



# Chloride binding in hydrated MK, SF and natural zeolite-lime mixtures



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## HIGHLIGHTS

- Supplementary materials such as Silica fume and Metakaolin proposed to have complex mechanism of chloride binding.
- The major contribution of alumina-rich SCMs on chloride binding mechanism is generally ascribed to the reactive alumina content of the mixtures through formation of Friedel's salt.
- In SF-lime mixtures enriched with reactive silica, chloride is bounded by the C-S-H phase and C-S-H binding capacity was obtained to be relevant to its calcium-to-silica ratio.
- A high C/A ratio, for the MK-lime mixture, increases the quantity of Friedel's salt by promoting the transformation of stratlingite and/or monocarboaluminate to Friedel's salt.
- The binding capacity of alumina-rich SCMs pastes was not only dependent on the alumina content of the mixture, but also on the C/A of the mixture.

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## ABSTRACT

Supplementary materials such as Silica fume and Metakaolin proposed to have complex mechanism of chloride binding. However, it has been established that the major contribution of alumina-rich supplementary cementitious materials on chloride binding mechanism is generally ascribed to the reactive alumina content of the mixtures through formation of Friedel's salt.

This work investigate the main contributions of silica fume, metakaolin and natural zeolite on binding mechanism and consequently to designing better mixtures in terms of durability through the use of silica fume–lime, metakaolin–lime and natural zeolite–lime mixtures containing different amounts of reactive  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . Results indicate that in SF-lime mixtures enriched with reactive silica, chloride is bounded by the C-S-H phase. The binding capacity of the C-S-H was obtained to be relevant to its calcium-to-silica ratio i.e., C-S-H with a higher C/S ratio leads to a greater binding capacity. For alumina-rich SCMs such as metakaolin or partly zeolite (MK-lime and NZ-lime mixtures), our results indicate that although the alumina content does have a significant influence on binding mechanism but the chloride binding capacity was also controlled by the calcium-to-alumina (C/A) and calcium-to-silica(C/S) ratios. Our finding confirms that a high C/A ratio, for the MK-lime mixture, increases the quantity of Friedel's salt by promoting the transformation of stratlingite and/or monocarboaluminate to Friedel's salt and improves durability of mixtures. For the NZ-lime mixture at high C/A ratio, our results show that clinoptilolite is the main compound which forms Friedel's salt at low chloride concentrations. Reduction of C/A ratio promotes the formation of stratlingite in the MK-lime mixture and increases the amount of clinoptilolite crystals in the NZ-lime mixture.

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## 1. Introduction

The capability of hydrating cements to bind chlorides in the form of Friedel's salt ( $\text{C}_3\text{A}\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ ) (chemically bound chlo-

ride) or to adsorb chloride to calcium silicate hydrates (C-S-Hs) (physically bound chloride) and/or present in the diffuse layer of the C-S-H phase in concrete is one of the significant parameters that controls the initiation of chloride-induced corrosion of steel reinforcement in concrete [1,2]. The remaining chloride ions are present in the pore solution, i.e., as free chloride and can ingress further toward the rebar. Ramachandran theory explains the

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several possible states of bound chloride in the hydration of tricalcium silicate in the presence of calcium chloride including: 1) a chemisorbed chloride layer on the surface of C-S-H, 2) chloride in the interlayer space and 3) incorporated  $\text{Cl}^-$  in the lattice of C-S-H [3]. However, it has been established that most part of the chloride ions are chemisorbed on the surface of hydrated  $\text{C}_3\text{S}$  [3]. One of the efficient approaches to enhance the chloride binding capacity of concrete is to partially replace Portland cement by alumina-rich supplementary cementitious materials (SCMs). The major contribution of alumina-rich SCMs on chloride binding is generally proposed to be ascribed to the alumina content of the mixes through formation of Friedel's salt. In addition, SCMs can improve the pore structure of concrete, which leads to higher strength and lower permeability.

It has been established that in general, Friedel's salt may originate from two sources: the  $\text{C}_3\text{A}$  phase of Portland cement (PC) and  $\text{Al}_2\text{O}_3$  (reactive alumina) of pozzolans [4]. In general, the pozzolanic reactivity of SCMs is mainly associated with the amorphous and/or glassy nature of reactive silica ( $\text{SiO}_2^-$ ) and reactive alumina ( $\text{Al}_2\text{O}_3^-$ ) [4,5]. The  $\text{SiO}_2^-$  is capable of reacting with  $\text{Ca}(\text{OH})_2$  to give rise to a C-S-H gel. In turn,  $\text{Al}_2\text{O}_3^-$  can form various hydrated calcium aluminates, particularly Stratling's compound ( $\text{C}_2\text{ASH}_x$ ); if sulfate ions are present in pore solution, AFm phase [8] and/or ettringite [10,11] are favored, but if chloride ions are present, Friedel's salt is formed. Furthermore, use of pozzolans to enhance the durability and service life of concrete structures are a common approach. Several studies have stated that chloride binding by the hydrated cement in concrete may affect the rate of chloride ingress and hence enhance the time to attain a threshold level of chloride ions at the steel surface. These studies also revealed that this time at the steel surface increases noticeably by use of fly ash, metakaolin, slag and decreases by use of silica fume [1–2,6–7].

It has been suggested that partial replacement of cement with silica fume results in a reduction in the pH value of the pore solution, a dilution of  $\text{C}_3\text{A}$  and finally an increase in the C-S-H content. In this regard, reduction of pH value and increase of C-S-H content lead to increase of chloride binding and dilution of  $\text{C}_3\text{A}$  conversely leads to reduction of chloride binding. It is not likely that the dilution of the  $\text{C}_3\text{A}$  can only illustrate the observed reduction in the binding capacity as a result of the partial replacement of cement with silica fume but instead it is established that this replacement leads to the formation of C-S-H with lower C/S ratio than the C-S-H formed without the presence of silica fume [8]. Beaudoin et al. [9] suggest that the degree of chloride binding in C-S-H is a function of the calcium/silica (C/S) ratio. They believe that with a lower ratio of C/S resulting in a lower degree of binding, which may explain the reduction in binding when silica fume is used.

The calcium silicate hydrate phases play a major role in assessing the performance of concrete and its sustainability [10]. An important stoichiometric parameter that describes a C-S-H phase is the molar ratio of CaO to  $\text{SiO}_2$  in its structure. A change in the C/S ratio of the C-S-H leads to different physical and chemical properties of the material [11]. Polymerization of C-S-H, i.e. the mean length of silicate chains which is usually used to describe the connectivity of silicate chains in the C-S-H systems, is significantly influenced by its compositional C/S ratio. By increasing C/S ratio, the silicate chain-length decreases remarkably and several bridging tetrahedra are removed from the silicate chains [12]. Indeed, the number of defect sites (i.e. locations of missing bridging tetrahedra) is strongly dependent on the C/S ratio. It was demonstrated that there are fewer sites at low C/S ratios as the length of the silicate chains enhances remarkably. This indicates that from low to high C/S ratio, the C-S-H's molecular structure shifts from layered to a more amorphous structure [12]. The C/S ratio in calcium silicate hydrates usually covers a range from 0.7 to 2.0 with an average value of 1.75 for that in hydrated Portland

cement in literature [11]. Taylor distinguished between low-lime calcium silicate hydrates (C-S-H (I)) with a C/S molar ratio  $<1.5$  and high-lime calcium silicate hydrates (C-S-H (II)) with a C/S molar ratio  $>1.5$  [13]. Incorporation of SCMs such as silica fume, in hydrated cement paste results in the formation of secondary C-S-H, which has a relatively lower C/S ratio of about 1.0 [11,14]. It has been shown that this type of C-S-H is more polymerized and thus, has different characteristics [15].

In this work, an additive containing medium and highly reactive alumina, contrary to silica fume i.e., natural zeolite (NZ) and metakaolin (MK) was studied and used as a pozzolanic material for mortar and concrete because of its high pozzolanic properties. The influence of MK on the durability and mechanical properties of mortar or concrete have been widely reported [16–18]. When metakaolin reacts with calcium hydroxide, the principal reaction is between  $\text{AS}_2$  ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) and CH, in the presence of water. This reaction depends on the  $\text{AS}_2/\text{CH}$  ratio and reaction temperature could form additional cementitious C-S-H gel along with crystalline products including stratlingite ( $\text{C}_2\text{ASH}_8$ ),  $\text{C}_3\text{AH}_6$  and calcium aluminate hydrate ( $\text{C}_4\text{AH}_{13}$ ) [19–22].

Natural zeolite as volcanic or volcano-sediment material is a crystalline mineral that contains silicon and aluminum oxide and has a three dimensional frame structure which is classified as a hydrated aluminosilicate of alkali and alkaline earth cations. Clinoptilolite is the most commonly mined natural zeolite. In recent years, there has also been a growing trend in the use of natural zeolite as a pozzolanic material in Iran [23–27]. Natural zeolite unlike other pozzolans which have a glassy or amorphous structure has been demonstrated to have pozzolanic properties despite its crystalline structure [23,25]. The large quantity of reactive  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in zeolite chemically incorporates with the calcium hydroxide created earlier by the hydration of cement to form additional C-S-H gel and aluminates, resulting in the improvement of the microstructure of hardened cement. Similar to other pozzolanic materials, replacement of cement by natural zeolite can improve the mechanical and durability properties of cement and concrete composites [23–29].

Most of the available investigations on the properties of SCMs concentrate on mechanical behavior or durability aspects of concrete mixtures including a specific pozzolan. However, there is scant information about the binding properties of silica fume, metakaolin and natural zeolite in the absence of  $\text{C}_3\text{A}$ . The aim of this work is to investigate chloride binding capacity in greater detail i.e., decreases or increases when silica fume and metakaolin or natural zeolite are added to cement respectively. The results of this work should prepare information not only on the binding capacity of the silica fume as a pozzolan, but should also give an idea about the mechanism of chloride binding of C-S-H in general since, due to the very high  $\text{SiO}_2$  content of silica fume, the hydrates produced in this case would be C-S-H gel.

## 2. Experimental

In this work the experimental setup, containing preparation of the pastes and the method (equilibrium approach) which used for obtaining the chloride binding isotherms follows procedures described recently [7,29,30].

### 2.1. Materials

The chemical composition of silica fume, metakaolin and natural zeolite used in this work is shown in Table 1. Silica fume (SF) obtained from Azna ferro-silicon alloy manufacture, includes greater than 90% silica, but almost no alumina. The silica and alumina content of the metakaolin (MK) is approximately equal proportions and is about 50% and 44.6% respectively. The silica and alumina content of the natural zeolite lies between that of SF and MK and is about 68% silica and 13% alumina. The source of natural zeolite (clinoptilolite type) used in this study was the mines from north of Semnan, Iran. The salt NaCl of laboratory grade were dissolved in distilled

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