

ADVANCED CHARACTERIZATION OF CHLORIDE BINDING IN OPC AND LC³ PASTES

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Abstract

The incorporation of supplementary cementitious materials (SCMs) in cement pastes enables both decreasing CO₂ emissions and increasing the concrete durability, notably with a better resistance against chloride ingress and thus retarding the chloride-induced corrosion of steel rebars. Nevertheless, a better understanding of the chloride fixation in cement pastes is required to build an accurate model for the transport of chlorides in new types of cementitious systems with SCMs. The purpose of this study is to characterize the chloride binding capacity of Limestone Calcined Clay Cement (LC³) pastes compared to Ordinary Portland Cement (OPC) pastes.

The binding of chlorides was investigated in hardened cement pastes equilibrated with 0.5M NaCl and 0.5M NaCl + 0.3M NaOH solutions whose chloride concentration is similar to that of sea water. The total chloride content was determined by acid dissolution of the paste after exposure, while chemically and physically bound chlorides were determined by X-Ray Diffraction (XRD) coupled with Rietveld analyses, Scanning Electron Microscopy with Electron Dispersive Spectroscopy (SEM-EDS) and water dissolution of the pastes.

The results showed that the higher content of AFm phases in LC³-50 pastes at 28 days did not lead to a higher chloride binding capacity compared to the reference OPC pastes, for both investigated chlorine solutions. XRD and SEM-EDS provided coherent estimates of chemically bound chlorides into AFm phases for each system (i.e., different solid solutions of Hemihydrate and Friedel's salt). These chlorides fixed in AFm were found to be lower than the difference between total acid-soluble chlorides and water-soluble chlorides (by 0.4 to 2.3 mg of fixed chlorides per gram of paste, depending on the system), suggesting other mechanisms of chloride binding such as physical binding on the C-A-S-H. Overall, the findings in this study suggest that the amount of the different kinds of chlorides fixed in cement pastes can be evaluated with relatively straightforward methods such as XRD/Rietveld and acid-soluble chloride titration.

Keywords: Chloride binding, AFm, Friedel's salt, limestone calcined clay cement

1. INTRODUCTION

In the search for a more accessible and durable binder for concrete with a lower carbon footprint, the addition of calcined clay and limestone to Portland cement was found to be a sustainable alternative while maintaining similar mechanical properties as 100 % Portland cement [1,2]. Chloride transport in cement pastes is a key parameter to predict the durability of the concrete, previous studies have shown significant increase of the resistance capacity against chloride ingress in LC³ systems compared to OPC systems, consequence of denser microstructure and porosity refinement in LC³ pastes [2-5].

Complete modelling of chlorides transport requires to consider the capacity of the hardened cement paste to fix chlorides in two ways: either by chemical binding in AFm by the replacement of the carbonate counter-ion by 2Cl⁻ (forming Friedel's salt), either by physical binding in C-A-S-H [6]. Chemically bound chlorides in AFm have been quantified in OPC by researchers using notably XRD [7] and previous work showed that carboaluminates and Friedel's salt can coexist within a solid solution [8,9]. The compounds released from calcined clays and limestone during hydration lead to higher content of carboaluminates [10] and thus to a potentially higher binding capacity of LC³ systems.

In this study, the total, chemically and physically fixed chlorides were quantified in OPC and LC³-50 hardened pastes equilibrated with a 0.5 M NaCl solution (chloride ingress in marine environment can be estimated using NaCl solutions [11]) at two different pH during 8 months with no renewal of the solution. XRD, SEM-EDS and titration of acid/water-soluble chlorides were employed to investigate the effect of both the binder and the pH on the amount of Friedel's salt. A further aim was to provide insights on the comparability between acid-soluble (total chlorides) and water-soluble (not bound chlorides) chloride contents in the studied systems in relation to the amount of chemically bound chlorides.

2. MATERIALS AND METHODS

The raw materials used in this study to produce the cement pastes are listed as follows: an industrial cement CEM I 42.5, an Indian calcined clay containing 45% of calcined kaolinite, fine limestone powder and gypsum of chemical grade. Chemical grade NaCl and NaOH were employed to prepare the exposure solutions. All the samples were prepared at the same water-to-binder ratio of 0.4 by mass and were cured in their pore solution for 28 days at room temperature.

2.1 Sample preparation

A series of OPC pastes was prepared by mixing CEM I with distilled water and a series of LC³-50 pastes was prepared by mixing 53 % of CEM I, 30 % of calcined clay, 15 % of limestone and 2 % of gypsum. The powders were homogenized using a paint mixer with ceramic balls for 10 minutes before mixing with distilled water. A high-shear mixer was used to mix the pastes at 1600 RPM for 2 min in air, followed by 1 min under vacuum at 450 RPM. A superplasticizer (polycarboxylate-based) was added to ensure a good workability. The fresh pastes were cast into cylindrical polypropylene recipients ($\varnothing = 33$ mm, $h = 55$ mm) sealed and left at room temperature for the first 24 hr. The hardened pastes were then cured at room temperature in slightly larger recipients filled with the lowest possible amount of water. A few grams of sacrificial finely ground sample (from the same batch) was added into each curing container to act as a leaching buffer and allow the curing in "pore solution".

After 28 days of curing, the cylinders were removed from the curing solutions and slices of about 2 mm thick were cut out using a water-lubricated saw, dismissing the first 2 mm of the cylinder's top and bottom. Slices were kept in a wetted tissue before being transferred in a slightly larger polypropylene cylindric container ($\varnothing = 36$ mm, $h = 60$ mm) filled with 40 ml of the host solution (0.5 M NaCl or 0.5 M NaCl + 0.3 M NaOH). Two slices were inserted per recipient along with two small polypropylene pieces inserted between slices to ensure the whole surface of the slices was in contact with the solution. Samples were stored at room temperature for about 8 months to reach equilibrium.

2.2 XRD and SEM-QEDS

The phase assemblage in the cement pastes was quantified by XRD coupled with Rietveld refinements on a 28-day cured sample as a reference and on the two samples exposed to high and low pH NaCl solutions. A slice was wet polished using its host solution for about 1 min with a 1200 carbide paper on both sides, it was then gently wiped with a wet paper and its Saturated Surface Dry (SSD) mass was recorded as well as its diameter and thickness. The slice was analyzed on a X'Pert PANalytical diffractometer in the Bragg-Brentano geometry using a $\text{CuK}\alpha$ source operated at 45 kV and 40 mA with a X-Celerator detector. The beam was constrained by fixed divergence and anti-scatter slits of 0.5° , with a mask of 15 mm. The 2θ range was $[5^\circ, 70^\circ]$ with a step size of $2\theta = 0.02^\circ$ and the scan lasted for 14 min. The external standard method was employed with a rutile standard. The phase assemblage quantification was carried out considering a Friedel's salt solid solution (Fs_{ssol}) between the Hemicarboaluminate (Hc) and pure Friedel's salt (Fs) phases, whose chemical composition was extracted from the position of the Friedel's salt peak, as illustrated in Figure 1 and described in [9].

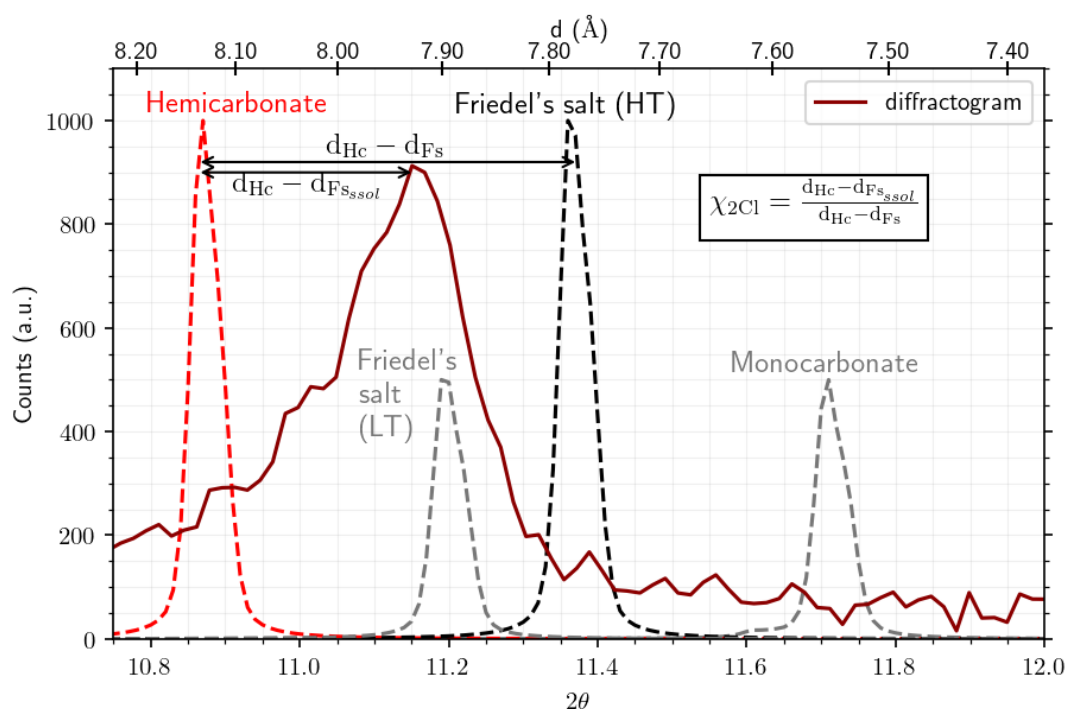


Figure 1: Determination of the chloride content within the Friedel's salt solid solution

The weight fraction of chemically fixed chlorides in AFm was calculated with Eq. (1):

$$\%Cl [\%wt] = f_{Fs_{ssol}} \cdot \frac{d_{Hc} - d_{Fs_{ssol}}}{d_{Hc} - d_{Fs}} \cdot \frac{2M_{Cl}}{M_{Fs_{ssol}}} \cdot 100 \quad (1)$$

where $f_{Fs_{ssol}}$ is the mass fraction [-] of the Friedel's salt solid solution obtained from the Rietveld refinement, d_X is the basal spacing of the phase X [Å] and M_{Cl} and $M_{Fs_{ssol}}$ are the molar mass of Cl and the Friedel's salt solid solution [g/mol].

After the analysis, the slice was dried using the solvent exchange method [12]: isopropanol was changed two times during the first 24 hr, then the sample was removed after 5–7 days of immersion and placed in a desiccator for at least 48 hr. A piece of the sample was then impregnated using a low viscosity epoxy resin. The sample's surface was polished using diamond suspensions (9 µm, 3 µm and 1 µm). The carbon-coated polished section was studied using by scanning electron microscopy on a Zeiss Cross Beam FEI equipped with an Oxford Ultim Max 170 energy-dispersive spectrometer. The EDS analyses were calibrated with standard reference materials (CaCO₃ for C, CaSiO₃ for O & Ca, Jadeite for Na, MgO for Mg, Al₂O₃ for Al, SiO₂ for Si, CaSO₄ for S, KCl for Cl & K, TiO₂ for Ti, and Fe₂O₃ for Fe). Quantitative chemical mappings were averaged from 12 frames at a resolution of 1024 x 768 with a pixel width of 0.0682 nm and a pixel dwell time of 256 µs.

The maps were analyzed with the *edxia* framework [13,14]. Representative points are extracted from the maps using a SLIC segmentation of a Si-Al-Ca composite image. These points are then analyzed using the Cl/Ca vs. Al/Ca ratio plots as described by Sui et al. [9], i.e. the composition of the pure AFm is given by the extrapolation of the mixture line between the C-S-H and the AFm to Al/Ca=0.5.

2.2 Acid-soluble and water-soluble chlorides

The second slice exposed to each host solution was wiped with a paper wetted with the host solution and broken up into two half disks by hand. The protocol described in ASTM C1152 [15] was adapted to determine the amount of acid-soluble chlorides in one half, whereas the amount of water-soluble chlorides in the second half was determined with a protocol adapted from ASTM C1218 [16]. Both protocols are described on a basis of 10 g of concrete, but given the homogeneity and the size of the cement paste specimens used in this study, the weight of each half-slice was only around 2 g. Therefore, every quantity of chemicals employed were scaled accordingly. In ASTM C1218 (water-soluble chlorides), filtration was performed through a PA 0.2 µm paper using a syringe rather than by gravity or by vacuum.

The weight fractions of acid-soluble and water-soluble chlorides were determined using Eq. (2):

$$\%Cl [\%wt] = V_{AgNO_3} \cdot c_{AgNO_3} \cdot M_{Cl} / m_{sample} \cdot 100 \quad (2)$$

where V_{AgNO_3} is the volume [L] resulting from titration, c_{AgNO_3} is the concentration of the AgNO₃ solution [mol/L] and m_{sample} is the mass of the powder used [g].

3. RESULTS AND DISCUSSION

3.1 Phase assemblage from XRD

Fig. 2 presents the mass fractions of the phases identified from Rietveld refinement in the investigated systems. The comparison of 28d samples and samples after equilibrium shows further hydration during the 8-month exposure in the NaCl solution, especially for the OPC system. As expected, the presence of calcite in both systems results in AFm in the form of carboaluminates instead of monosulfoaluminates [17]. Also, the Portlandite content was reduced during exposure, which can be explained with the leaching into the host solution. Moreover, the additional alumina, carbonate and calcium respectively released by calcined clays, limestone and portlandite in the LC³-50 system led to about twice the amount of carboaluminates compared to the OPC system. After exposure to chloride environment, carboaluminates were mostly transformed into a Friedel's salt solid solution, although non-negligible amount of carboaluminates remained in all systems except the LC³-50 system at a low pH (which also lost all its portlandite).

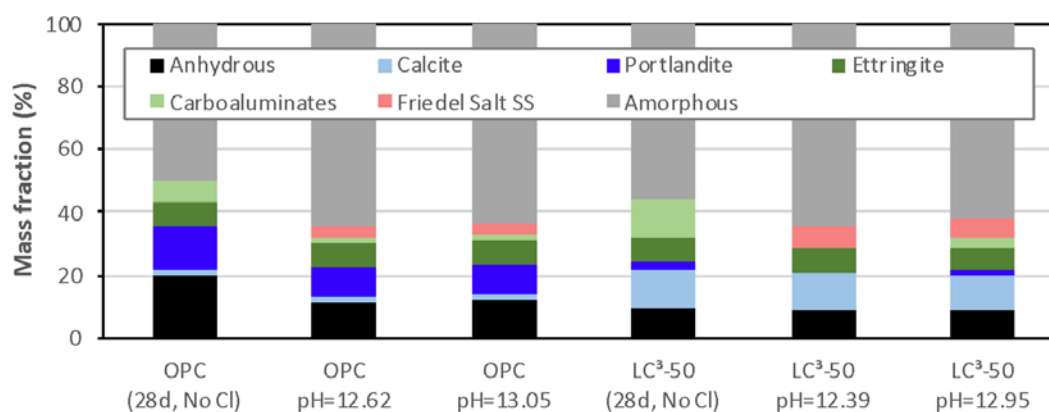


Figure 2: Phase assemblage from XRD coupled with Rietveld analysis

3.2 Chloride chemical binding in Friedel's salt solid solution

In all systems, “pure” Friedel's salt was not found for the NaCl concentrations investigated in this study, but solid solutions (Fs_{ssol}) were rather observed with different relative contents of Friedel's salt (Fs) and Hemicarboaluminate (Hc). The stoichiometry of Fs_{ssol} was investigated both from basal spacing of XRD patterns and from SEM-QEDS mappings (Fig. 3). The stoichiometry of the solid solution is given as the amount of chloride in the AFm phase. It is defined as $\chi_{2Cl} = 2Cl/Ca$. Notably, the two methods provided very coherent estimates of the AFm chloride content for both LC³-50 and OPC systems. This good agreement suggests that XRD basal-spacing analyses can be used to quantify the chemically bound chlorides in Fs solid solutions, allowing sustainable saving of time compared to SEM-QEDS mappings. The initial quantity of AFm in 28-days pastes is insufficient to estimate chloride binding in AFm phases after the exposure to the NaCl solution, given different equilibrium states and AFm chloride contents are reached despite identical protocols.

In addition, the lower pH of the host solution led to higher χ_{2Cl} , with a greater effect for LC³-50 than for OPC. The lowest value was obtained for the LC³-50 system at high pH. Moreover, χ_{2Cl} is higher for OPC at the same pH. XRD phase assemblage showed lower

amounts of carboaluminates in OPC pastes (Fig. 2), meaning there is less AFm to bind, eventually leading to a higher fraction of Friedel's salt per AFm than in LC³-50 pastes. However, the refined porosity in the latter limits significantly the chloride ingress as shown in [3]. Therefore, it cannot be excluded that the chloride transport properties of the porous network play a role in the chemical binding in AFm, by restricting the amount of chlorides in contact with the AFm.

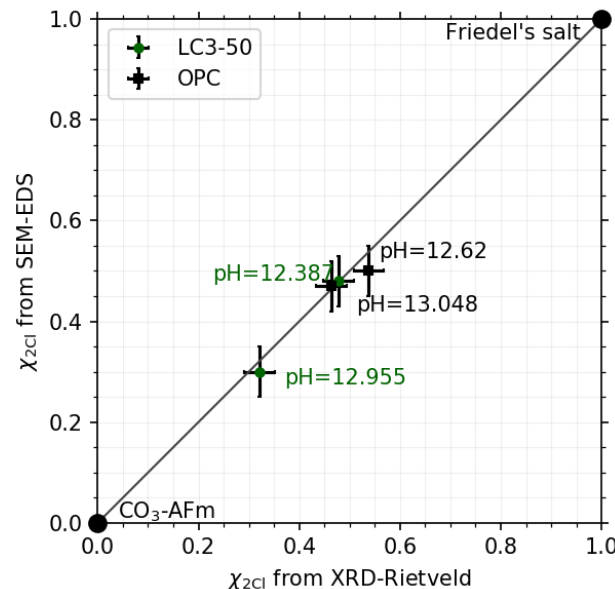


Figure 3: Comparison of the stoichiometry of the Fs + Hc solid solution (χ_{Cl}) between XRD and SEM-QEDS

3.3 Repartition of total chlorides between free chlorides and bound chlorides

Chloride content weight ratios obtained using Eq. (2) from acid-soluble and water-soluble chloride experiments were plotted in Fig. 4 along with the amount of chemically fixed chlorides in AFm determined with Eq. (1) from Rietveld refinements. Due to the complexity of the protocols, the analyses were performed on only one sample per system, therefore error bars cannot be provided.

LC³-50 systems showed lower water-soluble chloride content compared to OPC systems, which is consistent with previous studies on the chloride fixation in C-A-S-H in limestone-substituted binders [4]. The total amount of chlorides (acid-soluble chlorides) in LC³-50 appeared to be strongly dependent on the pH. Also, it is equal or lower than for OPC, although LC³-50 systems showed the highest content of AFm phases at 28 days. The chlorides bound in AFm represent about 25 % to 45 % of the total fixed chlorides, the highest fraction corresponding to LC³-50 systems and the cumulation of the chloride content in AFm with the water-soluble chlorides correspond to 78 % to 92 % of the total chloride amount, there is therefore in each system remaining chlorides that are not related to the chemical binding in AFm. Despite the fact the standard deviation of both ASTM 1152 and 1218 is negligible (~ 0.04 %), it cannot be excluded that this gap comes from experimental errors of the various experiments. However, these remaining chlorides may be fixed in other hydrates like C-A-S-H, suggesting that they are not water-soluble although being physically fixed. The latter

statement is beyond the scope of the current study, although it is part of ongoing work on characterization of the capacity of C-S-H and C-A-S-H to bind chlorides.

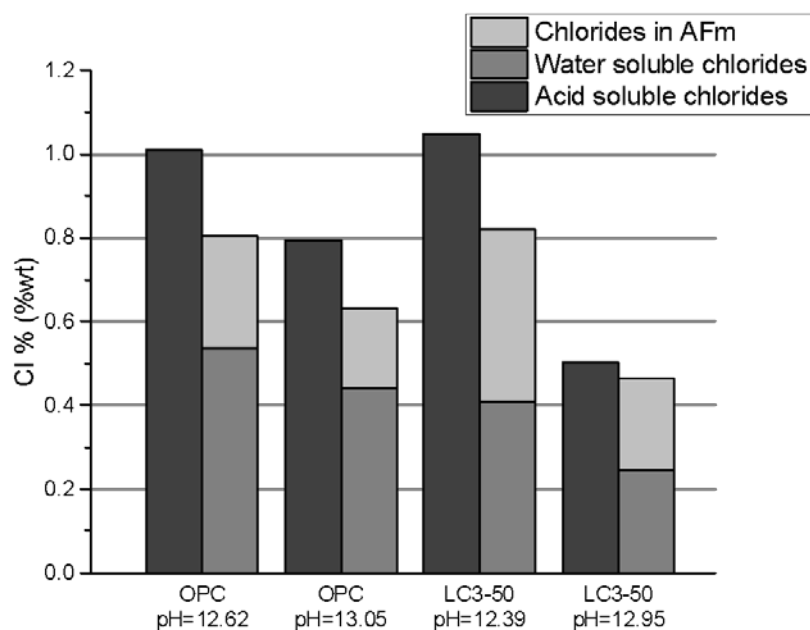


Figure 4: Acid/water-soluble chlorides + chlorides in AFm (XRD) weight fractions

4. CONCLUSIONS

Based on 8-month exposure of LC³-50 and OPC pastes to chlorine solutions, this study showed how chlorides were present in different quantities and bound with different mechanisms depending on the system and pH. Notably, chlorides were chemically bound in solid solutions of Fs and Hc (with variable χ_{Cl}) and most chlorides occurred as non-bound chlorides (water-soluble chlorides). The main findings of this study can be summarized as follows:

- No direct link was observed between the higher AFm content in LC³-50 pastes at 28 days (compared to OPC) and its capacity to chemically bind chlorides in Friedel's salt;
- The stoichiometry of Friedel's salt solid solutions was determined both from XRD patterns and from SEM-EDS mappings in very concordant estimations;
- The total binding capacity of LC³-50 pastes was found to be equal or lower than that of OPC pastes and strongly dependent on the pH of the chloride solution;
- The sum of chemically fixed chlorides in Friedel's salt and water-soluble chlorides was found to be lower than the total chloride content (acid-soluble) for both LC³-50 and OPC systems at both pH, suggesting non-negligible contents of chlorides are bound by other mechanisms (e.g., physical chloride binding).

In order to support and complete the presented characterization approach relying on acid/water-soluble chloride determinations and on the Rietveld refinement method, further ongoing investigation focusses on the physical binding capacity of C-A-S-H.

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