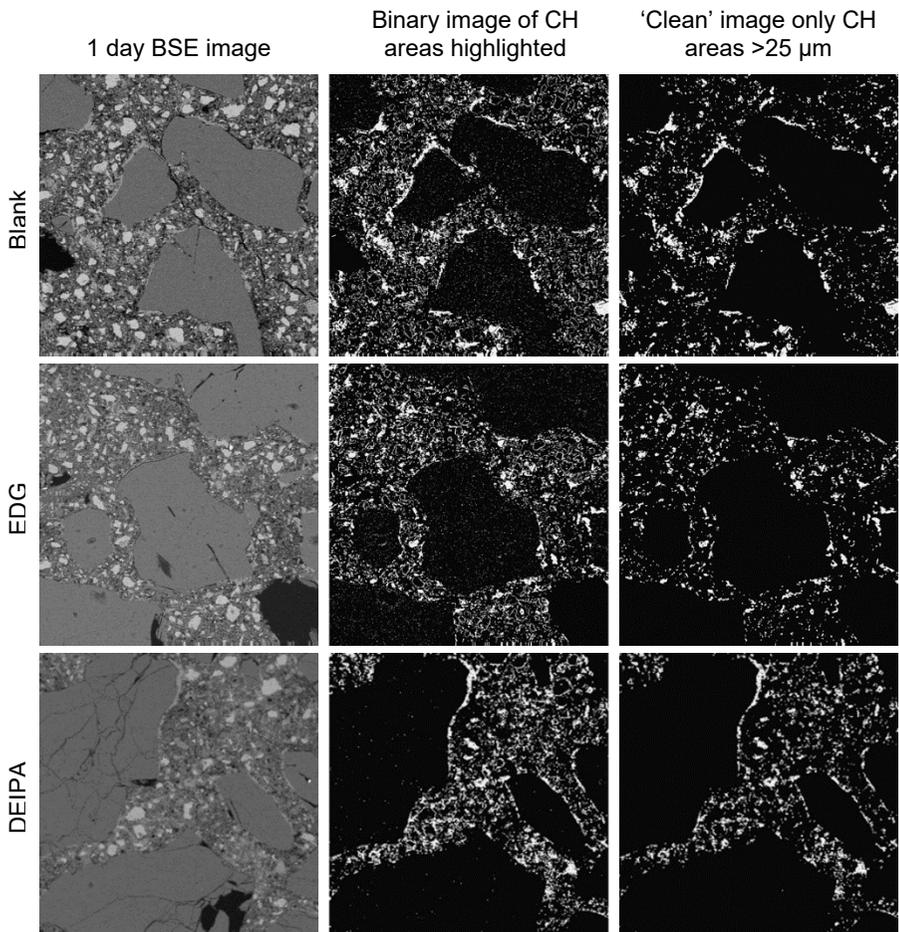


Figure 4: Binary maps produced from the BSE gray scale images used to highlight CH crystals. Image widths 620 microns.

Table 3: Size of CH crystals in the various samples (in microns).

days		Blank	EDG	DEIPA
1	Mean	95	84	77
	Mean of upper 50%	153	133	121
2	Mean	84	70	78
	Mean of upper 50%	134	106	121
3	Mean	120	87	82
	Mean of upper 50%	204	140	130

CONCLUSIONS

The results of this examination showed that the EDG additive appears to produce a noticeably more homogeneous and apparently denser cement paste particularly at early ages. The amounts of residual cement clinker grains also appear noticeably lower in the EDG and DEIPA sample at 1 and 3 days than observed in the blank sample, possibly suggesting increased dissolution of the cement at early age. However, it was most apparent that it lessened the amount and the size of CH crystal development, especially on the ITZ of the aggregates.

Therefore the observed strength improvements appear primarily to be the result of a combination of changes in cement clinker dissolution, paste homogeneity, pore size distributions and changes in CH crystals (volume, size and location). The cause for these CH morphology changes, cement clinker dissolution and C-S-H crystallization is not yet established, but may relate to rates of C-S-H and/ or CH seeding themselves a result of EDG being an enhanced calcium chelator. SEM-EDX analysis of outer C-S-H product showed no important changes in composition of that phase (reported on Silva et al, 2018) and was therefore not thought to be an important contributor to the strength differences observed.

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REFERENCES

- [1] Silva DA and Sibbick R (2018) Improving strength with a new grinding aid. *World Cement*, Volume.49, Issue 1, pp 53-56.
- [2] Silva, DA and Sibbick R (2019). Mechanistic study of two early strength enhancers: EDG and DEIPA. To be presented at the forthcoming 15th ICCI conference in Prague, Czech Republic.