

# Effect of using calcined clays, silica fume and limestone powder on the compressive strength and chloride binding capacity of cementitious pastes

Farnaz Bahman-Zadeh<sup>1\*</sup>, Ali Akbar Ramezani-pour<sup>2</sup>, Arash Zolfagharnasab<sup>1</sup>

<sup>1</sup>PhD candidate, department of civil and environmental engineering, Amirkabir university of technology, Tehran, Iran

<sup>2</sup>Professor, department of civil and environmental engineering, Amirkabir university of technology, Tehran, Iran

\* [farnaz1991@aut.ac.ir](mailto:farnaz1991@aut.ac.ir)

## Abstract:

Chloride ions ingress is one of the major reasons for the deterioration of reinforced concrete structures, particularly those exposed to marine environments. The use of supplementary cementitious materials (SCM) has been introduced by many researchers as a practical approach to reducing corrosion of embedded steel caused by chloride ions penetration. In addition to the effects of SCM on transfer properties of cement-based materials, their influence on the binders' chloride binding capacity should be studied to evaluate the durability of mixtures against chloride attack. In this investigation, the chloride binding capacity of pastes containing silica fume (SF), limestone powder (LS), and three samples of calcined clays (CC) as SCMs, have been compared with Portland cement (PC) paste. The chloride binding capacity has been measured by the equilibrium method for samples submerged in different concentrations of NaCl solution (0.1, 0.3, 0.5, 1 and 2 molar) for 42 days. Furthermore, compressive strength tests after 7, 28 and 90 days of curing, X-ray diffraction (XRD) analysis, and Friedel's salt (FS) quantification by thermogravimetric analysis have been carried out. Results indicated that by increasing the kaolinite contents of raw clays, the chloride binding capacity and FS amounts of samples submerged in 2 M NaCl solution have been increased up to 242.5% and 169.5%, respectively. While, samples with LS and SF had generally lower chloride binding capacity than PC paste. The 10% replacement of PC by SF and LS led to 37.5% and 9.8% lower formation of FS in samples submerged in 2 M NaCl solution.

## Keywords:

Chloride binding capacity, Supplementary cementitious material, Silica fume, Limestone powder, Calcined clay.

## 1. Introduction

The durability of reinforced concrete against the penetration of ions, e.g. chloride and sulfate, is a determinative factor for the serviceability of structures. The corrosion of embedded steel as a result of chloride ions ingress is one of the major reasons for the deterioration of reinforced concrete structures. Once the chloride ions accumulate on the rebar surface, the depassivation occurs, which results in the initiation of the reinforcement corrosion [1]. In this context, it should be considered that only free chloride ions that have not been bound to hydration products could move freely in pore solution and reach the surface of rebar [2].

Chloride ions can be physically adsorbed on the C-S-H phase (named as physical chloride binding) or react with alumina containing compounds which results in the formation of chloride bearing AFms, e.g. Friedel's salt (called chemical chloride binding-FS) [3]. Consideration of the chloride binding capacity of cementing materials exposed to corrosive environments is of utmost importance. The chloride binding capacity could be affected by many factors, e.g. cement composition, cation of chloride salt (for example  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , etc.), temperature, and supplementary cementitious materials (SCM) [4].

Several investigations have been carried out on the utilization of SCM and their effects on durability against chloride attack [5-7]. In addition to the positive influence of incorporating SCMs on reducing the permeability of cement-based materials, their role in altering chloride binding capacity needs to be considered for evaluating the durability properties of concrete structures against chloride ions ingress. According to researches, binders containing alumina-rich SCMs such as metakaolin and fly ash have higher chloride binding capacity than pure Portland cement (PC) mixture. In contrast, binders prepared with SCMs like silica fume (SF) that contain lower amounts of alumina possess lower contents of bound chloride ions [8, 9]. Additionally, the chemical composition of hardened cement paste has a significant role in mixtures'

chloride binding capacity, and well-formulated blends could have appropriate chloride binding capacity [10]. In fact, various hydration phases have different contribution to bound chloride ions, particularly by altering the chemical binding capacity and formation of FS [10, 11].

Due to the worldwide abundance and distribution of clay minerals, the incorporation of calcined clays in cement-based materials has received considerable interest [12, 13]. Calcination of clays in the range of 650-850 °C results in the transformation of clay minerals (e.g. kaolinite) into meta-stable phases (e.g. metakaolin) and production of pozzolanic material [14]. Most of the clay deposits on the earth are not adequately pure (with at least 85% of kaolinite) to provide metakaolin which is a highly reactive SCM [15]. In this context, some researches have been recently focused on the pozzolanic properties of low-grade kaolinitic clays [16, 17]. The studies on these clays have been mainly focused on the hydration, porosity, and mechanical properties of prepared mixtures [16, 18, 19] and the effect of using low-grade kaolinitic clays on the durability of cement-based materials should be more investigated.

Due to the lack of investigations on the chloride binding capacity of low-grade calcined clays and the high environmental and economic potential of using these SCMs, in this study, the different Iranian clay deposits with various amounts of kaolinite have been designated. Furthermore, the paste samples prepared with SF and limestone powder (LS) as conventional SCMs have been studied to compare their chloride binding capacity with PC mixture and domestic low-grade calcined clay containing pastes. In addition, the compressive strength test and X-ray diffraction (XRD) and thermogravimetric (TG) analyses were carried out to investigate the mechanical properties, phase assemblage and quantify the FS contents in different paste samples. The present study could help fill the research gap on the ability of chloride binding of blended cements concerning the chemical composition of binders with different SCMs. The findings of this investigation around chloride binding capacity might be employed as an indicator for further researches on the durability of cement-based materials against chloride ions attacks.

## 2. Experimental Program

### 2-1- Materials

In this study, type II PC was used to prepare the paste samples. In addition, SF, LS and three CCs were incorporated as SCMs in mixtures. It should be stated that the clay samples were provided from three different sources in Iran and had kaolinite contents of 20.8% (C1), 28.7% (C2) and 66.0% (C3). The kaolinite contents were determined by TG analysis (with heating rate of 10°C/min and under Ar atmosphere), using the tangent method to measure the mass loss related to dehydroxylation at around 400-600°C [20]. Clay samples were calcined in a laboratory scale fixed bed furnace at 800°C for one hour (the heating rate was 300 °C/h), and they were immediately cooled to the room temperature after calcination. Chemical composition and physical properties of cementitious materials are given in Table 1 and Table 2. The pozzolanic activity index was determined according to ASTM C311 [21].

In order to prepare pastes, the deionized water and a modified polycarboxylate ether-based superplasticizer (SP) were also employed.

Table 1. Chemical composition of Cementitious materials.

Materials	Chemical composition (wt.%)								
	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	L.O.I
PC	21.4	63.98	4.73	4.25	1.40	0.23	0.65	2.35	0.93
SF	93.5	0.49	0.43	0.94	1.00	0.82	1.04	0.71	0.67
LS	3.31	49.1	0.73	0.24	2.83	-	0.08	0.1	43.4
Calcined C1	77.1	1.71	19.1	0.18	0.09	0.04	0.18	0.08	1.42
Calcined C2	71.3	2.7	22.6	0.28	0.09	0.05	0.33	0.01	2.57
Calcined C3	16.2	2.1	55.4	17.4	1.22	0.03	0.37	0.06	0.6

Table 2. Physical properties of Cementitious materials.

Properties	PC	SF	LS	Calcined C1	Calcined C2	Calcined C3
Density (g/cm <sup>3</sup> )	3.02	2.16	2.62	2.57	2.55	2.57
Pozzolanic activity (%) -7 days	-	101.2	-	68.3	74.7	82.0
Pozzolanic activity (%) -28 days	-	114.3	-	85.6	90.3	99.7
Retaining on 45 µm sieve (%)	9.62	5.11	10.1	14.6	14.5	14.0

## 2-2- Mixture Proportions

Nine paste mixtures were considered to study the effects of SCM type and also cement replacement level. The mixture proportions are detailed in Table 3. The constant water to binder ratio of 0.4 was considered for all paste samples. The SP was added to the mixtures until similar flows to OPC mixture were achieved according to ASTM C1437 [22]. SP contents are mentioned as the percentage of total binder content in Table 3. Three PC replacement levels of 6%, 8% and 10% have been designated for SF based on the reported optimum utilizing range of this SCM [14]. Additionally, due to the beneficial environmental and economic aspects of calcined clay employment in blended cements, 30% replacement level was considered, which is almost the highest allowable replacement level of SCMs in accordance with the EN 197-1 [23]. Furthermore, 10% and 30% of PC were replaced with LS in LS-10 and LS-30 mixtures to compare the results with SF-10 and CC containing pastes.

Table 3. Mixture proportions.

Ingredients	Mixture ID*								
	OPC	SF-6	SF-8	SF-10	LS-10	LS-30	CC1-30	CC2-30	CC3-30
PC (kg/m <sup>3</sup> )	2100	1974	1932	1890	1890	1470	1470	1470	1470
SF (kg/m <sup>3</sup> )	-	126	168	210	-	-	-	-	-
LS (kg/m <sup>3</sup> )	-	-	-	-	210	630	-	-	-
Calcined C1 (kg/m <sup>3</sup> )	-	-	-	-	-	-	630	-	-
Calcined C2 (kg/m <sup>3</sup> )	-	-	-	-	-	-	-	630	-
Calcined C3 (kg/m <sup>3</sup> )	-	-	-	-	-	-	-	-	630
Water (kg/m <sup>3</sup> )	840	840	840	840	840	840	840	840	840
SP (%)	-	0.10	0.16	0.2	0.06	0.15	0.11	0.11	0.11

\* The mixture IDs introduce the cement composition and replacement level of SCMs.

The mixing procedure was in accordance with ASTM C305 [24]. The fresh mixtures were cast into  $5 \times 5 \times 5 \text{ cm}^3$  and  $4 \times 4 \times 16 \text{ cm}^3$  moulds. Subsequently, they were sealed with plastic sheets and kept in 95% relative humidity. After 24 hours, they were demoulded and cured in saturated calcium hydroxide solution (prepared with deionized water).

### 2-3-Test Procedures

To compare the mechanical properties of paste mixtures, the compressive strength test was carried out after 7, 28 and 90 days of curing. The test was conducted on three  $5 \times 5 \times 5 \text{ cm}^3$  samples.

The qualitative XRD analysis was also performed on ground paste samples to determine the phase assemblage of each mixture after 28 days of curing in saturated calcium hydroxide solution. In order to prepare the samples for XRD analysis, the hydration stoppage using the solution exchange method by isopropanol solution was carried out [25].

The equilibrium method recommended by Tang and Nilsson [2] was used to determine the chloride binding capacity. In this regard, the paste samples of  $4 \times 4 \text{ cm}^2$  with a thickness of 1-2 mm that were cut from  $4 \times$

4 × 16 cm<sup>3</sup> prisms were firstly dried for 3 days in a low pressure and CO<sub>2</sub> free vacuum desiccator containing soda lime and silica gel. Afterwards, the samples were transferred to a CO<sub>2</sub> free desiccator containing soda lime and saturated LiCl solution for 14 days. The dissectors were kept at room temperature and LiCl was used to provide the relative humidity of 11% in which it can be ensured that a monolayer of water was adsorbed by the C-S-H particles [2, 26]. At the end of drying period, the samples were immersed in 0.1, 0.3, 0.5, 1 and 2 M NaCl solutions. The saline solutions were saturated by calcium hydroxide to inhibit the leaching of calcium hydroxide (CH) from binder and the ratio of solution volumes to the mass of paste samples was equal to 4.00 cm<sup>3</sup>/g. Chloride ions concentrations of saline solutions were measured by potentiometric titration using 0.1 M AgNO<sub>3</sub> solution after 42 days. After this period, it could be ensured that the equilibrium between specimen and solution has been reached [2].

Eq. 1 was used to calculate the bound chloride ions contents ( $C_b$  in mg/g of sample):

$$C_b = \frac{35.45 \times V(C_i - C_f)}{W_d} \quad (1)$$

Where  $V$  is the volume of external chloride solution (ml),  $C_i$  is the initial chloride concentration (mol/l),  $C_f$  is the free chloride concentration at equilibrium (mol/l), and  $W_d$  is the mass of dry sample (g).

The TG analysis was also performed on chloride contaminated samples under a neutral atmosphere of Ar gas between 30-1000°C with a heating rate of 10°C/min. In this regard, the samples of 4 × 4 cm<sup>2</sup> with the thickness of 1-2 mm were prepared by a similar procedure to the equilibrium method and submerged in 2 M NaCl solutions for 42 days. Afterwards, the hydration stoppage was carried out by solution exchange method using isopropanol solution [25]. Then the samples were ground using pestle and mortar. The mass loss between 250-400°C, which is related to the dehydroxylation of six main layer water molecules of FS, were measured by integration method [20]. It should be noted that the specimens submerged in 2 M NaCl solution were chosen due to the highest contents of FS in these samples and consequently, the occurrence of the least relative errors in the quantification of FS by TGA method.

### 3. Results and discussion

The compressive strength test results are illustrated in Fig. 1. According to these results of this study, CC and LS containing pastes had 2.3%-31.3% lower compressive strengths than OPC mixture, while mixtures prepared with SF generally had similar or up to 36.3% higher compressive strength than OPC paste. The increase of curing time was resulted in higher compressive strengths due to hydration progress. In addition, increasing the cement replacement level by SF was led to higher compressive strengths. In the case of using LS as SCM, the increase in LS contents brought about between 17.3% and 33.2% reductions in compressive strength. This finding could be attributed to the dilution effect. In fact, according to the researches [27, 28], the use of LS in cement-based materials could result in the increase of compressive strength due to chemical reaction between calcium carbonate and alumina containing compounds of cement which led to the formation of carboaluminate phases and also because of nucleation effects of fine LS particles (in early ages). However, as the cement replacement levels were 10 and 30 wt. %, the dilution effect overcame the positive impacts of adding LS in this study. By comparing the CC containing pastes, it can be concluded that by increasing in kaolinite contents of clays, the compressive strengths were increased. This improvement was mainly related to the higher pozzolanic activity of CC containing binders with greater calcined kaolinite in their structures (see Table 2).



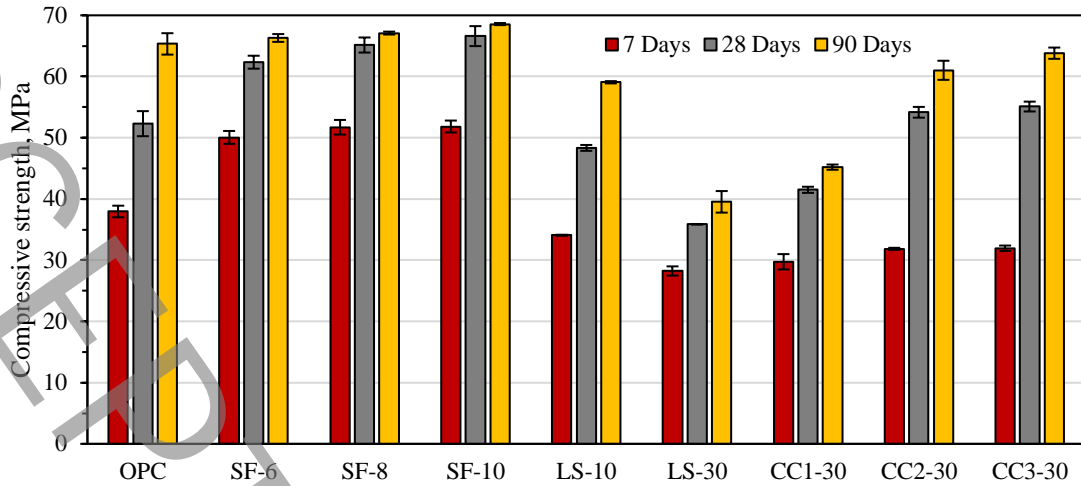


Fig. 1. Compressive strength test results.

The XRD patterns are given in Fig. 2. Peaks related to the presence of CH, quartz (Q) and calcite (Cc) are shown in the patterns. The CH contents decrease by increasing the SCM contents and pozzolanic activity due to dilution effect and CH consumption during pozzolanic reactions, respectively. As the cement replacement levels did not change significantly in SF containing pastes, the pozzolanic reaction and its impact on CH consumption had the predominant role in the CH contents of pastes after 28 days of curing. Therefore, SF-6 had higher amounts of CH than SF-8 and SF-10. In the case of pastes prepared with LS, LS-30 had lower CH contents due to the dilution effect. In addition, the peak related to the Cc could be observed in XRD patterns of LS pastes and this peak was intensified by increasing the LS content. The CH values in CC containing mixtures that had similar cement replacement levels were controlled by the pozzolanic activity of CC and the increment in kaolinite content of clays resulted in lower amounts of CH. This is in agreement with the findings of Avet and Scrivener [18].

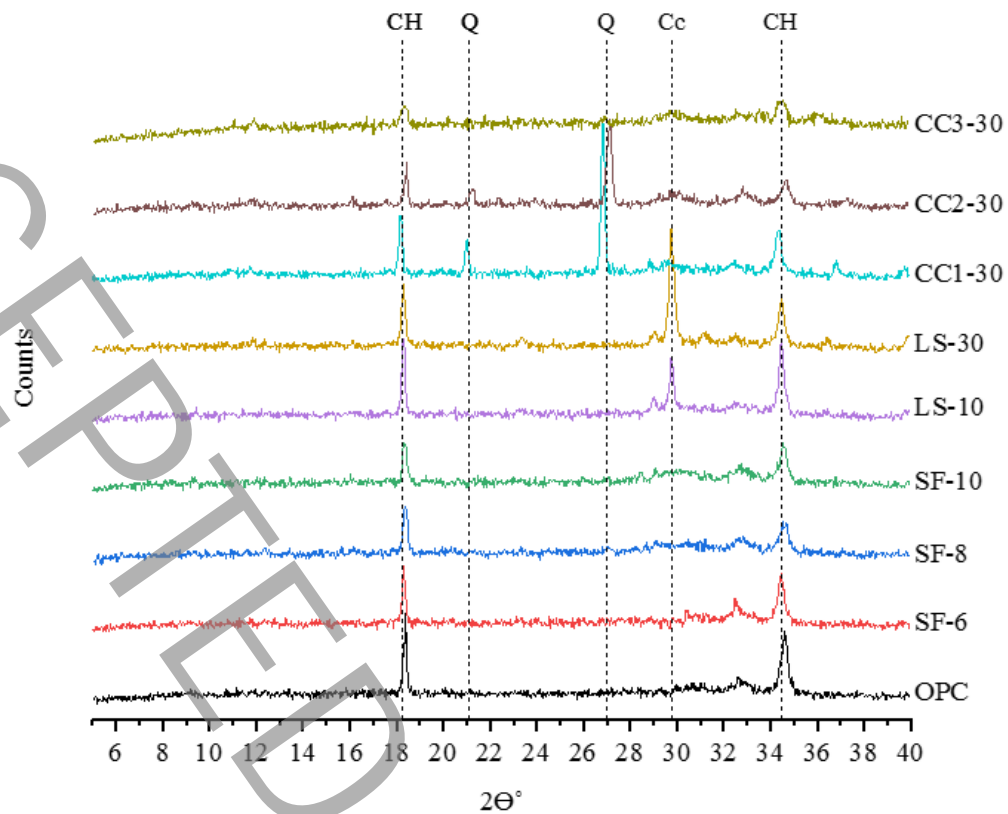


Fig. 2. XRD patterns.

The relation between the bound and free chloride ions contents (chloride binding isotherm) are shown in Fig. 3 to 5. The results indicated that the amounts of bound chloride ions were increased by increasing in the concentrations of NaCl solutions. According to Fig. 3, the SF containing pastes had generally lower chloride binding capacity than OPC. In SF-10 paste the contents of bound chloride ions were 18.8% and 34.4% higher than those of OPC in 1 and 3 M NaCl solutions, respectively. The investigations illustrated that the effects of physical chloride binding on chloride binding capacity were more significant in higher concentrations of chloride solutions [29]. In addition, due to the high surface area of SF containing binders, the physical chloride binding capacity could be increased. Thus, the improved chloride binding capacity of SF-10 mixture with higher amounts of SF than SF-6 and SF-8, in concentrations  $> 0.5$  M could be related to higher physical chloride binding.

In this study, the utilization of LS resulted in the reduction of chloride binding capacity. Moreover, LS-30 possessed down to 13.9% lower amounts of bound chloride ions than LS-10. The lower chloride binding capacity of LS containing binders is mainly due to the decrease of chloride-bearing AFm compounds and C-S-H gel that can bind chloride ions chemically and physically, respectively.

In mixtures containing CC, the chloride binding capacity were increased (see Fig. 5). In different concentrations of NaCl solutions, the chloride binding capacity of CC3-30 were between 34.5%-242.5% higher than OPC paste. In addition, the increase of kaolinite contents of here investigated clays led to the increase of bound chloride ions contents. For example, CC3-30 paste had 101.4% higher content of bound chloride ions than CC1-30 specimen submerged in 2 M NaCl solution. In fact, mixtures containing CCs with higher kaolinite contents had more amounts of alumina in the binder and therefore, both physical and chemical chloride binding capacities have been increased.

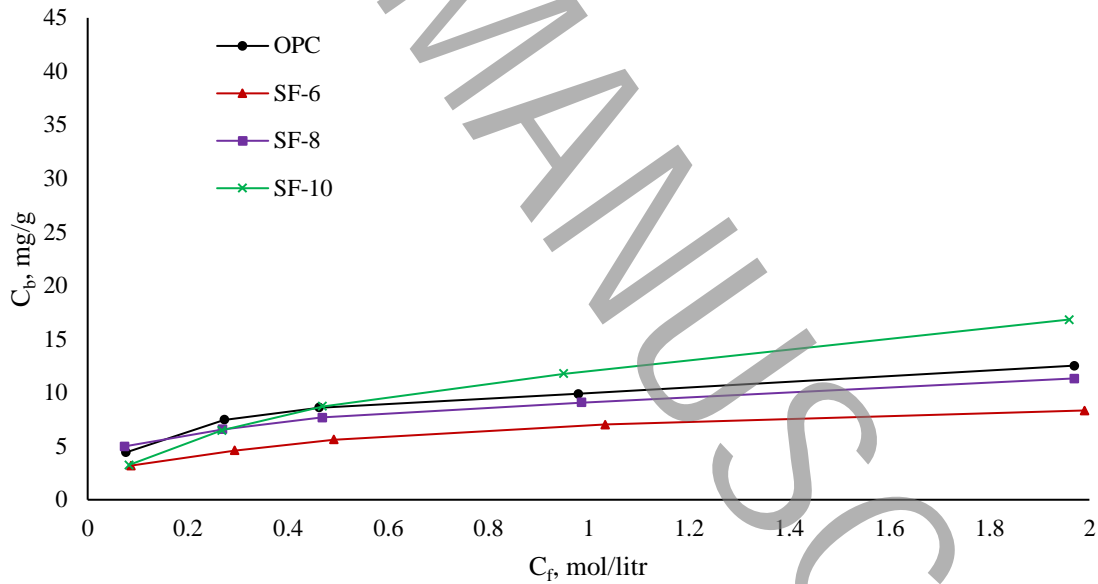


Fig. 3. Relation between  $C_b$  and  $C_f$  in SF containing mixtures.

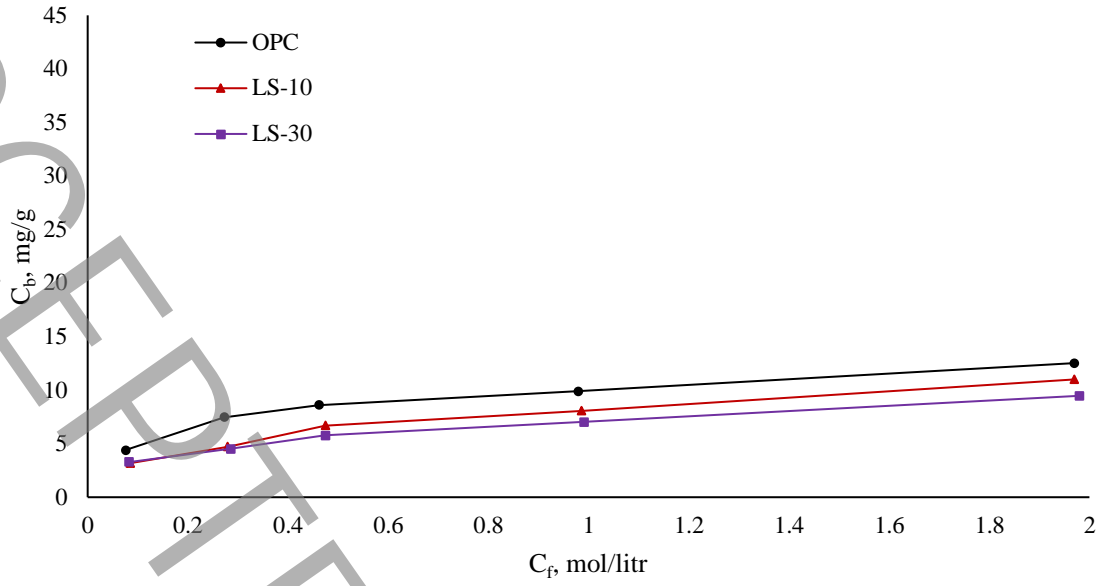


Fig. 4. Relation between  $C_b$  and  $C_f$  in LS containing mixtures.

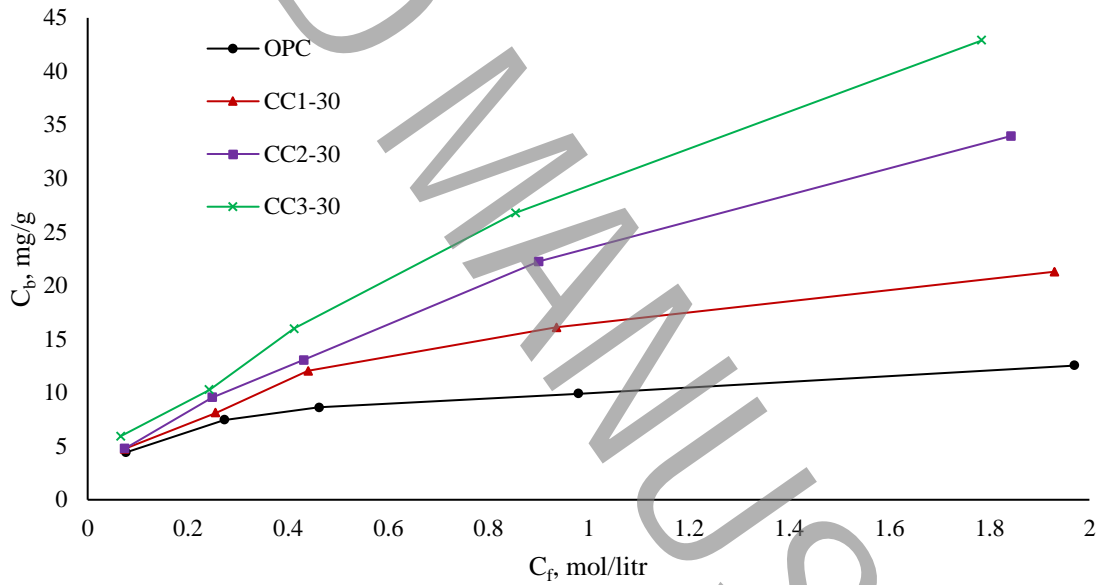


Fig. 5. Relation between  $C_b$  and  $C_f$  in CC containing mixtures.

The chloride binding isotherms were determined by two well-fitted isotherms of Freundlich and Langmuir (Eq. 2 and 3).

$$\text{Freundlich isotherm: } C_b = \alpha C_f^\beta \quad (2)$$

$$\text{Langmuir isotherm: } C_b = \frac{\alpha C_f}{1 + \beta C_f} \quad (3)$$

As mentioned in Table 4, Freundlich isotherm generally indicated a better correlation than Langmuir isotherm. This finding is in agreement with other investigations on the chloride binding capacity of cement-based materials [3, 30, 31].

Table 4. Chloride binding isotherms.

Mixture ID	Freundlich isotherm			Langmuir isotherm		
	$\alpha$	$\beta$	$R^2$	$\alpha$	$\beta$	$R^2$
OPC	10.348	0.287	0.977	65.804	4.935	0.945
SF-6	6.816	0.303	0.995	38.257	4.343	0.911
SF-8	9.327	0.255	0.993	79.515	7.292	0.779
SF-10	12.153	0.488	0.997	31.522	1.427	0.972
LS-10	8.297	0.391	0.986	29.842	2.370	0.923
LS-30	7.291	0.346	0.989	32.132	3.167	0.854
CC1-30	13.302	0.451	0.970	35.909	1.547	0.851
CC2-30	16.154	0.444	0.988	49.208	1.851	0.972
CC3-30	12.182	0.402	0.960	45.127	2.465	0.992

To clarify the effects of SCMs incorporation on chemical chloride binding capacity of pastes, the FS contents were quantified by TGA method. The FS amount was stated as a mass ratio of the anhydrous content by considering measured value from TGA to mass loss between 50-550°C that is attributed to bound water content [20]. The results are indicated in Fig. 6.

According to the results of this study, the FS contents were decreased by increasing the PC replacement level by SF due to the decrease of alumina contents in binders. This finding proves the above-mentioned results about the role of physical chloride binding of pastes with SF.

LS-10 and LS-30 mixtures also had 9.8% and 47.9% lower values of FS than OPC paste as a result of alumina dilution. Whereas, FS contents were increased between 86.8% and 169.3% in CC containing pastes. These increments are evidence of higher chemical chloride binding capacities of mixtures with CC due to their greater alumina contents. It should be mentioned that the higher the alumina was, the more chloride ions were chemically bound. In addition, Guo et al. [29] have reported the higher ability of C-A-S-H compounds than C-S-H in physical chloride binding, which means that the high alumina contents SCMs (like here studied CCs) could increase the physical chloride binding capacity, as well.

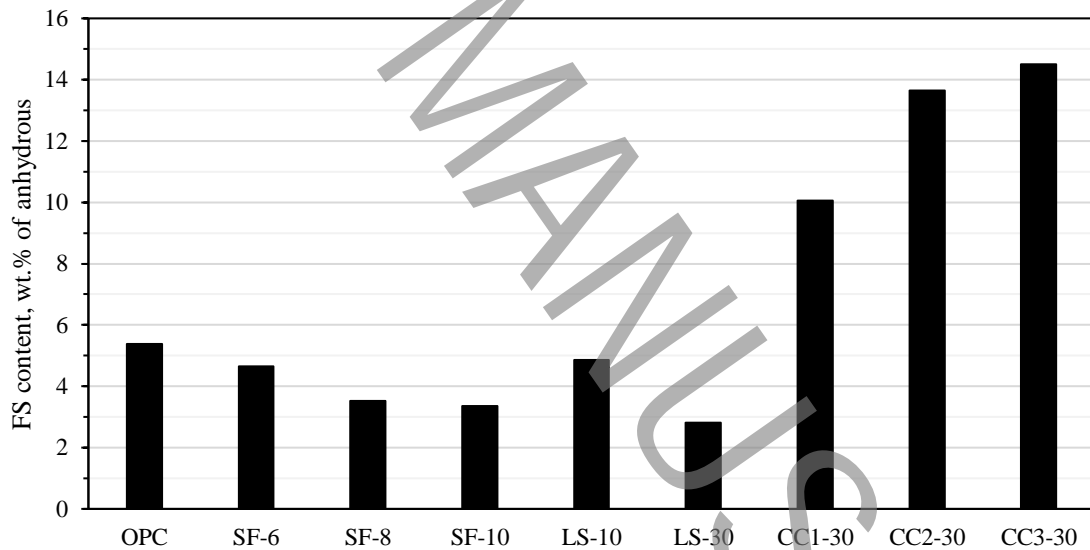


Fig. 6. FS contents of specimens immersed in 2M NaCl solution.

To evaluate the role of chemical binding of chloride ions in the chloride binding capacity, the bound chloride ions contents in FS from TG analysis and total chloride contents after 42 days immersion in 2M

NaCl solution from equilibrium method (Fig. 3-5) were calculated. The total chloride ions contents were also normalized to the anhydrous contents by considering the bound water values. In this study, the differences between the total bound chloride ions and bound chloride ions in FS were considered the contents of physically bound chloride ions. According to Fig. 7, as the SF and LS replacement level in pastes increased, the ratio of the bound chloride ions in FS to the total amounts of bound chloride ions decreased. For instance, the SF-10 mixture had 63.2% lower ratio of the bound chloride ions in FS to the total quantities of bound chloride ions than SF-6.

On the other hand, the partial replacement of PC with 10% of SF resulted in higher physical binding of chloride ions than LS-10 blend. In addition, the increment in kaolinite content of clays led to an inferior role of FS in chloride binding capacity of pastes (28.1% lower ratio of the bound chloride ions in FS to the total amounts of bound chloride ions for CC3-30 than CC1-30) and improvement of physical chloride ions binding as a result of C-A-S-H formation. This finding is consistent with the results of Maraghechi et al. [32]. It is worth mentioning that the FS content in CC3-30 was 6.3% and 44.3% higher than CC2-30 and CC1-30 pastes (see Fig.6) while the role of FS in total chloride binding capacity of CC3-30 paste was lower than CC2-30 and CC1-30 (see Fig.7).

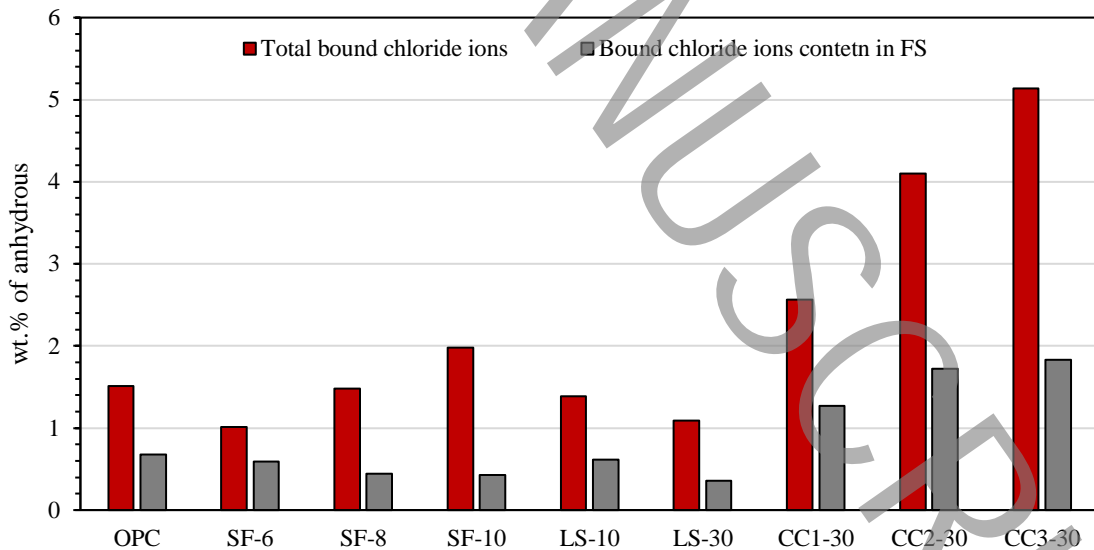


Fig. 7. Bound chloride ions contents in binder and FS after immersion in 2M NaCl solution.

It should be clarified that the considerable impact of incorporating low-grade calcined clays (even with kaolinite content < 30%) on the improvement of durability against chloride ions ingress by means of increasing the chloride binding capacity can be concluded. As a significant outcome of this research, the low-grade calcined kaolinitic clays, which have no or limited usage in other industries, could be introduced as novel SCMs with appropriate properties in the absorption of chloride ions and restraining their penetration into inner layers of cement-based materials. In addition, the environmental and economic beneficial aspects of replacing PC by here studied low-grade calcined clays highlights the high potential of using these materials as suitable SCMs.

#### **4. Conclusion**

In the present investigation, the effects of using SF, LS and CC with different kaolinite contents on compressive strength, phase assemblage and chloride binding capacity of pastes have been studied. The following conclusions can be drawn based on the materials and experimental program of this study:

- Utilization of SF resulted in a higher compressive strength than OPC mixture after 7 days of curing, while the partial replacement of PC with LS and CCs brought about decrements in compressive strengths due to the dilution effect.
- By increasing the kaolinite content of clays and the replacement level of PC by SF and LS, the calcium hydroxide contents of pastes have been reduced.
- The incorporation of CC improved the chloride ions binding capacity up to 242.5%. In addition, increasing the kaolinite content of clays led to higher amounts of bound chloride ions.



- In general, the partial replacement of PC by SF brought about decrements in chloride binding ability of pastes, except for SF-10 mixtures in NaCl solutions with concentrations above 0.5 M. The FS contents of all SF containing specimens immersed in 2M NaCl solution have been lower than that of OPC mixture. In addition, the physical chloride ions binding of SF-8 and SF-10 mixtures were higher than OPC paste in 2M NaCl solution.

Increasing the replacement level of PC with LS led to lower chloride binding capacities and less FS formation.

- Freundlich model provided better isotherms for indicating the relation between free and bound chloride ions contents than the Langmuir model.

## References

- [1] P.K. Mehta, P.J.M. Monteiro, Concrete: microstructure, properties, and materials, McGraw-Hill Education, 2014.
- [2] T. Luping, L.-O. Nilsson, Chloride binding capacity and binding isotherms of OPC pastes and mortars, *Cement and concrete research*, 23(2) (1993) 247-253.
- [3] A. Ipavec, T. Vuk, R. Gabrovšek, V. Kaučič, Chloride binding into hydrated blended cements: The influence of limestone and alkalinity, *Cement and Concrete Research*, 48 (2013) 74-85.
- [4] Q. Yuan, C. Shi, G. De Schutter, K. Audenaert, D. Deng, Chloride binding of cement-based materials subjected to external chloride environment—a review, *Construction and building materials*, 23(1) (2009) 1-13.
- [5] M. Kazemian, S. Sedighi, A.A. Ramezani pour, F. Bahman-Zadeh, A.M. Ramezani pour, Effects of cyclic carbonation and chloride ingress on durability properties of mortars containing Trass and Pumice natural pozzolans, *Structural Concrete*, (2021).
- [6] K.A. Gruber, T. Ramlochan, A. Boddy, R.D. Hooton, M.D.A. Thomas, Increasing concrete durability with high-reactivity metakaolin, *Cement and concrete composites*, 23(6) (2001) 479-484 % @ 0958-9465.
- [7] M. Zahedi, A.A. Ramezani pour, A.M. Ramezani pour, Evaluation of the mechanical properties and durability of cement mortars containing nanosilica and rice husk ash under chloride ion penetration, *Construction and Building Materials*, 78 (2015) 354-361.
- [8] M.D.A. Thomas, R.D. Hooton, A. Scott, H. Zibara, The effect of supplementary cementitious materials on chloride binding in hardened cement paste, *Cement and Concrete Research*, 42(1) (2012) 1-7 % @ 0008-8846.
- [9] H. Chang, Chloride binding capacity of pastes influenced by carbonation under three conditions, *Cement and Concrete Composites*, 84 (2017) 1-9.
- [10] M. Gbozee, K. Zheng, F. He, X. Zeng, The influence of aluminum from metakaolin on chemical binding of chloride ions in hydrated cement pastes, *Applied Clay Science*, 158 (2018) 186-194.
- [11] A. Machner, M. Zajac, M.B. Haha, K.O. Kjellsen, M.R. Geiker, K. De Weerd, Chloride-binding capacity of hydrotalcite in cement pastes containing dolomite and metakaolin, *Cement and Concrete Research*, 107 (2018) 163-181.
- [12] B. Sabir, S. Wild, J. Bai, Metakaolin and calcined clays as pozzolans for concrete: a review, *Cement and concrete composites*, 23(6) (2001) 441-454.
- [13] K.L. Scrivener, Options for the future of cement, *Indian Concr. J.*, 88(7) (2014) 11-21.

- [14] A.A. Ramezani pour, Cement replacement materials, Springer Geochemistry/Mineralogy, DOI, 10 (2014) 978-973.
- [15] H. Du, S. Dai Pang, High-performance concrete incorporating calcined kaolin clay and limestone as cement substitute, *Construction and Building Materials*, 264 (2020) 120152.
- [16] A. Alujas, R. Fernández, R. Quintana, K.L. Scrivener, F. Martirena, Pozzolanic reactivity of low grade kaolinitic clays: Influence of calcination temperature and impact of calcination products on OPC hydration, *Applied Clay Science*, 108 (2015) 94-101.
- [17] H. Du, S. Dai Pang, Value-added utilization of marine clay as cement replacement for sustainable concrete production, *Journal of Cleaner Production*, 198 (2018) 867-873.
- [18] F. Avet, K. Scrivener, Investigation of the calcined kaolinite content on the hydration of Limestone Calcined Clay Cement (LC3), *Cement and Concrete Research*, 107 (2018) 124-135.
- [19] F. Zunino, K. Scrivener, The reaction between metakaolin and limestone and its effect in porosity refinement and mechanical properties, *Cement and Concrete Research*, 140 (2021) 106307.
- [20] K. Scrivener, R. Snellings, B. Lothenbach, A practical guide to microstructural analysis of cementitious materials, Crc Press, 2018.
- [21] ASTM C311 / C311M-18, Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete in, ASTM International, West Conshohocken, PA, 2018.
- [22] ASTM C1437-20, Standard Test Method for Flow of Hydraulic Cement Mortar, in, ASTM International, West Conshohocken, PA, 2020.
- [23] EN 197-1, The new European standard on common cements specifications in, European Standard, 2011.
- [24] ASTM C305-20, Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency, in, ASTM International, West Conshohocken, PA, 2020.
- [25] R. Snellings, J. Chwast, Ö. Cizer, N. De Belie, Y. Dhandapani, P. Durdzinski, J. Elsen, J. Haufe, D. Hooton, C. Patapy, RILEM TC-238 SCM recommendation on hydration stoppage by solvent exchange for the study of hydrate assemblages, *Materials and Structures*, 51(6) (2018) 1-4.
- [26] C.L. Page, M.M. Page, *Durability of concrete and cement composites*, Elsevier, 2007.
- [27] P. Hawkins, P.D. Tennis, R.J. Detwiler, *The use of limestone in Portland cement: a state-of-the-art review*, Portland Cement Association, 1996.
- [28] B. Lothenbach, G. Le Saout, E. Gallucci, K. Scrivener, Influence of limestone on the hydration of Portland cements, *Cement and Concrete Research*, 38(6) (2008) 848-860.
- [29] Y. Guo, T. Zhang, W. Tian, J. Wei, Q. Yu, Physically and chemically bound chlorides in hydrated cement pastes: A comparison study of the effects of silica fume and metakaolin, *Journal of Materials Science*, 54(3) (2019) 2152-2169.
- [30] M. Thomas, R. Hooton, A. Scott, H. Zibara, The effect of supplementary cementitious materials on chloride binding in hardened cement paste, *Cement and Concrete Research*, 42(1) (2012) 1-7.
- [31] B. Martín-Pérez, H. Zibara, R. Hooton, M. Thomas, A study of the effect of chloride binding on service life predictions, *Cement and Concrete Research*, 30(8) (2000) 1215-1223.
- [32] H. Maraghechi, F. Avet, K. Scrivener, Diffusion And Interactions of Chloride Ions with Ternary Blends of Portland Cement-Limestone-Calcined Clay Binders, in: *International conference on advances in construction materials and systems*, 2017, pp. 173.