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A chemical/mineralogical investigation of the behavior of sulfoaluminate binders submitted to accelerated carbonation

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ABSTRACT

The paper addresses the carbonation of CSA based binders from the mechanical, chemical and mineralogical point of view. Three different binders have been investigated, revealing that many hydrated phases can protect ettringite against carbonation. In particular, the presence of AFm phases gives a significant contribution to buffer the pH in alkaline range and to preserve the protective film of steel reinforcement bars. In a carbonated environment AFm phases act as ionic exchangers: carbonate ions replace sulfates in the interlayer and in these conditions the released sulfate ions contribute to the formation of new ettringite, with a beneficial effect on compressive strength performances. Experimental data are compared with models and carbonation mechanisms are described.

1. Introduction

Among the possible chemical attacks that a concrete structure must front during its service life, carbonation is the prevailing one in urban and industrial areas, where the concentration of CO_2 in the air is high due to environmental pollution. The interaction of CO_2 with hydrated mineral phases of cement, in particular with $Ca(OH)_2$ abundantly formed in Ordinary Portland Cement (OPC) pastes, causes a decrease of the pH value of the cement paste and contributes to create condition where process of steel reinforcement bars corrosion may take place leading, at the end, to severe damages in buildings and infrastructures [1].

The ability of concrete to store CO_2 is also gaining more and more attention from a different point of view: thanks to their widespread diffusion, cement-based materials have a very high potential to become the largest CO_2 sequestrating agent in the world [2]. This aspect is nowadays a great challenge as a result of the urgent need to reduce the intake of anthropogenic CO_2 in the atmosphere [3], especially if combined with the possibility to develop new binders with low CO_2 embedded, such as binders with reduced clinker content, calcium sulfoaluminate cements (CSA), etc.

A deep knowledge of the mechanisms involved in CO_2 attack on innovative cement based materials is fundamental also in view of the use of alternative reinforcement of the concrete, such as glass fiber reinforcement polymers (GFRP) or carbon based reinforcement bars: these innovative materials are appealing solutions for the next future, since they would completely eliminate the risk of damage of concrete induced by steel corrosion and favor the spread of low clinker cements.

Calcium Sulfoaluminate Cement (CSA cement), is a non-Portland hydraulic binder produced from limestone, bauxite and gypsum and based on ye'elimite ($\mathbf{C_4A_3\bar{S}}$)[1] as main mineral phase [4,5]. Differently from OPCs, CSA based systems are high-performance binders characterized by fast setting and rapid hardening as well as high chemical resistance and reduced shrinkage, that they can counteract thanks to an expansive behavior [6,7]. These performances arise mostly as the consequence of the rapid formation of stable ettringite ($\mathbf{C_6A\bar{S}_3 \cdot H_{32}}$) crystals during the early hydration [8]; in a second time, phases such as monosolfoaluminate (monosulfate, $\mathbf{C_4A\bar{S} \cdot H_{14}}$) and strätlingite ($\mathbf{C_2ASH_8}$) also form [9,10]. When CSA clinker/cement is mixed with OPC, a wide range of products characterized by markedly different engineering features, such as high early compressive strength, tunable time of workability depending on the use of different additives, high resistance against frost, limited shrinkage, can be obtained [11]. In this case a different reaction for the formation of ettringite is established, consuming portlandite produced by the OPC component hydration [9].

Both when used alone and in mixture with OPC, a low-porous

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[1] Note that standard cement nomenclature is followed here, whereby C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, $\bar{S}$ = SO_3, $\bar{C}$ = CO_2 and H = H_2O.

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structure [12,13] is obtained, a distinguishing feature making CSA cements also less sensitive to possible interaction with external agents and, therefore, theoretically able to confer highest durability to concrete structure. Nevertheless, durability aspects of concrete based on CSA cements are still part of ongoing research activity and due to a very limited use of this binder in Europe, in the last decades there is low in-field practical experience (mainly experienced by cement companies in internal tests) to support laboratory tests.

As a general feature, CSA cements are considered less resistant to CO_2 penetration than OPC: the initial basicity of a CSA cement is actually lower than that of a Portland based paste, nevertheless it is high enough to guarantee the formation of the steel bar protective film [14]. Moreover, the sensitivity of ettringite towards CO_2 is well known and its decomposition into calcite, gypsum and aluminium hydroxide under CO_2 exposure is established [15–17]. Again, the absence of portlandite among the hydration products of a CSA cement is considered a disadvantage: in OPC, $Ca(OH)_2$ behaves like a sacrificial agent, able to capture CO_2 and slower its penetration inside the concrete. On the other hand, hydrated sulfoaluminate cement pastes are characterized by a hydrated phase assemblage which is completely different from that of an OPC, thus also chemical mechanisms involved in the carbonation process may be far different and require a deeper knowledge. In particular, the fundamental presence of AFm phases in sulfoaluminate cement pastes has been recently demonstrated for what concerns both hydration and durability issues [18,19]. Monosulfate, strätlingite and the other members of the AFm family are layered double hydroxide (LDH), i.e. structures composed by positively charged main layers $[Ca_2Al(OH)_6]^+$ and negatively charged interlayers $[X{\cdot}nH_2O]^-$, where X is one monovalent anion or half a divalent anion. A characteristic feature of LDHs is their high anion exchange ability: their interlayer can be easily replaced by a different anion depending on the environment in which they are placed.

It has been demonstrated that single synthesized AFm phases are relatively stable against CO_2 even in pressurized exposure conditions [20]. The direct use of LDH as additive for improving the carbonation resistance has also been tested [21].

A deeper knowledge of the formation and behavior of these phases inside a sulfoaluminate cement could significantly contribute to the possibility to specifically design binders with improved durability performances and to proof their stability against CO_2 attack. In the study hereafter described three sulfoaluminate cements have been submitted to accelerated carbonation by exposure in a 4% CO_2 environment and the carbonation depth has been measured up to 1 year. Carbonated mortars have been characterized through compressive strength test and mercury intrusion porosimetric analysis, while the effect of CO_2 on the mineralogical composition of pastes has been investigated by a combination of X-ray diffraction (XRD), thermogravimetric/differential scanning calorimetric analysis (TG/DSC) and $^{27}Al/^{29}Si$ nuclear magnetic resonance spectroscopy (NMR). In particular, solid state NMR (SSNMR) spectroscopy revealed to be a powerful technique for probing the molecular structure and assemblage of phases in a hydrated cement [22–24]. For example, ^{27}Al NMR has been used to study the identity and quantitative nature of aluminate phases formed during cement hydration [25,26]. With ^{29}Si NMR, C-S-H and C-A-S-H structure formation and evolution during long hydration times have been extensively studied [27,28]. Carbonation of cement paste leads to changes in the nature of both ^{27}Al and ^{29}Si containing phases, and SSNMR spectroscopy has been employed in this study to investigate the modifications happening at the molecular level [29,30]. Finally, carbonated phase assemblage has been modeled as a function of the amount of CO_2, with the double aim to help the interpretation of experimental data and to establish the different CO_2 storing capacity of each cement.

2. Materials and methods

The three investigated binders, supplied by Buzzi Unicem, are:

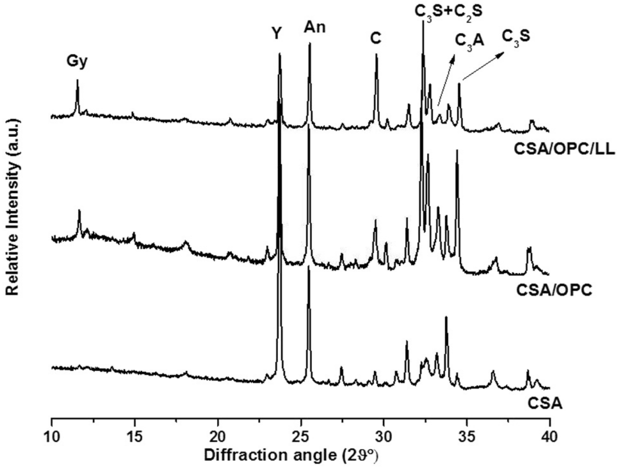

Fig. 1. XRD patterns of the investigated binders (Gy = gypsum; Y = ye'elimite; An = anhydrite; C = calcite).

- CSA: a pure CSA cement;
- CSA/OPC: a mixed binder based on CSA cement and CEM I 52.5R about 40:60;
- CSA/OPC/LL: a mixed binder based on CSA cement and CEM II/A-LL 42.5R about 40:60.

The mineralogical composition obtained by Rietveld refinement on X-ray diffraction patterns (Fig. 1) is summarized in Table 1, together with the chemical composition obtained by X-ray fluorescence after calcination at 950 °C. All the three binders had a surface area of about 4500 cm^2/g.

The carbonation chamber was set, on the basis of prTS 12390-12 [31], as to guarantee a 4% CO_2 concentration at 20 °C. In Fig. 2, a sketch of the chamber (modified Glove box, 900 × 650 × 700 mm) is shown, where it is possible to see:

- two gas bottles (air and CO_2 respectively);
- a two-flowmeter system, to set the flow of air and CO_2 respectively;
- a fan for allowing the recirculation of air;
- a $NaNO_2$ saturated solution, for maintaining internal moisture around 70%;
- a security valve to let out overpressure, if necessary.

Table 1
Mineralogical (above) and chemical (below) composition expressed as % in weight of the investigated binders (minor phases: MgO and C_2AS; minor elements: Na_2O, K_2O, TiO_2).

	ICDD reference number	CSA	CSA/OPC	CSA/OPC/LL
C_3S	31-0331	–	41.3	34.1
C_2S	33-0302	22.0	9.8	9.6
C_3A	38-1429	5.3	10.2	8.5
C_4AF	30-0256	5.7	2.8	2.7
$C_4A_3\bar{S}$	30-0256	41.1	15.9	16.2
Anhydrite	37-1496	17.1	11.6	10.8
Gypsum	33-0331	–	1.4	2.2
Calcite	05-0586	2.3	1.0	11.5
Dolomite	11-0078	1.3	2.3	2.0
Minor phases	–	5.2	3.7	2.4
CaO		42.2	56.4	53.4
SiO_2		9.3	12.9	11.8
Al_2O_3		24.3	11.9	11.2
Fe_2O_3		2.8	1.7	2.8
SO_3		15.4	10.8	11.8
Minor elements		3.6	4.0	3.1
LOI		2.4	2.3	5.9