Combined Use of Shrinkage Reducing Admixture and CaO in Cement Based Materials

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Abstract. The combined addition of a Shrinkage-Reducing Admixture (SRA) with a CaO-based expansive agent (CaO) has been found to have a synergistic effect to improve the dimensional stability of cement based materials. In this work, aimed to further investigate the effect, mortar and self-compacting concrete specimens were prepared either without admixtures, as reference, or with SRA alone and/or CaO. Their performance was compared in terms of compressive strength and free shrinkage measurements. Results showed that the synergistic effect in reducing shrinkage is confirmed in the specimens manufactured with SRA and CaO. In order to clarify this phenomenon, the effect of SRA on the hydration of CaO as well as cement was evaluated through different techniques. The obtained results show that SRA induces a finer microstructure of the CaO hydration products and a retarding effect on the microstructure development of cement based materials. A more deformable mortar or concrete, due to the delay in microstructure development by SRA, coupled with a finer microstructure of CaO hydration products could allow higher early expansion, which might contribute in contrasting better the successive drying shrinkage.

1. Introduction
The exposure of a cement based system to non-saturated environment causes drying shrinkage due to water evaporation [1]. Shrinkage is one of the main reasons of mortar and concrete failures like curling, cracks formation and de-bonding.

Cracks greatly increase the concrete surface permeability, since they represent preferential paths for penetration of aggressive ions such as sulphates and chloride in polluted area and coastal zone [2-4] promoting concrete deterioration and corrosion of embedded reinforcements [5]. Since the cost of repairing cementitious structures is very high, one of the most used method to mitigate deterioration include hydrophobic admixtures due to their ability to make concrete less susceptible to water saturation, even in the presence of cracks [6-9].

However, to guarantee the dimensional stability of concrete structures to extend their service life, recently the practice of using expansive agents has been recommended to manufacture shrinkage-compensating concretes, provided that an adequate wet curing is carried out. Quite recently, also the use of a shrinkage reducing admixture (SRA) [10, 11] has been suggested to improve the concrete performance in terms of lower risk of cracking related to drying shrinkage.
However, neither expansive agent nor SRA, when used separately, can definitely and safely avoid the risk of cracking caused by drying shrinkage in real concrete structures under practical curing conditions on many job-sites. On the other hand, the combined addition of a SRA with an expansive agent as CaO has been found to be very successful in producing restrained expansion in laboratory specimens [12-14] and concrete for outside industrial floor [15], even in the absence of any wet curing.

The aim of this work is to further investigate the still not clear synergistic effect on the shrinkage reduction when SRA and a CaO-based expansive admixture are used together in different types of cement-based materials, trying to account for this effect through the obtained results.

2. Experimental
Firstly, the study was performed by detecting the compressive strength development and the free shrinkage/expansion of mortars (M) and self-compacting concretes (SCC) without admixtures as well as with SRA alone and/or CaO.

Subsequently, in order to clarify the obtained results, the influence of SRA on CaO as well as cement hydration was investigated by TG (thermogravimetry), SEM (scanning electron microscopy), XRD (X-ray diffraction analysis) and temperature rise test, at different curing times.

2.1. Materials
A commercial portland-limestone blended cement type CEM II/A-L 42.5 R according to the European Standards EN-197/1 was used. The Blaine fineness of cement was 0.415 m²/g and its density was 3050 kg/m³. The chemical composition of cement is reported in Table 1. Natural sand with 5 mm maximum size, volume mass of 2620 kg/m³ and water absorption of 3% was used as aggregate. In the case of SCC, crushed limestone aggregate (12 mm maximum size), a commercial filler based on limestone powder with specific gravity equal to 2.70 g/cm³, a 30% aqueous solution of an acrylic-based superplasticizer together with a viscosity modifying agent (VMA), based on biopolymers, were also used. A shrinkage reducing admixture (SRA) based on propylene-glycol ether and a calcium oxide based expansive agent (CaO) were considered.

| Table 1. Chemical analysis of cement. |
|--------------------------------------|
| Oxide   | (%) |
| SiO₂    | 29.67 |
| Al₂O₃   | 3.74  |
| Fe₂O₃   | 1.80  |
| TiO₂    | 0.09  |
| CaO     | 59.25 |
| MgO     | 1.15  |
| SO₃     | 3.25  |
| K₂O     | 0.79  |
| Na₂O    | 0.26  |
| L.O.I.  | 11.62 |

2.2. Mechanical tests and free shrinkage/expansion measurements
Mechanical tests and free shrinkage/expansion measurements have been carried out on two different systems: mortars (M) and self-compacting concretes (SCC).

Mortars with cement to sand ratio 1:3 (by weight) and water/cement (w/c) of 0.50 were manufactured. Self-compacting mixtures with w/c of 0.60 were manufactured by using a limestone
filler, an acrylic based superplasticizer and a viscosity modify agent in order to guarantee a slump flow of at least 600 mm.

Mortars or self-compacting concretes were manufactured either without admixtures (labelled in the text as Ref) and with 10% (by cement weight) of CaO-based expansive admixture partially replacing sand (labelled in the text as CaO), or with 2% (by cement weight) of a shrinkage reducing admixture (labelled in the text as SRA) and with both admixtures (labelled in the text as SRA+CaO). In this last case, the shrinkage reducing admixture was dosed at 2% by cement+CaO weight. The amount of mixing water was reduced by a volume corresponding to that of SRA. The mixture proportions of the manufactured mortars and self-compacting concretes are reported in Table 2.

### Table 2. Mortar (M) and self-compacting concrete (SCC) mixture proportions (kg/m3).

| Mixture                      | Ref | SRA | CaO | SRA+CaO | Ref | SRA | CaO | SRA+CaO |
|------------------------------|-----|-----|-----|---------|-----|-----|-----|---------|
| Water                        | 256 | 246 | 256 | 245     | 188 | 182 | 188 | 181     |
| Cement                       | 512 | 512 | 512 | 512     | 305 | 305 | 305 | 305     |
| Natural sand                 | 1536| 1536| 1485| 1485    | 660 | 660 | 630 | 630     |
| Crushed aggregate           | -   | -   | -   | -       | 900 | 900 | 900 | 900     |
| Limestone filler             | -   | -   | -   | -       | 236 | 236 | 236 | 236     |
| Superplasticizer             | -   | -   | -   | -       | 3   | 3   | 3   | 3       |
| VMA                          | -   | 0.3 | 3   | 3       |
| SRA                          | -   | 10.2| 11.3| 6.1     |
| CaO                          | -   | 51.2| 51.2| 30.0    |

Measurements of compressive strength were carried out at curing times of 2, 7, and 28 days on cube specimens (100 x 100 x 100 mm) wet cured at 20°C.

For each mixture, prismatic specimens (100 x 100 x 500 mm) were also prepared according to Italian Standard UNI 6555-73 “Hydraulic Shrinkage Determination”. The mortar specimens were demoulded at the setting time (about 6-8 hours after mixing), while the SCC specimens at 22 hours after mixing. Then the specimens were permanently stored at constant temperature (20 ± 2 °C) and relative humidity (50 ± 2 %) all the test time long.

### 2.3. Physical, morphological and chemical analyses

Physical, morphological and chemical analyses have been carried out on CaO and cement pastes through temperature rise test, thermogravimetric, X-ray diffraction analyses and SEM observations.

In particular, CaO pastes were manufactured by mixing the CaO-based expansive agent with tap water, with water/CaO = 0.8 in the absence or in the presence of SRA (2% by CaO weight). Concerning with temperature rise test, CaO pastes were mixed at a temperature of 20±1°C for 3 minutes and then poured into a semi-adiabatic container equipped with a thermocouple and a monitoring system. The temperature was recorded at intervals of 30 seconds.

The effect of SRA on CaO hydration was investigated, in addition to the temperature rise test, by thermogravimetric analysis carried out on CaO pastes at 2, 6 and 24 hours after mixing as well as by X-ray diffraction analysis carried out on CaO pastes at 2 hours after mixing.

The effect of SRA on cement hydration was investigated by thermogravimetric analysis carried out on cement pastes with w/c = 0.5 in the absence or in the presence of SRA (2% by cement weight) at 2, 6 and 24 hours after mixing.
The effect of SRA on the hydration of shrinkage compensating cement pastes was investigated by thermogravimetric analysis, carried out on cement pastes with w/c = 0.5 containing CaO (10% by cement weight) in the absence or in the presence of SRA (2% by cement+CaO weight), after 2, 6 and 24 hours of hydration and by SEM morphological observations and EDXA analysis after 7 and 20 hours of hydration.

Concerning with thermogravimetric analysis, calcium hydroxide formed in CaO and cement pastes was determined. For each deadline, the hydration was stopped by removing unbound water through acetone and the resulting dried powder kept in a vacuum dryer until the test.

3. Discussion of test results

3.1. Mechanical properties and free shrinkage/expansion measurements

The data reported in Figure 1 (data are average values obtained by three measurements) show that the specimens containing SRA, either mortar or SCC, are characterized by lower compressive strength than the reference specimens without admixture, thus confirming the results already reported in the literature [12]. On the other hand, this effect is counterbalanced when CaO is added to the mixture, probably due to the reduction in actual w/c caused by the consumption of a small part of mixing water in the transformation of CaO into Ca(OH)$_2$, as reported by Collepardi et al. [12]. However, this effect was not observed by Maltese et al. [16], probably due to the lower CaO dosage.

![Figure 1. Compressive strength development of mortars (left) and SCC (right).](image-url)

Figure 2 (each datum is the average value obtained by five measurements) shows that the drying shrinkage of SRA mortar or SCC is significantly lower than that of the reference mixtures, where the reduction in drying shrinkage (about 50%) is related to the reduction in water surface tension caused by the presence of SRA [1]. However, the addition of SRA admixture to shrinkage-compensating mortar or SCC (SRA+CaO) increases dramatically the expansion value detected when only a CaO-based expansive agent is added (CaO). There is a synergistic effect in the shrinkage reduction when SRA and CaO-based expansive agent are used together, confirming the results reported by Maltese et al. [16] and Collepardi et al. [12].
3.2. Physical, morphological and chemical analyses

Concerning the effect of SRA on CaO hydration, the results obtained from the temperature-rise test, reported in Figure 3, make clear that SRA does not influence significantly the hydration rate of CaO. The very slight delay in calcium oxide hydration in the presence of SRA is probably due to the reduction of water permittivity by SRA [18] as an organic hydrophobic molecule. X-ray diffraction analysis (Figure 4) and calcium hydroxide determination (data are average values obtained by three measurements) through thermogravimetric analysis (Figure 5a), carried out on CaO pastes with and without SRA reveal a slight higher amount of calcium hydroxide in the presence of SRA probably due to the SRA ability to reduce the water solubility of calcium hydroxide [18].

On the other hand, thermogravimetric analysis carried out on cement pastes (Figure 5b) underlined that in general SRA hindered calcium hydroxide formation. Morphological SEM observation of shrinkage compensating cement pastes evidenced that after 7 hours of hydration (Figure 6), the presence of SRA induces a finer microstructure of the hydration products of CaO. After 20 hours of hydration (Figure 8) the presence of SRA inhibits the growth of fibers-like calcium silicates hydrates, which are responsible for mechanical strength and stiffness of cement-based materials, confirming the observations of He et al. [17] although through other techniques.
Figure 4. XRD pattern of CaO pastes in the presence (right) and in the absence (left) of SRA after 2 hours of hydration.

Figure 5. Calcium hydroxide content determined by thermogravimetric analysis in CaO pastes (left) and in the cement pastes (right).

A finer microstructure of CaO hydration products together with a delay in the solid microstructure development of cementitious materials by SRA, could induce higher deformability of mortars and concretes and, therefore, greater expansion.

Figure 6. SEM micrograph of cement pastes with CaO (10% by cement weight) in the absence of SRA (left) and in the presence of SRA (2% by cement+CaO weight), after 7 hours of hydration.
Figure 7. SEM micrograph of cement pastes with CaO (10% by cement weight) in the absence (left) and in the presence (right) of SRA after 20 hours of hydration.

4. Conclusions
A synergistic effect is produced by the combined use of a propylene glycol ether-based SRA and CaO-based expanding agent to obtain cement based materials less sensitive to free shrinkage.

The results obtained by this work show that SRA induce a finer microstructure of the hydration products of CaO and a retarding effect on the microstructure development of cement based materials.

A more deformable mortar or concrete, due to the delay in microstructure development by SRA, coupled with a finer microstructure of the hydration products of CaO can allow higher early expansion, which might contribute in contrasting better the successive drying shrinkage.

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