Influence of Mineral Admixture in CSA Cement on Chloride Binding Capacity

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Abstract. Increasing chloride binding capacity of hardened cement paste is an effective method in reducing corrosion risk of reinforcement in concrete structures exposed to marine environment and guarantee its designed service life. Compared with traditional Portland Cement, Calcium Sulfoaluminate Cement (CSA) has been proved for its better chloride binding capacity in practice. However, in order to save cement consumption and reduce environmental pollution, it is important to investigate the influence of mineral admixture on the Cl- binding capacity of CSA cement. Based on this background, authors of this paper studied influence of key parameters within CSA-Cl- mix proportion, i.e. mixtures like Calcium carbonate (C), Slag (S), Fly ash (F) and Metakaolin (M) and use of gypsum and studied its effect on the chloride binding capacity. Meanwhile, the Cl- binding mechanism was also explored by means of XRD and TG. From the results obtained, it can be concluded that the use of gypsum led to an increase in ettringite, which caused a severe drop in chloride binding capacity; the addition of mixtures led to an increase in chloride binding capacity.

Keywords: calcium sulfoaluminate cement; chloride ion; gypsum; mixtures; binding capability

1. Introduction
In order to solve the major resource gaps that exist in the construction process, especially qualified problem of sand and gravel aggregate and the shortage of fresh water resources, the use of the rich marine resources of the sea sand given birth. However, the appearance of Cl- introduced into the interior of the concrete from the material components will cause corrosion of the steel bars, crack concrete and decline bearing capacity [1].

Recent studies show that the main factor causing the corrosion of the steel inside the concrete structure is the free Cl- in the pore liquid inside the structure, while the Cl- consolidated in the concrete has almost no obvious effect on the reinforcement [2,3]. Renaudin [4] et al. synthesized high-purity Friedel's salt crystals formed by ordinary Portland cement solidified Cl- by using pure chemical reagents Ca(OH)2, Al(OH)3 and CaCl2, confirmed that the Al element played the most important role in curing Cl- in the hydration products of ordinary Portland cement. For high-aluminum phase materials, in the 1970s, China Building Materials Science Institute successfully developed sulphoaluminate cement (CSA), which is mainly composed of calcium sulfoaluminate.

The existing research clearly indicates that in the CSA cement system, ettringite does not promote the consolidation of Cl-, and even the physical adsorption capacity is small, and the decisive effect on the consolidation of Cl- is the AFm phase formed by hydration. Zhenguo Shi [2] describes the distribution of Cl- and F salts in mortar samples, and describes that F salt is the main hydration product of consolidation of Cl-, and the Cl- consolidation ability of F salt is related to the monocarbonate consumed in the system. Many studies have shown that CSA cement has a higher resistance to Cl- erosion than PC, which can bind Cl inside the structure effectively [5,6]. Based on its excellent
binding capacity, some scholars have studied the use of CSA cement to treat industrial waste containing Cl\textsuperscript{-}. Adel Mesbah [7] studied the use of CSA cement hydration for superior Cl\textsuperscript{-} consolidation capacity to treat radioactive chlorides that may be produced by decommissioning old nuclear reactors.

The addition of mineral admixture in the cement system can not only reduce the amount of cement, save resources, and reduce the amount of CO\textsubscript{2} produced in the production process. Moreover, the addition of mineral admixture can effectively improve the performance of cement. Zhengguo Shi [2] studied the Cl\textsuperscript{-} binding ability in the portland-metakaolin-limestone blends system, and explained that the addition of a metakaolin mixture resulted in the formation of a large amount of Friedel's salt in the system, which significantly improved the Cl\textsuperscript{-} binding ability. Some scholars have also found that the presence of fly ash and slag improves the Cl\textsuperscript{-} consolidation ability of cement systems in the process of improving the anti-Cl\textsuperscript{-} erosion of cement systems [8,9]. The above mineral admixture promotes the Cl\textsuperscript{-} consolidation ability of the cement system to a certain extent, but for calcium carbonate, as reported by andrej ipavec [1] and Zhengguo Shi [2], the Cl\textsuperscript{-} binding capability tends to decrease, because the presence of calcium carbonate only serves as a filling, and to some extent, the amount of cement is reduced. These studies are based on the influence of different mineral admixtures on the Cl\textsuperscript{-} binding ability of the PC system, and the improvement of the consolidation capacity is related to the Al phase contained in the mineral admixture. For CSA cement systems with high aluminum content, different mineral admixtures have little research on Cl\textsuperscript{-} binding ability.

Based on existing research, it can be found that there is a problem with the CSA system. There is a lack of corresponding data comparisons on the mechanism of Cl\textsuperscript{-} binding and the effect on binding capacity in different mineral admixtures in high-aluminum phase CSA cement systems.

The authors use the higher Cl\textsuperscript{-} binding ability of CSA cement system with different mineral admixtures to effectively solve the adverse effects of Cl\textsuperscript{-} introduced by material components on reinforced concrete. The author used a purification reagent to prepare a real seawater Cl\textsuperscript{-} concentration solution (1.9\%) to participate in the preparation of cement paste samples to simulate the Cl\textsuperscript{-} concentration introduced during the use of seawater and sea sand in actual engineering. The material CSA as a basic cement system, and different mineral admixtures, calcium carbonate, slag, fly ash and metakaolin are added. The purpose of this study was to investigate the effects of different mineral admixtures on the ability to binding Cl\textsuperscript{-} in different cement systems.

2. Experiments

2.1. Materials and Mix Proportion

In this study, CSA clinker and commercial PC were used, which were manufactured by Beijixiong Cement Co., Ltd (China) and Guangzhou Zhujiang Cement Co., Ltd.(China). Their chemical and mineral compositions are summarized in Table 1. One PC mix was used to be reference for evaluating performances of binding capacity of the CSA samples. The density of CSA clinker is 2.90 g/cm\textsuperscript{3}.The chemical composition of Calcium carbonate (C), Slag (S), Fly ash (F) and Metakaolin (M) used in this work are presented in Table 1. Water used in the present study was deionized. The salt NaCl (reagent grade) was dissolved in deionized water.
Table 1. Chemical and mineral compositions of materials used (wt%)

| Chemical composition | CSA  | C   | S   | F   | M   | PC  |
|----------------------|------|-----|-----|-----|-----|-----|
| CaO                  | 45.34| 98.4| 40.23|15.34|0.35|64.47|
| Al₂O₃                | 34.34| 0.24|14.19|20.07|45.97|4.92|
| SO₃                  | 7.96 | -   | 2.69|1.82 |0.23|3.48|
| SiO₂                 | 7.01 | 0.38|31.35|45.87|49.67|20.35|
| Fe₂O₃                | 1.75 | 0.08| 0.7 |9.09 |1.61|3.06|
| MgO                  | 1.44 | 0.79| 8.66|1.58 | -  |2.34|
| TiO₂                 | 1.4  | -   | 0.8 |0.89 |1.96|0.16|
| Loss on ignition     | 0.76 | 0.11|1.38 |5.34 |0.21|1.72|

| Mineral composition  | CSA  | PC  |
|----------------------|------|-----|
| C₂S                  | 21.2 | 7.71|
| C₄A₂S                | 69.7 |
| C₄AF                 | 3.8  | 8.78|
| CTI                  | 2.5  |
| C₃S                  | 72.38|
| C₃A                  | 11.13|

In the used mixes, the water/binder ratio of CSA cement mixes was 0.5. CSA cement pastes were casted with two levels gypsum (G:CaSO₄·2H₂O) mass ratios (0% and 20%) [10,11]. Mineral mixtures with different mixture/binder ratio by mass (1:10 and 3:10) were developed and tested for their chloride binding capacity. In this purpose different types of pastes were listed in Table 2.

Table 2. Mix proportions of CSA samples

| Notation | Content (g) | Key factor (%) |
|----------|-------------|----------------|
|          | CAS | Gypsum | Water | NaCl | X | Gypsum/CSA | Water/binder |
| G0-0     | 100.0 | 0.0 | 48.4 | 1.6 | 0 | 0 | 0.5 |
| G1-0     | 83.3 | 21.1 | 44.0 | 1.6 | 0.2 | 0.2 | 0.5 |
| G0-10X   | 90.0 | 0.0 | 48.4 | 1.6 | 10 | 0 | 0.5 |
| G1-10X   | 75.0 | 19.0 | 44.5 | 1.6 | 10 | 0.2 | 0.5 |
| G0-30X   | 70.0 | 0.0 | 48.4 | 1.6 | 30 | 0 | 0.5 |
| G1-30X   | 58.3 | 14.8 | 45.3 | 1.6 | 30 | 20 | 0.5 |
| PC       | 100.0 | 0.0 | 48.4 | 1.6 | 0 | 0 | 0.5 |

X: Calcium carbonate (C), Slag (S), Fly ash (F) and Metakaolin (M).

2.2. Tests Carried Out

Chloride binding capacity: The chloride ions extraction test was measured according to (RILEM TC 178-TMC(RILEM,2002) d). Obtain the ratio in water-soluble (Vw) and acid-soluble (Vs) titration values and calculate the sample's binding capacity, the formula is:

\[ P = \frac{V_s - V_w}{V_s} \times 100\% \]

P—binding capacity, %
Vs—Silver nitrate solution consumption under acid-soluble conditions, ml
Vw—Silver nitrate solution consumption under water-soluble conditions, ml
X-ray power diffraction and thermogravimetric analysis: The powder samples tested by XRD and TG were the same as chloride-ions titration samples.
3. Results and Discussion

3.1. Cl⁻ Binding Capacity

The Cl⁻ binding percent of the samples aged with 3, 7 and 28 days are shown in Table 3. In order to compare the Cl⁻ binding capacity in the CSA system more intuitively, the result is compared with PC. From the results we can know that the binding percent of 3, 7 and 28d basically unchanged, in other word, the CSA cement have accomplished the initial Cl⁻ binding capacity before 3 days. So the average of the sample binding percent on 3, 7 and 28 days represent the Cl⁻ binding capacity of each sample (Fig.1). The following relationships can be observed from the results:

Table 3. Cl⁻ binding percent after 3, 7 and 28 days of hydration (%).

| Notation | 3d  | 7d  | 28d  | average | Notation | 3d  | 7d  | 28d  | average |
|----------|-----|-----|------|---------|----------|-----|-----|------|---------|
| G0-0     | 32.4| 42.8| 40.7 | 38.6    | G1-0     | 2.8 | 3.2 | 5.8  | 3.9     |
| G0-10C   | 39.7| 37.8| 43.7 | 40.4    | G1-10C   | 14.5| 16.9| 19.1 | 16.8    |
| G0-10S   | 33.6| 36.5| 51.5 | 40.5    | G1-10S   | 14.8| 18.8| 18.9 | 17.5    |
| G0-10F   | 51.5| 46.6| 50.1 | 49.4    | G1-10F   | 11.6| 8.1 | 14.6 | 11.4    |
| G0-10M   | 47.1| 44.6| 46.7 | 46.1    | G1-10M   | 14.0| 11.1| 12.1 | 12.4    |
| G0-30C   | 45.3| 45.6| 44.5 | 45.1    | G1-30C   | 12.2| 7.5 | 10.9 | 10.2    |
| G0-30S   | 37.5| 38.7| 39.1 | 38.5    | G1-30S   | 5.0 | 7.7 | 9.7  | 7.5     |
| G0-30F   | 42.9| 43.0| 54.6 | 46.8    | G1-30F   | 7.3 | 11.9| 10.9 | 10.0    |
| G0-30M   | 33.1| 40.7| 55.0 | 42.9    | G1-30M   | 6.7 | 10.9| 12.0 | 9.9     |
| PC       | 5.5 | 5.5 | 4.9  | 5.3     |

Figure 1. Cl⁻ binding capability of CSA cement paste.

(1) It can be seen that the Cl⁻ binding capacity of containing-gypsum CSA pastes is much littler than equivalent free-gypsum CSA pastes. In pure CSA pastes without mixtures, the Cl⁻ binding capacity of free-gypsum CSA paste is about 4 and 8 times of containing-gypsum CSA paste, which even slightly lower than the binding capacity of PC paste.

(2) The addition of mixtures makes the Cl⁻ binding capacity of CSA paste improved. For the free-gypsum paste, the increase of mixtures on binding capacity is pretty lower, among which F has the highest lifting amplitude (the binding percent of CSA with 10% content F is 49%), and the effect of mixture content of binding capacity is not obvious. For the containing-gypsum paste, mixtures make the binding capacity significantly ascend, in which the highest value of binding percent achieves 4 times of binding percent of CSA paste without
mixture, and the binding capacity decreased slightly with the addition of mixture content from 10% to 30%, but with a small amplitude.

(3) The incorporation of mixtures greatly improves the Cl\(^{-}\) binding capacity of the containing-gypsum CSA paste, and to some extent reduces the difference in binding capacity of containing-gypsum and free-gypsum. On the whole, the free-gypsum paste of Cl\(^{-}\) binding capacity is more than twice as high as that of containing-gypsum.

In order to clarify the main reason for more chloride binding capacity to free-gypsum samples and CSA cement with mixtures, it is necessary to identify the main hydration products by XRD and TG and to investigate the morphology of hydration products by SEM. The results of each test are described as follows.

3.2. XRD and TG

Figure 2. XRD patterns of CSA paste. E: ettringite, Ms: calcium monosulfoaluminate hydrate, A: AH\(_{3}\), Y: ye’elimite, G: gypsum, Fs: Friedel’s salt, Str: strätlingite, Mc: calcium monocarboaluminate hydrate, C:CaCO\(_3\)
Table 4. Results of the XRD patterns of paste

|      | AFt | CAH₁₀ | Ms  | AH₃ | Y   | Fs  | Str | Mc  | C   | Binding |
|------|-----|-------|-----|-----|-----|-----|-----|-----|-----|--------|
| G0-0 | *   | ***   | *   | *   | *   | *   | *   | *   | *   | 38.6   |
| G0-30C | **  | *     | *** | *   | **  | *   | *   | *   | **  | 45.1   |
| G0-30S | **  | ***   | *   | *   | *** | *   | *   | *   | *   | 38.5   |
| G0-30F | **  | ***   | *   | *   | **  | *   | *   | *   | *   | 46.8   |
| G0-30M | **  | ***   | *   | *   | *** | *   | *   | *   | *   | 42.9   |
| G1-0  | ***** | *    | *** | *** | *   | *   | *   | *   | *   | 3.9    |
| G1-30C | **** | **    | *** | *   | **  | **  | *** | *   | **  | 10.2   |
| G1-30S | **** | **    | *** | *   | **  | **  | *** | *   | *   | 7.5    |
| G1-30F | **** | **    | *** | *   | **  | **  | *** | *   | *   | 10.0   |
| G1-30M | **** | **    | *** | *   | **  | **  | *** | *   | *   | 9.9    |

Figure 3. DSC-TG curves of CSA cement paste

The XRD patterns show that the main crystalline hydration products detected in the CSA paste are AFt, calcium monosulphoaluminate hydrate, aluminum hydroxide and ye’elimite (Fig. 2). The relative crystallinity comparison results of the respective proportions of hydration products are obtained from the XRD results in Fig. 2, as shown in the table 4. From the results we can see that the most obvious difference is that the hydration production of CAH₁₀ is only found in the free-gypsum paste, and the balance equation was showed in (1). This hydration products CAH₁₀ is usually known to be mainly formed at low temperature (below 15°C) during the hydration of CSA cement, but it has also been reported to precipitate at higher temperature (from 15 to 35°C), together with C₂AH₈ and AH₃ in the study of many scholars [10,13], and that the existence of CAH₁₀ is due to the CSA clinker contains C₁₂A₇.

There is a better AFt crystal peak than the containing-gypsum samples to the free-gypsum samples, and it can be seen in the TG curve that the AFt loss peak of the containing-gypsum samples is significantly larger than the AFt+CAH₁₀ loss peak in the free-gypsum samples (Fig. 3). It is because that the gypsum directly influences and determines the hydration rate and hydration products of the clinker minerals in the cement, especially the formation of AFm or AFt in the early stage of hydration. The hydration reactions show as (2) and (3) [11,12]. Furthermore, from the reactions we can know that much water will be consumed. AFt is clearly detected by the hydration of CSA cement in the absence of calcium sulfate, and it is formed by the transformed from the AFm of the hydration of the original cement system (Eq. (4)). Thus, it is more favorable to form a mixtrix of AFm, AFt and aluminium hydroxide rather than only AFm phases and aluminium hydration.
Ca\(^{2+}\)+2AlO\(_2\)+10H\(_2\)O→CAH\(_{10}\)  \(\text{(1)}\)

\[
\text{C4A3S} + 2\text{CSH2} + 34\text{H} \rightarrow \text{C3A.3CS.H32} + 2\text{AH3}  \(\text{(2)}\)
\]

\[
\text{C4A3S} + 18\text{H} \rightarrow \text{C3A.CS.12H} + 2\text{AH3}  \(\text{(3)}\)
\]

\[
4\text{C4A3S} + 8\text{OH}- \rightarrow \text{C3A.3CS.H32} + \text{C3A.CS.H12} + 2\text{C3AH6} + 8\text{AH3}  \(\text{(4)}\)
\]

From the Fig.1 we can know that the Cl' binding capacity of CSA paste is significantly larger than of PC paste, except the containing-gypsum pure CSA paste. The main reason for more Cl' binding capacity to the CSA paste system is the existence of Friedel’s salt, which can be found in all the samples of XRD. It is well known that Friedel’s salt has two formation mechanisms, the first is the cementation mechanism, Cl' directly enters the \([\text{Ca}_2\text{(Al)}(\text{OH})_6]^-\) interlayer structure to balance the interlayer charge and participates in the formation of Friedel’s salt\[14\]; and the second is the ion exchange mechanism, the free-Cl' in pore solution enters the interlayer structure of the AFm to directly replaces the anions in the interlayer to form Friedel’s salt by the ability of gain or lose electrons. Therefore, from the direction of Friedel’s salt formation, C binding capacity is closely related to the formation of \([\text{Ca}_2\text{(Al)}(\text{OH})_6]^-\) interlayer structure and various type of AFm phase in the system \[15,16\].

It is worth noting that the presence of gypsum makes a significant difference in the containing-gypsum and free-gypsum pastes system, as shown in Table 4. First, with the addition of gypsum, there is no CAH\(_{10}\) in the hydration product and the proportion of the hydration product AFt phase is much larger than that in the free-gypsum pastes; second, there is more Ms, Fs and Str in the free-gypsum CSA, which is relate to the Cl' binding capacity. Combined with the results of Cl' binding capacity, it can be assumed that the AFt in the paste system does not promote the binding capacity and the presence of gypsum in the paste inhibits the appearance of CAH\(_{10}\). It can be concluded that Cl' binding capacity has a great relationship with the material morphology of cement hydration products, like CAH\(_{10}\) Ms, Fs and Str. This explains why the Cl' binding capacity of free-gypsum paste is much greater than of containing-gypsum paste.

With the participation of different mixtures in different CSA paste, the Cl' binding capacity is not consistent, and the ratio of 10% and 30% fly ash has the highest binding capacity in free-gypsum paste, which is completely different from the results in containing-gypsum paste. This is because fly ash has a unique spherical structure compared with the other mixtures and made the dilution and nucleation effect in the paste work better, which is more conducive to the hydration products CAH\(_{10}\) (Fig. 3-b). The addition of calcium carbonate makes the CSA paste (including containing-gypsum and free-gypsum) have a better Cl' binding capacity, it is quiet different from the effect of binding capacity of calcium carbonate on PC cement paste. It is because the most important thing in improving the Cl' binding capacity is to increase the content of Al in PC cement paste. Other types of mixtures such as fly ash, slag and metakaolin have a higher Al content, and Alkali excitation occur in the system due to the higher pH, which leads to a better Cl' binding capacity in the PC cement paste.

However, a higher Al content is not the important part for the binding capacity in CSA paste, the mixture of calcium carbonate can bring amount of CO\(_2\)\(^{\circ}\) to the pore solution and leads to the appearance of Mc, which can be found in containing-gypsum and free-gypsum paste. As a special structure of AFm phase, Mc has a more stable crystal structure compared with other types of AFm and it can substitute or adsorb Cl' in the system, thus achieving a better binding capacity in the presence of calcium carbonate, especially in the containing-gypsum paste. As for the addition of metakaolin mixture, it does greatly increase the al content in CSA paste, but does not significantly improve the binding capacity as in PC paste. It is because that the increase of Cl' binding capacity is related to the hydration product of chemical binding and physical adsorption of Cl' in CSA paste, and its formation is not only related to the single Al content, but also to the ratio of C/A \[16\]. This also explains the
lowest Ca content of metakaolin have a not obvious improvement of binding capacity in CSA paste.

4. Conclusion

This paper is the most important part of the research on the corrosion damage of steel bars introduced by Cl\textsuperscript{−} in the marine environment seawater sand using CSA cement. In particular, this study focused on the effect of different admixtures on Cl\textsuperscript{−} binding capacity of CSA-Cl\textsubscript{−} system. The following conclusions can be drawn:

1) The presence of gypsum has a significant impact on the properties of the CSA cement system. Due to the addition of gypsum, it greatly reduces the Cl\textsuperscript{−} binding ability of the CSA cement system.

2) The presence of admixtures has some effects on the properties of different cement systems (containing-gypsum and free-gypsum systems). The addition of different mineral admixtures increased the Cl\textsuperscript{−} binding ability of the sample and it have a higher promoting effect on the Cl\textsuperscript{−} binding ability of containing-gypsum samples.

3) Cl\textsuperscript{−} binding ability is related to the type of ions and the ion ratio present in the hydration process. In the presence of gypsum, gypsum provides a sufficient amount of SO\textsubscript{4}\textsuperscript{2−} for the cement system, which results in the presence of a large amount of AFt in the system and inhibits the formation of AFm to some extent. The addition of mineral admixture metakaolin increases the Al content in the system, but due to the lower Ca content, the effect of improving the consolidation capacity is not obvious, which explains the improvement of the binding capacity is related to the ratio of C/A.

4) The increase of Cl\textsuperscript{−} binding ability of mineral admixtures in CSA system is also related to the structure type and chemical composition of mineral admixtures.

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