

CHLORIDE BINDING ASSESSMENT IN C₃S SYSTEMS WITH CALCINED CLAY

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Abstract

Chloride binding is an important factor for chloride transport in cementitious materials, which can fix the chloride on the solid phase and decrease the free chloride content. As an alumina-rich supplementary cementitious material, calcined clay can be applied to improve the binding capacity of the system. While the contribution of calcined clay to chemical binding (through the formation of Friedel's salt) is clear, its influence on physical binding (adsorption on hydration products) is still under debate. In this study, pure C₃S instead of cement was used to assess the binding capacity on the presence of calcined clay. In addition, extra limestone was added to investigate the synergetic effect between calcined clay and limestone on binding capacity. Binding capacity was evaluated by an equilibrium method between free chloride in the solution and bound chloride in the solid phase. The evolution of the phase assemblage was analyzed using XRD-Rietveld, the pore structure, and the specific surface area were measured with the nitrogen adsorption method. It was observed that the systems with calcined clay present higher binding capacity than the reference. In addition, the binary system demonstrates similar bound chloride content compared to the ternary system. Characterization results were used to correlate the microstructural properties of cementitious materials to chloride binding capacity. Results showed that the calcined clay contributes to the chemical binding and, that there is no clear relation between specific surface area and physical binding in cementitious materials.

Key words: Chloride binding, Calcined clay, C₃S

1. INTRODUCTION

Supplementary cementitious materials (SCMs) incorporated in cements and concrete are by far the most realistic means to increase the performance [1]. The “classic” SCMs are fly ash (FA), slag, silica fume and so forth. Nowadays, kaolinitic clay, calcined at 700-850°C, is an important source of additional SCMs. However, the performance of samples with calcined clay has not been comprehensively investigated.

Steel corrosion, caused by chloride ingress, is one of the most serious durability issue for cementitious materials. A high chloride binding capacity can fix the chloride ions on solid phase to avoid chloride ions reaching steel [2]. There are two kinds of chloride binding: chemical binding and physical binding. Alumium-rich AFm phase (monosulfoaluminate (Ms), Monocarboaluminate (Mc) or Hemicarboaluminate (Hc)) can react with chloride to form Friedel’s salt or Kuzel’s salt, which is called chemical bound chloride [3]. Some other chloride ions can be adsorbed on the surface of hydration products like C(-A)-S-H, which is treated as physical bound chloride [4,5].

For the calcined clay, there is abundant aluminum in the materials and calcined clay is a pozzolanic material [6]. Therefore, calcined clay has the potential to improve the chloride binding of cementitious materials. This work focused on the chloride binding capacity of C₃S and the mechanism of calcined clay to improve chloride binding capacity. Microstructure characterization was made to get a better understanding of the factors affecting chloride binding.

2. MATERIALS AND METHODS

This study used a C₃S powder, a limestone powder (LS) and an industrial calcined clay (calcined kaolinite content is 48%). The chemical composition is shown in Table 1.

Table 1: Chemical composition (wt. %) of cementitious materials

	CaO	SiO ₂	Al ₂ O ₃
C ₃ S	73.4	26.6	
Calcined clay		54.5	45.5
Limestone	55		

Four paste mixtures were studied, with the name of C₃S 0.5, C₃S 1.0, C₃S+Clay, C₃S+Clay+LS. The water to solid (w/s) ratio for all the systems is 0.5, except for the C₃S 1.0, which is 1.0. In binary system, calcined clay was used to replace 30% of C₃S while in ternary system, extra limestone was employed to substitute a further 15% of C₃S. The paste preparation procedure included blending of the dried powders, followed by mixing with deionized water for 2 min at 1600 rpm. Fresh paste was sealed for 24 h and after that submerged in water (minimum amount of water to avoid leaching) for further curing. For the water to C₃S ratio of 1.0 system, rotation was used for the first 24 hours to avoid bleeding.

The following methods are used to characterize the performance of the samples.

Binding capacity: After 28 days of curing, approximately 25g samples were weighed and placed in 100 ml of 0.1, 0.3, 0.5, 1, 3 M NaCl solution for 10 weeks until the equilibrium between free chloride and bound chloride was reached. The host solutions were then analyzed for chloride concentration by means of potentiometric titration using 0.05 M AgNO₃.

XRD analysis, coupled with Rietveld refinement, was employed to quantify the main phases in 28 days fresh paste samples. A PANalytical X'Pert Pro MPD diffractometer in a θ - θ configuration using Cu-K α source ($\lambda=1.54 \text{ \AA}$) with a fixed divergence slit size of 0.5° was used.

Mass balance: Along with the XRD analysis, a simplified mass balance calculation was used to quantify the C(-A)-S-H content in hydrated pastes:

(1) Total amounts of reacted oxides are quantified from reaction degrees of C₃S and CaCO₃, by using XRD Rietveld analysis.

(2) The Ca(OH)₂ (CH), AFt, AFm and calcite content are taken directly from XRD-Rietveld refinement, and the CaO included in them are subtracted from the initial reacted oxides.

(3) All CaO in remaining oxides is incorporated into C(-A)-S-H (CaO.aAl₂O₃.bSiO₂.4(a+b)H₂O, in this work a=0 and b=0.55 for pure C₃S system, a=0.065 and b=0.67 for systems with calcined clay from previous research [7]), assuming the molar ratio of H₂O/(Si+Al) to be 4 [8].

Nitrogen adsorption (N₂ adsorption): nitrogen adsorption with Barrett Joyner Halenda (BJH) model and Brunauer Emmett Tellerwas (BET) model were used for finding the pore size distribution and surface area of hydrated samples, respectively.

3. RESULTS

3.1 Binding capacity

Binding isotherm curves are shown in Fig. 1. Freundlich isotherm ($C_b = \alpha \cdot C_f^\beta$) was used to fit the experimental data. The parameters are provided in Table 2. Since several binding modes may coexist (physical and chemical binding), these parameters are only mathematical parameters without physical meaning. However, these parameters can be used to compare the binding capacity of different systems. C₃S+Clay system exhibits the highest bound chloride content among all the systems. When limestone is added, bound chloride content decreases a bit compared to the C₃S+Clay system. Systems with pure C₃S presents the lowest bound chloride content. In addition, pure C₃S systems demonstrate similar bound chloride content with the w/s ratio of 0.5 and 1.0, which means that the w/s shows little effect on chloride binding capacity. In Table 2, C₃S+Clay system shows the highest values of α , while C₃S 1.0 presents the lowest values. The higher values of α , the higher the binding capacity. Besides, the fitting curves for pure C₃S systems seem not as good as other systems. However, as a binding capacity evaluation indicator, the parameters from the Freundlich isotherm fitting can still be used.

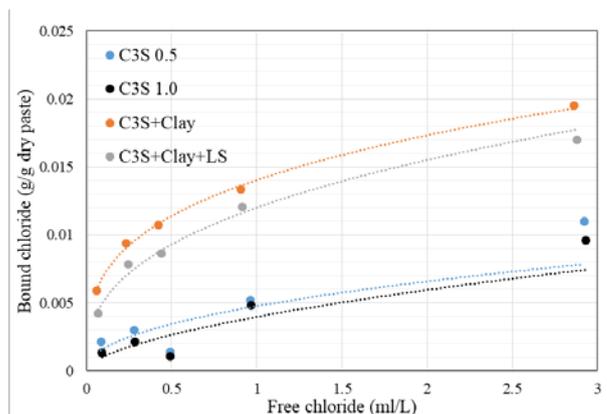


Figure 1: Binding isotherm of the investigated systems

Table 2: Binding coefficients for Freundlich isotherm

	α	β	r^2
C ₃ S 0.5	0.0048	0.467	0.5802
C ₃ S 1.0	0.0040	0.586	0.6915
C ₃ S+Clay	0.014	0.303	0.9975
C ₃ S+Clay+LS	0.012	0.370	0.9861

3.2 XRD/Rietveld analysis and mass balance results

Fig. 2 presents the XRD spectrums for C₃S and C₃S+Clay+LS. For C₃S 0.5 and C₃S 1.0 systems, the main hydration products are C(-A)-S-H and Ca(OH)₂. In C₃S+Clay+LS system, Hc and Mc were found thanks to the limestone reaction with the aluminum phase.

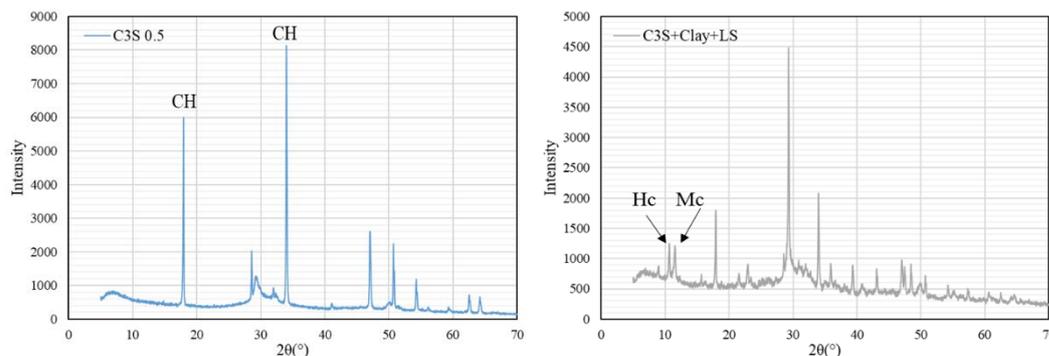


Figure 2: XRD spectrum for part of the investigated systems

Table 3 is a summary of the phase assemblage of the investigated systems from XRD/Rietveld analysis and mass balance calculation. It is clear that higher w/s ratio leads to higher degree of hydration in pure C₃S systems. For systems with calcined clay, AFt and AFm

were formed because of the Al and impurities of clay. Therefore, in C_3S +Clay and C_3S +Clay+LS systems, when NaCl solution is added, chemical binding of chloride may happen.

Table 3: Phase assemblage from mass balance (g/100g solid)

	CH	C(-A)-S-H	Calcite	AFt	Mc	Hc	Other phases	Free water
C_3S 0.5	39.32	95.98	0	0	0	0	0	10.01
C_3S 1.0	30.32	107.12	0	0	0	0	0	61.15
C_3S +Clay	13.16	104.36	2.42	5.29	0	0	7.07	14.50
C_3S +Clay+LS	6.28	89.50	12.52	2.68	7.68	2.97	3.55	23.72

3.3 N₂ adsorption analysis

N₂ adsorption method was used for pore structure and surface area comparison. Fig. 3 shows the pore size distribution of the investigated systems. For the pure C_3S system, there is a peak around 5nm. However, when calcined clay is added, the peak shifts to bigger size and becomes wider. Systems with calcined clay and limestone exhibits similar pore size distribution to the one with only calcined clay. This suggests that when supplementary cementitious materials are added to C_3S system, the pore size will become bigger. In addition, Table 4 presents the pore volume from N₂ adsorption method. The result shows that C_3S +Clay+LS shows the highest pore volume while the pure C_3S displays the lowest pore volume.

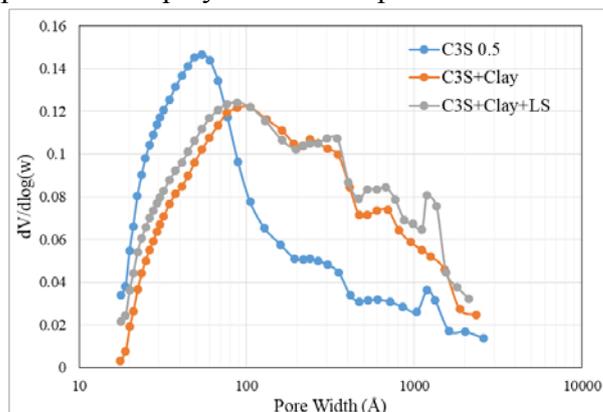


Figure 3: Pore size distribution from N₂ adsorption for 28d samples

Table 4: Pore volume from N₂ adsorption for the investigated systems

	C_3S 0.5	C_3S +Clay	C_3S +Clay+LS
Pore volume (cm ³ /g)	0.138	0.169	0.184

Surface area is very important for the physical binding capacity. It is found in some literature that when the surface area is higher, there are more chloride ions bound on C(-A)-S-H [9]. Fig.

4 is the surface area distribution curves for the investigated systems. The critical pore size are quite similar, around 2-4 nm, which may come from the representative pore size of C(-A)-S-H. However, it is clear that the total surface area decreases when calcined clay is present. In addition, sample with calcined clay and limestone exhibits higher surface area than the one with calcined clay in Table 5. Therefore, from the N₂ adsorption results, the addition of calcined clay increases the pore volume while decreases the surface area.

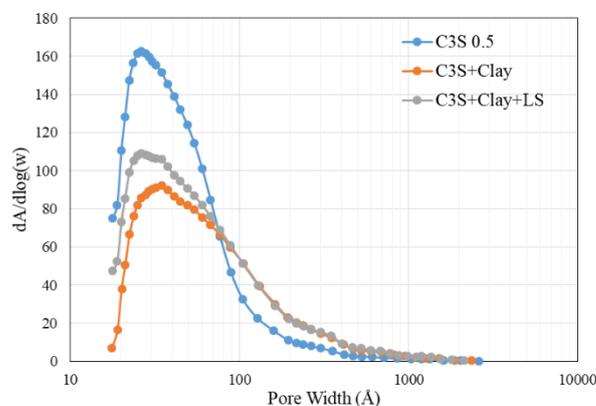


Figure 4: Surface area distribution from N₂ adsorption for 28d samples

Table 5: BET surface area from N₂ adsorption for the investigated systems

	C ₃ S	C ₃ S+Clay	C ₃ S+Clay+LS
BET surface area (m ² /g)	77.12	59.08	66.44

4. DISCUSSION

From the results session, when calcined clay was added to the system, binding capacity increases. In pure C₃S systems, only physical binding exists. However, for C₃S+Clay+LS system, physical binding and chemical binding both happen because of the C(-A)-S-H and AFm phases. For C₃S+Clay, even though no AFm was found in XRD spectrum, the Friedel's salt could still be formed in the presence of Al from the pore solution.

Since the Al content in C₃S+Clay and C₃S+Clay+LS systems are similar, we assume that the Friedel's salt in these two systems are same. Therefore, the values for chemical bound chloride could be estimated from the AFm content in C₃S+Clay+LS system. Fig. 5 correlates the surface area with physical bound chloride in 3M NaCl solution. The physical bound chloride content is from the total bound chloride subtracting the chemical bound chloride, under the assumption that all the AFm transformed to Friedel's salt. In Fig. 5, there is no clear relation between surface area and the physical bound chloride. There are two possible reasons for this: the Ca/Si of C(-A)-S-H ratio are different; the pH values of the NaCl solution are different. The Ca/Si ratio for pure C₃S system is 1.82 while it is 1.49 for systems with calcined clay. From previous study, the higher Ca/Si ratio, the higher binding capacity of C(-A)-S-H [10]. Table 6 shows the final pH of the NaCl solutions. The pure C₃S system presents lower pH values compared to the

systems with calcined, which is good for physical binding [11]. However, the reason for C_3S +Clay showing higher bound chloride than C_3S +Clay+LS is not clear. The reason may come from the higher C(-A)-S-H content in the former system. Therefore, the physical binding is a complicated process. More research is needed for the mechanism.

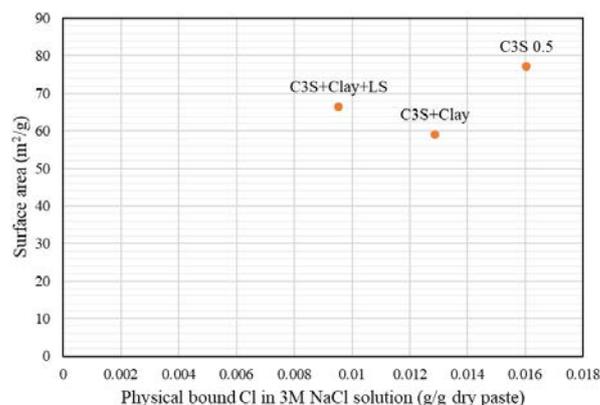


Figure 5: Relationship between N₂ adsorption results and physical bound Cl

Table 6: pH values of the NaCl solution after equilibrium

	C ₃ S 0.5	C ₃ S 1.0	C ₃ S+Clay	C ₃ S+Clay+LS
0.1M	12.622	12.61	12.695	12.658
0.3M	12.585	12.533	12.69	12.628
0.5M	12.568	12.523	12.624	12.59
1M	12.47	12.391	12.564	12.504
3M	12.188	12.092	12.257	12.249

5. CONCLUSION

This study investigated the chloride binding of C_3S systems in related to calcined clay. It is found that the presence of calcined clay can improve the chloride binding capacity, which comes from the improved chemical binding capacity; The W/C ratio shows little effect on chloride binding; There is no clear relation between the surface area and physical bound chloride. Surface area, Ca/Si ratio of C(-A)-S-H, pH of the final NaCl solution and C(-A)-S-H content could affect the physical binding of chloride.

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