Chloride Desorption Isotherms of Cementitious Systems Exposed to Low-pH Environments

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Table of Contents

1	Ι	NTRODI	UCTION 1		
	1.1	Proble	m Statement 1		
	1.2	Object	tives of the Study		
	1.3	Resear	rch Significance		
	1.4	Backg	round		
	1.5	Organi	ization of Report		
2	Ι	LITERAT	FURE REVIEW		
	2.1	Chlori	de Binding 8		
	2.2	Factor	s Affecting Chloride Binding11		
	2	2.2.1 Bi	inder Chemical Composition11		
	2	2.2.2. The	Effect of Water-to-Binder Ratio 16		
	2.2.3. The Effect of the Curing Method16				
	2.2.4. The Effect of Cation of Chloride-Bearing Salt				
	2.2.5 The Effect of Sample Type 1				
	2.2.6 The Effect of Exposure Condition				
	2	2.2.7 TI	he Effect of Sample Saturation State21		
	2	2.2.8 TI	he Effect of Admixtures		

	2.3	Cl	hloride Desorption	22
3]	EXPE	ERIMENTAL WORK	29
	3.1	Μ	laterials	29
	3.2	2 Cl	hloride Binding Experiment	30
	3.3	B Cl	hloride Desorption Experiment	32
	3.4	A	nalytical Measurements	35
	3.5	5 М	Iass Change	36
4	(CHLO	ORIDE BINDING RESULTS	37
	4.1	H	ydration Characterization of Binary Blended Cement Pastes	37
	4.2	2 Cl	hloride Binding Isotherms of Binary Blended Cement Pastes	39
	4.3	3 X	RD Analysis of Chloride Binding Products	44
	4.4	+ T(GA Analysis of Chloride Binding Products	48
	4.5	5 Di	iscussion	55
	2	4.5.1	The Role of pH of Exposure Solutions in Chloride Binding	55
	2	4.5.2	The Role of The Salt Cation in Chloride Binding	56
5	(CHLO	ORIDE DESORPTION RESULTS	59
	5.1	Cl	hloride Desorption of Ca(OH) ₂ in a Model System	59
	5.2	e Cl	hloride Desorption of Binary Blended Cement Pastes	61

5.3	Visual Inspection of Samples After Chloride Desorption Test	
5.4	XRD Analysis of Chloride Desorption Products	74
5.5	TGA Analysis of Chloride Desorption Products	80
5.6	Sample Mass Change After Chloride Desorption Test	
5.7	Discussion	
5.7	7.1 The Role of pH in Chloride Desorption	
5.7	7.2 The Role of The Salt Cation in Chloride Desorption	
6 C0	ONCLUSION	100
6.1	Recommendations for Future Works	101
REFEI	RENCES	103
APPEN	NDIX A	111
APPEN	NDIX B	119

List of Figures

Figure 1.1. (a) The influence of volumetric addition of 1:1 nitric acid on the pH of the solution					
containing OPC samples, (b) the influence of pH on chloride disassociation of bound chlorides					
[11]5					
Figure 1.2. The formation of hydrogels due to the addition of 20 ml dilute (1:1) nitric acid to					
ground OPC 6					
Figure 2.1. The relationship between measured free and bound chlorides superimposed with fitted					
Langmuir, Freundlich, and linear chloride binding isotherms9					
Figure 3.1. Environmental chamber (left) and vacuum oven (right)					
Figure 3.2 Schematics of solution preparation and titration testing					
Figure 3.3 Schematics of chloride desorption testing procedure					
Figure 3.4. The Experiment setup for chloride binding (left) and desorption tests (right)					
Figure 3.5. The analytical tools used to characterize chloride binding and desorption products.					
XRD (left); TGA (middle); and a digital microscope (right)					
Figure 4.1. The XRD scans of 56-d paste samples containing different SCMs (E: Ettringite, C:					
C4AF, M: Monocarbonate, F: Ferrite, CH: portlandite, Cc: Calcite, C2S: Belite					
Figure 4.2. The DTG analysis of 56-d hydrated paste samples containing different SCM (E:					
Ettringite and CH: portlandite)					

Figure 4.3. The chloride binding isotherms of OPC pastes exposed to NaCl, CaCl₂, and MgCl₂. Figure 4.4. The chloride binding isotherms of OPC+ fly ash paste exposed to NaCl, CaCl₂, and Figure 4.5. The chloride binding isotherms of OPC+ slag pastes exposed to NaCl, CaCl₂, and Figure 4.6. The chloride binding isotherms of OPC+ silica fume pastes exposed to NaCl, CaCl₂, Figure 4.7. The XRD results for OPC samples after two weeks of exposure to salt solutions (FS: Figure 4.8. The XRD results for fly ash samples after two weeks of exposure to salt solutions (a) FA15; (b) FA30 (FS: Friedel's salt, CH: Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, Figure 4.9. The XRD results for slag samples after two weeks of exposure to salt solutions. (a) SG25; (b) SG50) (FS: Friedel's salt, CH: Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, Figure 4.10. The XRD results for silica fume samples after two weeks of exposure to salt solutions, (a) SF5; (b) SF10 (FS: Friedel's salt, CH: Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, Figure 4.11. The DTG results of OPC paste samples after exposure to chloride solutions....... 49

Figure 4.12. The DTG results of fly ash paste samples after exposure to chloride solutions; (a)
FA15 and (b) FA30
Figure 4.13. The DTG results for slag paste samples after exposure to chloride solutions; (a) SG25
and (b) SG50
Figure 4.14. The DTG results of silica fume paste samples after exposure to chloride solutions; (a)
SF5 and (b) SF10
Figure 4.15. The mass fraction of Friedel's salt in paste samples made with OPC, fly ash, slag, and
silica fume
Figure 5.1. pH change and its effect on chloride binding in a model Ca(OH) ₂ system. (a) pH
change; (b) bound chlorides
Figure 5.2. Measured free chlorides after desorption in samples containing OPC. (a) NaCl; (b)
CaCl ₂ ; (c) MgCl ₂
Figure 5.3. Measured free chlorides after desorption in samples containing FA15. (a) NaCl; (b)
CaCl ₂ ; (c) MgCl ₂
Figure 5.4. Measured free chlorides after desorption in samples containing FA30. (a) NaCl; (b)
CaCl ₂ ; (c) MgCl ₂
Figure 5.5. Measured free chlorides after desorption in samples containing SG25. (a) NaCl; (b)
CaCl ₂ ; (c) MgCl ₂
Figure 5.6. Measured free chlorides after desorption in samples containing SG50. (a) NaCl; (b)
CaCl ₂ ; (c) MgCl ₂

Figure 5.7. Measured free chlorides after desorption in samples containing SF5. (a) NaCl; (b)
CaCl ₂ ; (c) MgCl ₂
Figure 5.8. Measured free chlorides after desorption in samples containing SF10. (a) NaCl; (b)
CaCl ₂ ; (c) MgCl ₂
Figure 5.9. Measured free chlorides in OPC samples exposed to salt solutions before and after
adding nitric acid. (a) NaCl; (b) CaCl ₂ ; (c) MgCl ₂ 64
Figure 5.10. Measured free chlorides in FA15 samples exposed to salt solutions before and after
adding nitric acid. (a) NaCl; (b) CaCl ₂ ; (c) MgCl ₂ 64
Figure 5.11. Measured free chlorides in FA30 samples exposed to salt solutions before and after
adding nitric acid. (a) NaCl; (b) CaCl ₂ ; (c) MgCl ₂ 64
Figure 5.12. Measured free chlorides in SG25 samples exposed to salt solutions before and after
adding nitric acid. (a) NaCl; (b) CaCl ₂ ; (c) MgCl ₂ 65
Figure 5.13. Measured free chlorides in SG50 samples exposed to salt solutions before and after
adding nitric acid. (a) NaCl; (b) CaCl ₂ ; (c) MgCl ₂ 65
Figure 5.14. Measured free chlorides in SF5 samples exposed to salt solutions before and after
adding nitric acid. (a) NaCl; (b) CaCl ₂ ; (c) MgCl ₂ 65
Figure 5.15. Measured free chlorides in SF10 samples exposed to salt solutions before and after
adding nitric acid. (a) NaCl; (b) CaCl ₂ ; (c) MgCl ₂
Figure 5.16. The released bound chlorides and measured pH after two weeks of exposure to nitric
acid in samples containing OPC67

Figure 5.17. The released bound chlorides and measured pH after two weeks of exposure to nitric
acid in samples containing fly ash. (a) FA15; (b) FA30
Figure 5.18. The released bound chlorides and measured pH after two weeks of exposure to nitric
acid in samples containing slag. (a) SG25; (b) SG5069
Figure 5.19. The released bound chlorides and measured pH after two weeks of exposure to nitric
acid in samples containing silica fume. (a) SF5; (b) SF1070
Figure 5.20. Images of OPC samples after two weeks of exposure to nitric acid
Figure 5.21. The XRD results for OPC samples before and after exposure to 25 ml acid. Samples
were first exposed to 2 M salt solutions (FS: Friedel's salt, CH: Portlandite, Cc: Calcite, C2S:
Belite, E: Ettringite, B: Brucite)
Figure 5.22. The XRD scans of fly ash samples before and after exposure to 25 ml acid. Samples
were first exposed to 2 M salt solutions. (a) FA15; (b) FA30 (FS: Friedel's salt, CH:
Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, B: Brucite)
Figure 5.23. The XRD scans of slag samples before and after exposure to 25 ml acid. Samples
were first exposed to 2 M salt solutions. (a) SG25; (b) SG50 (FS: Friedel's salt, CH:
Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, B: Brucite)77
Figure 5.24. XRD scans of silica fume samples before and after exposure to 25 ml acid. Samples
were first exposed to 2 M salt solutions. (a) SF5; (b) SF10 (FS: Friedel's salt, CH: Portlandite,
Cc: Calcite, C2S: Belite, E: Ettringite, B: Brucite)
Figure 5.25. Sample preparation for testing the chemical composition of corroded layer (OPC paste
exposed to 25 ml acid addition)

Figure 5.26. The XRD results of the corroded layer of OPC paste exposed to 25 ml acid (Q:
Quartz, Gi: Gibbsite, G: Gypsum B: Brucite, CN: calcium nitrate)
Figure 5.27. The DTG results for OPC sample before and after 25 ml acid addition 80
Figure 5.28. The DTG results of fly ash-containing samples before and after exposure to 25 ml
nitric acid (a) FA15 and (b) FA30
Figure 5.29. The DTG results of slag-containing samples before and after exposure to 25 ml nitric
acid (a) SG25 and (b) SG50
Figure 5.30. DTG results of silica fume-containing samples before and after exposure to 25 ml
nitric acid (a) SF5 and (b) SF10
Figure 5.31. Salt crystallization within the cracks after drying of samples exposed to 2 M salt
solutions
Figure 5.32. Discoloration and corrosion of outer layer of samples as a result of exposure to 25 ml
acid for two weeks
Figure 5.33. Percent mass change in OPC samples after exposure to nitric acid at different volumes.
Figure 5.34. Percent mass change in samples containing fly ash after exposure to nitric acid at
different volumes. (a) FA15; (b) FA30
Figure 5.35. Percent mass change in samples containing slag after exposure to nitric acid at
different volumes. (a) SG25; (b) SG50

List of Tables

Table 2.1. Most reported variabilities affecting chloride binding results. 11
Table 2.2. Reported findings on the impacts of SCMs on chloride binding capacity. 12
Table 3.1. The oxide analysis of cement and SCMs. 29
Table 3.2. Mix design proportions (FA: Fly ash, SG: Slag, SF: Silica fume). 30
Table 3.3. Effect of various molarities of nitric acid on the pH of exposure solutions
Table 4.1. The Langmuir and Freundlich isotherms parameter estimates
Table 4.2. Measured mass fraction of Friedel's salt in different cementitious systems 50
Table 4.3. Average measured pH of containers containing salt solutions and a paste after two
weeks
Table 4.4. Average measured bound chlorides in different paste samples when exposed to 2 M salt
solutions
Table 5.1. Samples after exposure to 25 ml nitric acid
Table 5.2. Measured mass fraction of Friedel's salt in a temperature range of 240 to 420 for before
and after adding 25 ml acid

1 INTRODUCTION

1.1 Problem Statement

The surface of concrete pavements and reinforced concrete bridge decks are commonly treated with chloride-bearing deicing and anti-icing salts during winter to minimize freezing risk. The frequent application of these salts can result in the ingress of chlorides into the concrete. When enough chlorides reach the surface of the reinforcing bars, localized corrosion can occur. The corrosion of the reinforcing bars can ultimately reduce the structure's service life and result in significant repair or rehabilitation costs. One of the several reported factors that can delay the corrosion initiation of the embedded reinforcing steel in concrete is the chloride-binding capacity of the concrete matrix. Chloride binding mechanisms remove a portion of free chlorides from the pore solution that can participate in corrosion. However, under certain circumstances (e.g., carbonation, sulfate attack, acid attack) and as a result of a drop in the pH of the concrete pore solution, bound chlorides can disassociate from the hydration products and return to the pore solution, leading to an increased risk of corrosion. The current state-of-the-art in service-life modeling of concrete structures often incorporates a sink term to account for the role of chloride binding in estimating the remaining service life of a structure. However, a recent review indicates that little is known regarding the disassociation kinetics of chlorides as a function of the pH of the pore solution. More research is needed to incorporate the influence of chloride desorption in service-life models. Ignoring the desorption of bound chlorides can lead to overestimating a structure's remaining service life, resulting in significant maintenance costs.

1.2 Objectives of the Study

The overall objectives of this project are to understand the kinetics of chloride desorption mechanisms and develop empirical chloride desorption isotherms for cementitious systems that contain ordinary Portland cement (OPC), fly ash, slag, and silica fume. More specifically, this research project has three objectives; first, it investigates the chloride binding capacity of various cementitious systems using paste samples; second, it studies the chloride desorption behavior of these cementitious systems when exposed to low-pH environments; and third, it looks into the chemical reactions that take place as a result of the reduction in the pH, and quantifies the physicochemical properties of the produced hydrogels. A methodic experimental plan will be followed to determine the portion of bound chlorides that can disassociate after exposure to solutions at various pH levels.

1.3 Research Significance

The primary output this research achieves necessarily improves service-life estimates' reliability. It also quantifies the durability and performance of concretes exposed to low-pH environments. Furthermore, the quantification and sound understanding of chloride desorption mechanisms and the ability to extrapolate critical physical properties such as chloride desorption capacity of cementitious systems in potentially aggressive environments constitutes a significant step forward. The current ACI 222-guide to the protection of reinforcing steel in concrete against corrosion provides unambiguous information to the users of this document regarding the role of chloride binding in corrosion initiation. Although ACI 222 document acknowledges the potential release of bound chlorides due to pH-drop in the pore solution, no further information or discussion

is provided regarding what percentage of bound chlorides can be disassociated and the role that SCMs can play in retaining or release of bound chlorides.

The state-of-the-art report on service-life prediction published by ACI 365 also acknowledges the role of chloride binding in extending the service life of structures. However, it provides no additional information on how the disassociation of bound chlorides can affect structures' remaining service life. Unfortunately, there are no standardized tests or procedures to study the desorption behavior of bound chlorides in low-pH environments. Thus, this project will be one of the first studies investigating the kinetics of chloride desorption methodically. The current data in the literature also provides limited value for determining the chloride desorption isotherms of cementitious systems.

Given that the knowledge of available free chloride content in the pore solution is essential for a reliable service-life estimate, this project will fill this knowledge gap by developing empirical desorption isotherms incorporated in service-service life models. The data from this project is expected to provide the baseline for addressing the disassociation of bound chlorides in ACI 222 and 365 documents. Moreover, a standardized test will be proposed to measure cementitious systems' chloride desorption capacity.

1.4 Background

Extensive research has been conducted on chloride binding of various cementitious systems. These researches have adequately highlighted the prime role of chloride binding mechanisms in delaying chloride ingress and the onset of reinforced corrosion [1]. In non-carbonated concrete that has not been exposed to low-pH environments, the chemical and physical bonds that form between the cement hydrates and chlorides can immobilize a portion of ingressed chlorides and slows the transport of free chlorides in the pore solution [2-4]. This phenomenon has been addressed in Fickian service-life models by incorporating the chloride binding capacity of a cementitious system in the chloride diffusion coefficient or as a sink term in service-life models using the Nernst-Plank equation [5-7].

In terms of durability, the disassociation of bound chlorides is an unfavorable mechanism, and the desorption behavior of the cementitious system is worth investigating. Three main factors that can affect the chloride binding behavior of cementitious systems are (i) the cation type of the chloride salt [2, 4, 8], (ii) the type of cement and supplementary cementitious materials used in the concrete mixture [9, 10], and (iii) the pH of the cementitious system [5, 6].

The PI of this research proposal hypothesizes that cementitious systems that develop a strong bond with chlorides are more durable in low-pH and release fewer chlorides into the concrete pore solution. Figure 1 shows the preliminary study results by the PI of this project on the effects of the chloride cations and pH of the exposure solution on the chloride desorption behavior of ground OPC paste samples. These results show that the breakdown of physical or chemical chloride bonds in ground paste samples exposed to MgCl₂ and CaCl₂ solutions requires a lower pH value. Therefore, it can be hypothesized that chlorides from magnesium- and calcium-based salts can develop relatively stronger bonds with cement hydration products than sodium-based salts. This is an important finding because most currently used anti-icing and deicing salts are made of NaCl, suggesting that bound chlorides from these salts are more prone to disassociation in a low-pH environment.



Figure 1.1. (a) The influence of volumetric addition of 1:1 nitric acid on the pH of the solution containing OPC samples, (b) the influence of pH on chloride disassociation of bound chlorides [11].

The concrete industry is currently using blended cement types containing OPC and many other cementitious materials such as fly ash, slag, and silica fume. Therefore, to better understand the disassociation behavior of chlorides in a low-pH environment, this project proposes a methodic and comprehensive study of the chloride binding and desorption behavior of paste samples made of OPC, fly ash, slag, and silica fume exposed to NaCl, MgCl₂, and CaCl₂ solutions at various pH values.

As a result of a significant drop in the pH, the PI observed that a hydrogel was produced (Figure 2). However, the formation of such hydrogel is more distinct in powdered paste samples than in solid samples. This can be attributed to an increased reaction surface area between hydration products and nitric acid to produce calcium nitrate and silicon nitride [12]. However, little is known about the influence of these hydrogels on chloride binding and desorption in cementitious systems. Therefore, it can be hypothesized that, in a low-pH environment, these hydrogels can

absorb some of the free chlorides from the exposure solution, resulting in the downward trend in chloride desorption isotherm shown in Figure 1b. As an extension to the PI's preliminary findings, the current proposal will also look at these gel-like materials' chemical and physical properties and their influence on chloride binding/desorption.



Figure 1.2. The formation of hydrogels due to the addition of 20 ml dilute (1:1) nitric acid to ground OPC.

1.5 Organization of Report

The report is composed of six sections and one appendix. Section 1 overviews the objective of the study and research significance. Section 2 provides a detailed literature review of previous findings on chloride binding of cementitious systems and mechanisms which lead to chloride desorption. Section 3 includes material properties and experimental procedures for chloride binding and desorption tests. Section 4 discusses chloride binding results of binary blended cement pastes, which include hydration characteristics, chloride binding isotherms, and analytical results. Section 5 consists of chloride desorption results of binary blended cement pastes, including chloride desorption results, analytical tests on sample after exposure to a low pH environment, visual inspection, and sample mass change after chloride desorption test. Finally, section 6

summarizes conclusions and provides recommendations for future works. Appendix A includes images of binary blended cement pastes samples after desorption tests.

2 LITERATURE REVIEW

2.1 Chloride Binding

Chloride-induced corrosion is one of the reinforced concrete infrastructures' most researched environmental deterioration phenomena. The ingress of chlorides in concrete and the depassivation of the protective layer formed on the surface of reinforcements is the main reason leading to chloride-induced corrosion [13]. Chloride ions entering the concrete can originate from external or internal sources. The external sources can come from the marine environment or recurrent application of chloride-bearing dicing and anti-icing salts during the winter [8]. The internal chloride can enter the concrete with concrete constituent materials such as aggregate, cement, admixtures, and even water [9, 14] during the mixing process.

Irrespective of how chlorides enter the concrete, chlorides can exist in concrete in two forms: free and bound chlorides [10]. Free chlorides are the ones that can freely move inside the concrete pores filled with concrete pore solution and, if they reach the surface of the steel in sufficient quantities, are the primary cause of chloride-induced corrosion in concrete structures [13]. The accumulation of these free chlorides on the steel surface can lead to the breakdown of the protective passive layer formed on the steel surface during the hydration process and contribute to the onset of the corrosion process. Bound chlorides are those chloride ions that are adsorbed by the concrete matrix and cannot participate in active corrosion under normal conditions. Therefore, chloride binding refers to a process by which chlorides form a physical or chemical bond with cement hydration products and are removed from the concrete pore solution. Broadly speaking, chlorides can be physically adsorbed onto the surface of cement hydrates, especially calcium silicate hydrate

(C–S–H), and/or they can bind chemically with the hydrated aluminate phases of cement to form calcium chloroaluminate hydrates, known as Friedel's salt (C₃A.CaCl₂.10H₂O) [15, 16].

The relationship between the concentration of free and bound chlorides in concrete at a given temperature can be characterized using binding isotherms; plotting bound versus free chlorides, as shown in Figure 2.1, constitutes a binding isotherm.



Figure 2.1. The relationship between measured free and bound chlorides superimposed with fitted Langmuir, Freundlich, and linear chloride binding isotherms

Eqs. (1) and (2) show the Langmuir and Freundlich isotherms, respectively, which are two of the most widely used empirical chloride-binding isotherms in the literature. In previous reports, the units used to measure free and bound chlorides have varied. For example, Sergi et al. [17] used mol/l and mmol/g cement to report free and bound chlorides, respectively. The present study expresses free and bound chlorides in M and mg/g concrete, respectively.

$$C_b \Big|_{Langmuir} = \frac{\alpha_L C_f}{\left(1 + \beta_L C_f\right)} \tag{1}$$

$$C_b \big|_{Freundlich} = \alpha_F C_f^{\beta_F} \tag{2}$$

where $\alpha_{.}$ and $\beta_{.}$ are empirical values determined numerically by fitting Eq. (1) or Eq. (2) to the experimental results, C_f is free chloride, and C_b is bound chloride.

In a particular case, when β in the Langmuir isotherm is zero, the equation for this isotherm changes into a line equation, often referred to as a linear chloride binding isotherm. One of the most significant differences between the Langmuir and Freundlich isotherms lies in their behavior at high chloride concentrations. While the slope of the Langmuir isotherm approaches zero asymptotically at high free-chloride concentrations, the slope of the Freundlich isotherm can increase perpetually. Intuitively, the concrete matrix comprises a finite amount of hydration products that can physically and chemically bind chlorides. Therefore, once the available hydration sites and hydration products are exhausted, no more binding can occur (i.e., the rate of chloride binding approaches zero). Thus, chloride binding capacity. The binding capacity of a cementitious system in the literature is often expressed as the rate of change in bound with respect to free chloride. Eqs. (3) and (4) show the binding capacity associated with the Langmuir and Freundlich isotherms, respectively.

$$\frac{\partial C_b}{\partial C_f}\Big|_{Langnuir} = \frac{\alpha_L}{\left(1 + \beta_L C_f\right)^2} \tag{3}$$

$$\frac{\partial C_b}{\partial C_f}\Big|_{Freundlich} = \alpha_F \beta_F C_f^{\beta_f - 1} \tag{4}$$

2.2 Factors Affecting Chloride Binding

Numerous factors potentially impact the chloride binding mechanism. For example, table 2.1

summarizes the most commonly reported factors affecting chloride binding results.

Variable	Explanation	Reference
Binder chemical composition	Chemical composition of cementitious materials	[18-22]
Water to binder ratio	Amount of water in the mixture	[23-25]
Curing method	Curing time and temperature (fixed or gradient)	[22, 26]
Cotion type	Chloride solution type and molarity (NaCl,	[11, 27, 28]
Cation type	CaCl ₂ , etc.)	
Sample type	Paste, mortar, and concrete	_
Sample form	Disk, powder, or synthesized pore solution	_
Exposure condition	Exposure time, temperature, condition	[15, 29-31]
Samples saturation	Dried, saturated, wet/dry cycles	—
Admixtures	Admixtures type	[32-35]

Fable 2.1. Most reported	variabilities affecting	chloride binding results.
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2.2.1 Binder Chemical Composition

Numerous studies investigated the influence of binder type composition on the chloride binding mechanism [22, 36, 37]. The inclusion of SCMs that alter the binder's chemical composition affects the chloride binding capacity of concrete [22, 24, 38]. However, there are contradictory results regarding the impacts of various SCMs on chloride binding capacity. Table 2.2 presents some recent studies on the effects of SCMs on the chloride binding capacity of different cementitious systems. Using fly ash and slag promotes more chloride binding, whereas silica fume reduces the binding capacity. The bound chloride capacity of a cementitious system with SCMs strongly depends on the aluminum content of the SCM [39]. In addition, incorporating an SCM can change the pore solution chemistry and, in most cases, reduce its pH [40]. The reduction of pore solution

pH as a result of adding an SCM to the system can be owing to the pozzolanic reaction, in which portlandite is consumed to produce C-S-H [41, 42].

SCM type	Salt solution	Bound	Fitted	Reference
SCIVI type		chloride	isotherm	
8% silica fume	NaCl (0.1 M to 3 M)	\downarrow	Freundlich	[23]
8% metakaolin	NaCl (0.1 M to 3 M)	\uparrow	Freundlich	[23]
25% fly ash	NaCl (0.1 M to 3 M)	↑	Freundlich	[23]
25% slag	NaCl (0.1 M to 3 M)	↑	Freundlich	[23]
6% silica + 25% fly ash	NaCl (0.1 M to 3 M)	↑	Freundlich	[23]
6% silica + 25% slag	NaCl (0.1 M to 3 M)	↑	Freundlich	[23]
15 silica fume	NaCl (0.005 M to 0.1 M)	\downarrow	Freundlich	[22]
15% Metakaolin	NaCl (0.005 M to 0.1 M)	\uparrow	Freundlich	[22]
10, 20 and 30%	NaCl (0.53 M)	↑	-	[43]
Metakaolin		I		
20% fly ash	NaCl (0.1 M to 2.5 M)	↑	Freundlich	[25]
40% slag	NaCl (0.1 M to 2.5 M)	↑↓	Freundlich	[25]
5% silica fume	NaCl (0.1 M to 2.5 M)	↑↓	Freundlich	[25]
20% fly ash	NaCl (0.1 M to 1 M)	↑	-	[26]
20% slag	NaCl (0.1 M to 1 M)	↑	-	[26]
10% silica fume	NaCl (0.1 M to 1 M)	\downarrow	-	[26]
20, 40, 60% fly ash	CaCl ₂ (0.1 M to 5.5 M)	1	-	[36]

Table 2.2. Reported findings on the impacts of SCMs on chloride binding capacity.

2.2.1.1 The Effect of Aluminum Content

Rasheeduzzafar et al. [18, 44] reported that an increase in C_3A promotes chemical chloride binding and the formation of Friedel's salt, and more chlorides can be bound if they are present in the mixture as admixed chlorides rather than chlorides that enter the concrete from external sources later. Ipavec et al. [39] conducted an experimental study to investigate the impact of SCM type (fly ash, slag, and silica fume) and the inclusion of limestone on the chloride binding mechanism. Their results indicated that chloride-bearing AFm compounds such as calcium monochloroaluminate hydrate (Friedel's salt) are the primary forms of chemically bound chlorides. In terms of chloride binding, there is a subtle difference between C-S-H and AFm phases (such as monosulfate). AFm has a more robust chloride binding capability compared to C-S-H. However, since a hydrated cementitious system usually contains a significantly higher amount of C-S-H than AFm phases, the portion of chemically bound chlorides in the form of Friedel's salt compared to adsorbed chlorides on C-S-H depends on the concentration of free chlorides [28]. When chloride concentration is lower than 1 M, chemical binding is the dominant binding mode. However, at higher chloride concentrations, the physical binding can supersede the formation of Friedel's salt [28].

2.2.1.2 The Effect of Ca/Al₂O₃

The CaO-to-Al₂O₃ ratio (C/A) of the binder is another factor that affects chloride binding capacity. CaO and Al₂O₃ can help form C-S-H and AFm phases, both promoting chloride binding. Based on a review of previously published experimental studies using binders with varying chemical compositions, Wang et al. [45] reported that when C/A < 3, there will be an excessive amount of alumina in the system, and calcium content becomes a limiting factor in chloride binding. On the other hand, when C/A > 7, chloride binding is highly dependent on the aluminum phase content. Based on these findings, Wang et al. [45] reported an increase in chloride binding with an increase in C/A from 3 to 7.

2.2.1.3 The Effect of Alkali Content

The effect of the alkali content on chloride binding is twofold. Firstly, increased alkali content inhibits chloride binding because chloride ions and alkalis can bind with hydration products such as C-S-H, so high concentrations of alkalis lower the chance of chloride ions binding. Secondly, a

higher alkali content increases the pH of the pore solution [46], which in turn lowers the value of CI^{-}/OH^{-} [18]. Quite a few studies concluded that the depassivation of reinforcements is a function of the pore solution's Cl-/ OH- rather than chloride concentration [20, 21, 44]. According to Tritthart et al. [47], there is an inverse relationship between the OH⁻ concentration in pore solution and the number of bound chlorides because Cl⁻ and OH⁻ ions compete for adsorption on hydrated cement.

2.2.1.4 The Effect of Fly Ash

Geng et al. [38] reported that replacing 30% of OPC with class F fly ash and slag improved chloride binding capacity, with samples with fly ash having a higher chloride binding capability. Xu et al. [52] found a similar result and reported that the inclusion of silica fume led to a reduction in chloride binding, but a partial replacement of cement with fly ash and slag increased the chloride binding and reduced the release of bound chloride. Ramirez-Ortiz et al. [48] studied the chloride binding performance of different cement pastes containing OPC+10% silica fume, OPC+20% fly ash, and OPC+40% fly ash, which were immersed in NaCl solutions at various concentrations using ultrasonic detectors (500 kHz longitudinal wave transducers). The silica fume and fly ash contained 0.03% and 20.38% Al₂O₃, respectively. They reported that incorporation of 40% fly ash resulted in the highest chloride binding, followed by 10 % silica fume, 20 % fly ash, and OPC.

2.2.1.5 The Effect of Silica Fume

Silica fume in concrete can improve the concrete's microstructure and permeability against the ingress of harmful species. Since fewer chlorides can penetrate a silica fume-containing system than a neat OPC system, the quantity of bound chlorides samples made with silica fume is lower.

In addition, since silica fume is mainly made of silica, it can dilute the C_3A content of the system if used in large quantities. Thomas et al. [49] confirmed that the incorporation of 8% SF decreased the chloride binding capacity of ternary concrete. Xu et al. [50] also reported that the partial replacement of silica fume could negatively affect chloride binding capacity due to its influence on (i) reduction of pore solution pH, (ii) reduction of Ca/Si ratio, and (iii) dilution of C_3A .

2.2.1.6 The Effect of Metakaolin

Shi et al. [51] reported that the incorporation of metakaolin (25.5% and 31.9%) as an aluminum source in a ternary binder increased the number of bound chlorides compared to OPC samples [51]. Huang et al. [22] reported that replacing 15% metakaolin with high-ferrite Portland cement increased the total bound chloride because metakaolin enhances the generation of more aluminate hydrates, verified to be AFm phases in the cement matrix.

2.2.1.7 The Effect of Calcite

Ipavec [39] investigated the influence of adding limestone to cement on chloride binding and found that it can slightly reduce the chloride binding capacity of the system. The underlying reason was reported to be due to the formation of carboaluminate phases (CO₃-AFm) as the main constituent of limestone, which has a lower chloride binding than AFm phases.

Then [52] investigated the chloride binding of portland limestone cement (PCL) containing various SCMs and concluded that bound chloride contents in PCL specimens containing up to 15% interground limestone were not statistically different from those of OPC samples. Sui et al. [53] analysis revealed that when the proportion of calcite in the binder is more than 5%, a solid solution

containing Friedel's salt and hemicarboaluminate is formed, with the latter having a lower chloride binding capability.

2.2.2. The Effect of Water-to-Binder Ratio

It is well known that the w/b significantly impacts the concrete microstructure [53]. A higher w/b can increase the micropores' degree of hydration and coarseness, promoting chloride binding [50]. Thomas et al. [49] reported that reducing the w/b from 0.5 to 0.3 significantly reduced the binding capacity of pastes containing metakaolin, slag, and fly ash. They claimed that insufficient water content, especially when SCMs are included in the binder, stifled the hydration and pozzolanic reactions, and a considerable number of aluminum-rich phases did not become available to bind chloride ions. Yuan et al. [25] tested 12 concrete mixtures containing diverse SCMs and made with the w/b of 0.35, 0.48, and 0.6, and observed a higher chloride binding in samples made with w/b = 0.6. They argued that increased chloride bindings were due to increased hydration. In addition, a high w/b can make the system more porous, providing more adsorption sites for chloride ions. Thus, selecting an appropriate w/b would help to improve the chloride binding capacity at no cost.

2.2.3. The Effect of the Curing Method

Curing concrete is an important step that can enhance and improve the durability of concrete structures [54] and affect the chloride binding capacity of concrete. Huang et al. [22] reported that an elevated curing temperature is detrimental to concrete pore structure and decreases the binding capacity of the system. A recently published study by Chen et al. [26] investigated the impacts of three curing regimes, including standard ($20 \pm 2^{\circ}$ C, RH > 95%), steam (55°C for 5 h), and autoclave (180°C for 8 h) on chloride binding of cementitious systems containing portland cement,

and different SCMs including fly ash (20%), slag (20%), and silica fume (10%) with a w/b of 0.32. A higher porosity is observed in autoclaved curing, followed by steam and standard curing, which provide a chloride ions transport path inside samples. However, chloride binding capacity in autoclave curing was lower compared to two other procedures due to the reduction of AFm and C-S-H phases as the primary phases capable of binding chlorides. The precast concrete industry has vastly grown, and more comprehensive investigations on the effect of curing methods on chloride binding are needed.

2.2.4. The Effect of Cation of Chloride-Bearing Salt

One of the main factors affecting the chloride-binding behavior of a cementitious system is the cation type of chloride salt. Previous research has shown that the pH of the pore solution increases in the presence of NaCl and decreases in the presence of CaCl₂ and MgCl₂ [8, 32, 33]. In general, an increase in the pH of the pore solution leads to a decrease in the number of bound chlorides [34, 35, 55]. This is because chlorides first form a chemical bond with tricalcium aluminate or its hydrates to form Friedel's salt C₃A.CaCl₂.10H₂O [36]. The solubility of Friedel's salt is pH-dependent, and, therefore, the rise in pH as a result of the exposure to NaCl solution can increase the solubility of Friedel's salt and reduce the concentration of bound chlorides [18, 37]. Ca²⁺ from calcium-bearing salts, however, can contribute to the development of more C–S–H, which can take up more chlorides from the solution and release H⁺ back into the solution in return, leading to a significant reduction in the pH of the solution [47]. Similarly, the presence of Mg²⁺ can lead to the formation of brucite and an increased Ca/Si ratio in the C–S–H gel, which in turn can increase the chloride uptake capability of the C–S–H [41]. NaCl is one of the most commonly used de-icers, and research has shown that long-term exposure to NaCl can result in the dissolution of portlandite

in concrete pavements through the reaction described in Eq. (5) [8]. This reaction makes the concrete surface more porous and susceptible to durability issues, such as scaling and corrosion [21].

$$NaCl + Ca(OH)_2 \rightarrow CaCl_2 + 2NaOH$$
(5)

CaCl₂ is another standard de-icer that, when used in high concentrations, can react with portlandite and produce calcium hypochlorite, as Eq. (6) shows. CaCl₂ can also form calcium oxychlorides at near-freezing temperatures, which are very expansive and can significantly affect the integrity of hardened concrete [30]. In addition, CaCl₂ can react with anhydrous C₃A to form Friedel's salt, as shown in Eq. (7). In general terms, the degree of concrete deterioration is higher with CaCl₂ exposure compared to NaCl exposure. Notably, CaCl₂ causes more damage in concrete-containing dolomite aggregates [56].

$$CaCl_2 + 3Ca(OH)_2 + 12H_2O \rightarrow 3CaO.CaCl_2.15H_2O$$
(6)

$$CaCl_2 + C_3A + 10H_2O \rightarrow C_3A.CaCl_2.10H_2O$$
⁽⁷⁾

Cody et al. [57] demonstrated that MgCl_{2 could} cause more severe deterioration to concrete than NaCl or CaCl₂. When MgCl₂ remains in melting ice, Mg²⁺ and Cl⁻ ions make damaging changes to the cement hydrates. These changes reduce the strength and increase the porosity of concrete. MgCl₂ can react with portlandite to form magnesium hydroxide and CaCl₂, as shown in Eq. (8), thus reducing the alkalinity of the pore solution. MgCl₂ can also lead to the decalcification of C–S–H, which is the primary cause of strength reduction in concrete. Upon exposure to MgCl₂, C–S–H can also be converted into magnesium silicate hydrate (M-S-H), as detailed in Eq. (9). M-S-H is non-cementitious and reduces the strength and increases the porosity of concrete.

$$MgCl_{2} + Ca(OH)_{2} \rightarrow CaCl_{2} + Mg(OH)_{2}$$
(8)

 $MgCl_2 + CSH \rightarrow CaCl_2 + MSH$ (9)

2.2.5 The Effect of Sample Type

There is not enough information in the literature regarding the role of sample type (i.e., paste vs. mortar vs. concrete) and its form (powder vs. disk) in the mechanism of chloride binding. Jiřičková et al. [58] compared the chloride binding isotherms of four building materials, including cement paste, and used both small but not crushed specimens and ground samples. They concluded that ground OPC paste showed a higher bound chloride content than not-crushed specimens due to the higher specific surface area and the fact that chloride ions get into direct contact with almost all binder hydrated grain, which is highly improbable for real concrete elements and not crushed specimens.

A literature review suggests that most researchers manually use ground powder from paste samples for chloride binding tests. Due to the lack of uniformity in these tests, there is a significant variation in the reported binding capacity of similar binders. Therefore, there is a need for standardizing chloride binding tests. During cold seasons, deicing or anti-icing agents are used on the roads, concrete pavements, and bridge decks, which gradually penetrate the concrete structures. Therefore, a disk (not-crushed samples) seems more representative of the actual conditions than powder samples. Therefore, it is highly recommended to investigate the impacts of sample type and shape on chloride binding results for future works.

2.2.6 The Effect of Exposure Condition

There are contradictory results regarding the impacts of temperature on chloride binding. While Roberts et al. [29] reported that higher exposure temperatures always lead to a lower amount of bound chlorides, Zibara [59] claimed that the relationship between chloride binding and temperature depends on salt solution concentration. Zibara [59] reported that at chloride concentrations lower than 1 M and when temperature changes from zero to 38°C, a decrease in chloride binding is observed, but a reverse relationship (increase in bound chloride) is detected at solution concentrations higher than 3 M.

Panesar et al. [60] studied the effects of cold temperature exposure ranging from 22° C to -3° C on the chloride binding capacity of ternary paste containing OPC and ground granulated blast furnace slag (GGBFS). Their results showed a higher chloride binding capacity at 22° C, followed by -3° C, 13° C, and finally 5° C. Due to ice formation, they attributed the higher chloride binding capacity at -3° C to more physical binding and a higher chloride concentration in the exposure solution.

Qiao et al. [36] studied the effect of exposure temperature (i.e., 5°C vs. 23°C) on chloride binding and reported that Friedel's salt formation is independent of the exposure solution temperature. However, their results showed fewer bound chlorides (both physically and chemically) at the lower temperature.

Yuan et al. [25] investigated chloride binding for concrete samples containing different SCMs at 5°C, 20°C, and 40°C and reported a higher chloride binding in samples exposed to higher temperatures. In a similar trend, an increase in temperature from 20°C to 38°C led to an increase inbound chloride amount in slag blended cement [27].

2.2.7 The Effect of Sample Saturation State

Most researchers [30, 37, 39, 61] follow Tang and Nilsson's [62] method to determine the chloride binding capacity of cementitious systems, which requires soaking a crushed dried sample in a salt solution for some time and then testing the supernatant solution for the concentration of free chlorides. Using oven-dried samples in this method is popular due to its simplicity [58]. However, in an actual condition, when a concrete structure is exposed to a salt solution, it is neither saturated nor fully immersed in the salt solution. Moreover, structures typically experience numerous wetting-drying and freezing-thawing cycles. The saturation state of samples influences the diffusivity of cement-based materials [63-65]. For example, when samples are saturated, chloride can penetrate the sample via diffusion as the governing transport mechanism, whereas in unsaturated samples, advection is the dominant transport mechanism. Since chloride ingress via diffusion is significantly slower than in advection, fewer chlorides can enter saturated samples, resulting in lower binding results relative to unsaturated samples. [65]. Jin et al. [66] studied the effects of rainfall intensity on the chloride binding capacity of concrete with different saturation levels. Their results reveal a direct relationship between sample saturation and chloride bindingthe binding capacity declines with a reduction in the saturation level.

2.2.8 The Effect of Admixtures

The application of admixtures in precast and ready-mix concrete suppliers is widespread. Polycarboxylate-based superplasticizers, one of the widely used water-reducing admixtures, can potentially reduce the chloride binding capacity of the cementitious system [33]. The key reason is the adsorption of superplasticizer on the cement surface, leading to the formation of a repulsive force between the cement surfaces and chloride ions, reducing the possibility of chloride binding. The content of COO⁻ ions in the pore solution rises when polycarboxylate superplasticizer is added to the mixture leading to a reduction in bound chloride amount owing to the competition between COO⁻ and Cl⁻ ions to react with positive ions and form ion pairs.

Phosphate corrosion inhibitors are widely used to reduce the risk of chloride-induced corrosion. For example, commonly used phosphate corrosion inhibitors (MFP, DHP, and TSP) noticeably reduce the chloride binding capacity of concrete owing to the reduction of chemically bound chloride. In addition, Friedel's salt formation is suppressed in the presence of phosphates because phosphates have a higher priority than chloride ions during ion exchange in AFm phases [35].

The surfactants are mainly used as water-reducing, shrinkage-reducing, and air entraining admixtures. The impact of surfactants on chloride binding is mainly on the physical absorption of chloride ions and is influenced by cationic, anionic, and nonionic characteristics. Surfactants have a negligible effect on the chemical reaction of chloride with AFm phases regardless of when they are added to the mixture [32].

2.3 Chloride Desorption

Under certain circumstances, bound chlorides can dissociate from the hydration products and return to the pore solution. One of the main goals of this project is to ascertain the extent of chloride binding reversibility and investigate the chloride desorption mechanisms in binary systems containing OPC and other SCMs. Although the positive impacts of SCMs on increased chloride binding capacity are well documented [4, 30], the role of SCMs in resisting the release of bound chloride when the pH of pore solution drops is still unclear. In one study, Jian et al. [67] used synthesized concrete pore solution with pH of 13.3, 12.6, and 11.6 and found that the chloride
binding is dependent on the pH of the concrete pore solution and free chloride concentration. They reported that the binding capacity in pH of 12.6 and free chloride concentration of more than 1.5 M is higher than in pH of 11.6, mainly due to the dissolution of AFm phases at pH values lower than 12. In addition, increased binding capacity was observed in solutions with a higher $CI^{-}/(CI^{-}+ OH^{-})$ value. The pH value of the exposure solution can also influence the desorption of bound chloride. The pH of concrete pore solution in OPC ranges from 13 to 13.8 [68]. Long et al. [69] reported that when pH drops to a lower level, 88% of chlorides disassociated when powder OPC samples were transferred from a 3M NaCl solution to a NaOH solution prepared by deionized water at a pH =9. The release of bound chlorides due to the reduction in pore solution alkalinity (pH reduction) can initiate with carbonation [70], sulfate attack [71], and acid attack [42].

2.3.1. The Effect of Carbonation

Atmospheric carbon dioxide (CO₂) penetrates concrete, forming carbonic acid (H₂CO₃) in the concrete pore solution. Carbonic acid can lower the pH of the pore solution and subsequently react with main hydration products, including portlandite and C-S-H, to form calcium carbonate (CaCO₃), which has a very low solubility [72], as shown in Eqs. (10) and (12). There are mixed findings regarding the pH level for fully carbonated concrete. While Chang [73] observed a pH=7, Geng et al. reported [74] a higher pH level of around 9, Sun et al. found pH =8.3 [75], and Guo et al. observed pH=7.9.

$$CO_2 + H_2O \to H_2CO_3 \tag{10}$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$$
(11)

$$CO_2 + H_2O + C-S-H \rightarrow CaCO_3 + SiO_2.nH_2O$$
(12)

Carbonation can also influence the chloride binding capacity of cementitious systems by decomposing the hydration products (such as C-S-H) capable of binding chlorides [3]. In addition, carbonation can dissolve Friedel's salt [76], as shown in Eq. (13). These phenomena can release the physically or chemically bound chloride ions from hydrated phases into the binder's pore solution and increase the concentration of free chlorides.

$$3CaO.Al_2O_3.CaCl_2.10H_2O + 3CO_2 \rightarrow 3CaCO_3 + Al_2O_3 + Ca^{+2} + 2Cl^{-} + 10H_2O$$
 (13)

In binders containing SCMs, carbonation ingress and the extent to which C-S-H is carbonated is higher than OPC at the same exposure condition due to a lower portlandite content [70, 77]. Zheng et al. [70] investigated the impacts of carbonation on chloride binding in binders containing different compositions and w/b values. They observed a lower pH level in binders containing SCMs and a reduction in chloride binding with a proportional reduction in pH. Chang [73] studied the chloride binding capacity of two groups of binders– the first group was first carbonated and then exposed to chlorides, and the second group was first exposed to chlorides and then carbonated. Their results showed that the bound chloride level of all samples approached zero after total carbonation, regardless of whether carbonation or chloride exposure occurred first. It should be noted that because chloride diffusion is faster compared to carbonation ingress, it is more practical to expose the concrete to chloride-bearing solutions first before carbonation [76].

2.3.2. The Effect of Sulfate Attack

Sulfate ions can originate from seawater, soil, groundwater, and industrial wastes. When sulfate ions enter the concrete, they react with portlandite, forming gypsum (CaSO₄). Then the formed gypsum reacts with C3A to form Aft (ettringite), as shown in Eq. (14) through (17) [50, 78].

The presence of sulfate ions in pore solution reduces the chloride binding capability of the system due to the formation of more ettringite, which has no chloride binding capability. Sulfate ions can also react with Friedel's salt and convert it to AFt, as shown in Eq. (18) [79]. This reaction increases the free chloride concentration in pore solution, increasing the risk of chloride-induced corrosion. Moreover, sulfate ions compete with chloride ions to physically adsorb on C-SH phases. In addition, C-S-H preferentially reacts with sulfate ions and incorporates more sulfates instead of chlorides, resulting in lower chloride binding capacity in concrete [50, 79, 80].

$$Na_{2}SO_{4} + Ca(OH)_{2} + 2H_{2}O \rightarrow CaSO_{4}.2H_{2}O + 2 NaOH$$
(14)

$$K_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.2H_2O + 2KOH$$
(15)

$$Mg_{2}SO_{4} + Ca(OH)_{2} + 2H_{2}O \rightarrow CaSO_{4}.2H_{2}O + Mg(OH)_{2}$$
(16)

$$3(CaSO_4.2H_2O) + 3CaO.Al_2O_3(C3A) + 26H_2O \rightarrow 3CaO·Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$
(17)

$$3(CaSO_4.2H_2O) + 3CaO.Al_2O_3.CaCl_2.10H_2O \rightarrow 3CaO\cdotAl_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$
(18)

The exact mechanism for chloride desorption in the presence of sulfate ions is proposed by De Weerdt et al. [13], that claimed sulfate ions initiate AFm conversion to ettringite and C-S-H include more binding with sulfates.

Geng et al. [38] studied the stability of chloride binding in pastes under Na₂SO₄ and MgSO₄ attacks and observed that while most bound chlorides are released due to sulfate attack, in MgSO₄ due to the formation of brucite and its blocking effect on ionic transport, less transformation of Fridle's salt to Aft (ettringite) (Eq. (8)) is observed. The same observation was reported in [80].

The release of bound chlorides due to the dissolution of portlandite in the outer layers of concrete happens in concrete samples exposed to marine environments [4]. Seawater's sulfate (SO42-) concentration is relatively high, nearly 2700 ppm SO_4^{2-} [81]. Xu et al. [50] reported chloride desorption in paste samples containing 10% SF, 30% FA, and 50% SG and exposed to 5% Na₂SO₄, K₂SO₄, and MgSO₄ solutions, mainly due to the conversion of Friedel's salt to ettringite. Among various sulfate salts, exposure to K₂SO₄ led to the highest amount of chloride desorption. It was found that the amount of released bound chloride is mainly affected by the water to binder ratio, total chloride content, and cation type of sulfates.

2.3.3. The Effect of Acid Attack

Acid attacks on cementitious materials comprise several complicated processes and usually lead to a sharp pH reduction, resulting in the dissolution and decomposition of hydrated phases [82]. Therefore, it affects the chloride binding capacity of binders. Chemical reactions of an acid (with a general formula of HA) with cement hydration products that cause dissolving main phases and formation of calcium salt are shown in Eqs. (19) and (20) [82].

$$2HA + Ca(OH)_{2} \rightarrow CaA_{2} + 2H_{2}O$$
⁽¹⁹⁾

$$2xHA + xCaO \times ySiO_2 \times nH_2O \rightarrow CaA_2 + ySi(OH)_4 + (x+n-2y)H_2O$$
⁽²⁰⁾

During the acid attack, a degraded layer with high porosity forms on a concrete (or paste) surface, which, based on its solubility, acts as a protective layer and is combined with white (hydrated SiO₂) and light-brown (ferric hydroxide) layers [83, 84]. The acid diffusion rate governs the deterioration through the corroded layer to reach undamaged concrete, so the solubility and composition of the degraded layer are deciding factors [82, 85]. Shrinkage of the corroded layer

and formation of cracks on the surface also pronounce the deterioration magnitude. For instance, in the case of nitric acid, the calcium salt is highly soluble calcium nitrate, and considerable volume contractions on the degraded layer form numerous cracks and increase permeability in concrete [82, 86]. Therefore, when chloride ions are present, they can ingress through concrete through this highly permeable surface.

Hemstad et al. [42] investigated the chloride binding mechanism for OPC subjected to HCl acid solution and reported reduced chloride binding magnitudes in OPC paste samples when pH drops below 12 and no binding when the pH drops to 9. They proposed that due to the corrosion of paste samples in a low-pH environment, the AFm content reduces due to dissolution. There are two controversial issues in Hemstad et al. [42] investigation. First, while they used up to 17 ml of 4 M HCl, reported instant pH values for solutions (salt+powder+acid) range from 9 to 13. And, using HCl can cause errors and complex conditions in chloride binding calculations because it contains chlorine ions. Second, Gutberlet et al. [85] observed the conversion of monosulfate to Friedel's salt and ettringite during exposure of hydrated portland cement slices to HCl. They explained that required calcium sources are provided through C-S-H decalcification and portlandite dissolution. However, they did not investigate the chloride binding capacity due to Friedel's salt formation and leaching of capitulum-bearing phases.

Based on the current findings, pH reduction, whether triggered by carbonation, sulfate, or acid agents, can significantly influence the chloride binding mechanism, leading to chloride desorption in cementitious systems. In terms of acid attack, complex processes can happen, including but not limited to leaching of cement hydration products, formation of new phases, alteration of microstructure, cracking, and higher concrete permeability. A few investigations provided mechanisms on the impacts of pH reduction due to the addition of acid on chloride desorption of cementitious systems. In addition, while chloride binding mechanisms for various cementitious composites have been investigated, it is not clear yet what proportion of bound chlorides is released and returned to the concrete pore solution when SCMs are included in a binder and exposed to a low-pH environment,

This project addresses these knowledge gaps by investigating the impacts of the inclusion of SCMs on chloride desorption at a wide range of pH levels.

3 EXPERIMENTAL WORK

3.1 Materials

OPC conforming to the ASTM C150 [87] and AASHTO M 85 [88] specifications for Type I– II portland cement, and three supplementary cementitious materials, namely Class F fly ash (FA), slag (SG), and silica fume (SF), were used as binders in this study. Table 3.1 shows the oxide composition of these binders. The binders' mill reports showed that OPC had a specific gravity of 3.15, FA had a density of 2.39 g/cm³, SG had a Blaine fineness of 547 m²/kg, and SF had a bulk density of 0.63 g/cm³ and specific surface area (BET) of 20 m²/kg.

Table 3.1. The oxide analysis of cement and SCMs.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	LOI
OPC	19.24	3.80	2.75	59.05	1.5	2.49	0.17	0.60	9.90
FA	54.24	18.16	10.42	7.37	1.46	1.30	1.24	2.71	1.13
SG	31.4	15.7	0.4	37.7	8.6	2.5	_	_	0.6
SF	95.40	0.9	1.3	0.9	1.4	_	_	_	1.70

3.1.1. Paste Samples

In this study, paste samples were used to investigate various cementitious systems' chloride binding and desorption properties. Paste samples were prepared with a w/b = 0.4 in a 5-liter mortar mixer (Humboldt Mfg) according to ASTM C305 [89] mixing procedure. Table 3.2 shows the mixture proportions of the paste systems. After mixing, samples were cast into circular disc-shaped molds with a diameter of 33 mm and depth of 15 mm. Samples were then sealed and stored in an environmental chamber maintained at 25°C and RH of 95%. These samples were demolded after 24 h. After removing the samples from their molds, they were kept inside Ziplock bags and sealed-

cured inside the environmental chamber, maintained at 25°C and RH of 95%, for 56 d. Before exposing the paste samples to the chloride solutions, they were dried in a vacuum oven (Figure 3.1) at 55°C to obtain a constant weight. During the drying process, soda lime and moisture-absorbent silica gel were placed inside the oven to prevent carbonation and moisture buildup.

ID	Cement %	SCM type	Replacement level (%)
OPC	100	None	0
FA 15	85	FA	15
FA 30	70	FA	30
SG 25	75	SG	25
SG 50	50	SG	50
SF 5	95	SF	5
SF 10	10	SF	10

Table 3.2. Mix design proportions (FA: Fly ash, SG: Slag, SF: Silica fume).



Figure 3.1. Environmental chamber (left) and vacuum oven (right)

3.2 Chloride Binding Experiment

Three salt solutions, including NaCl, CaCl₂, and MgCl₂, were made in six concentrations. First, reagent-grade NaCl, CaCl₂, and MgCl₂ salts were dissolved in distilled water to make a solution with a two molar (M) chloride concentration. Subsequently, this solution was diluted to prepare solutions with concentrations of 0.1, 0.3, 0.5, 0.7, 1, and 2 M, as shown in Figure 3.2. After

dilution, the actual concentration of the diluted solutions was measured to reduce calculation errors.



Figure 3.2 Schematics of solution preparation and titration testing.

Subsequently, the samples were exposed to 60 ml chloride solutions for 14 d in capped glass containers at ambient temperatures of $23^{\circ}C \pm 2^{\circ}C$. Two samples were tested at each chloride concentration. The free chloride concentration in the exposure solution was measured using an automatic chloride titrator (T5, Mettler Toledo). Two hundred fifty-two samples (two replicates × seven mixes × six chloride solutions × three salts) were used for the chloride binding experiment. The bound chloride concentration was calculated using Eq. (21):

$$c_{b} = \frac{\left(c_{i} - c_{f}\right) \times V \times 34.45}{m_{dry}}$$
(21)

where c_b is the bound chloride concentration (mg Cl⁻/g paste); c_i is the initial chloride concentration of the exposure solution (M); c_f is the measured free chloride concentration (M) after 14 d; *V* is the volume of the exposure solution (ml) (i.e., 60 ml); m_{dry} is the sample's oven-dried weight (g), and 34.45 is the molar mass of chlorine (g/mol).

3.3 Chloride Desorption Experiment

In order to quantify the released bound chlorides in samples exposed to low-pH environments; first, ten replicate paste samples from each mix were exposed to 2 M salt solutions for 14 d. This step was similar to the chloride binding procedure discussed above. A total of 210 (10 replicates \times seven mixes \times three salt solutions) were used to assess the chloride desorption of different cementitious systems.

After two weeks, the pH of the equilibrated solutions was measured at room temperature using a pH meter (SevenCompact, Mettler Toledo), as shown in Figure 3.3. The pH sensor was tested with a standard buffer solution at a pH of 9 before every measurement to reduce measurement errors.

Subsequently, 1-molar nitric acid in volumes 5, 10, 15, 20, and 25 ml were added to the containers to reduce their pH. The nitric acid concentration was determined using a series of experiments on OPC samples exposed to a 2 M NaCl solution. For this purpose, various molarities of nitric acid ranging from 0.5 M to 3 M and at different volumes were added to a solution containing an OPC paste sample exposed to a 2 M NaCl solution for two weeks. The pH of the solutions was monitored for one week, and the results are shown in Table 3.2. The results showed that 1 M nitric acid would give a suitable range of pH values after it reached an equilibrium with the solution. Therefore, 1 M nitric acid was selected to reduce the solutions' pH and quantify the desorption properties of various blended paste samples.

	pH measurement time						ime					
Agid		1 d				4 d				7 d		
volume					Ac	Acid concentration						
vorunie	0.5 M	1 M	2 M	3 M	0.5 M	1 M	2 M	3 M	0.5 M	1 M	2 M	3 M
								IVI				
5 ml	12.1	1.8	1.5	1.6	12.2	11.5	8.1	5.2	12.2	11.6	11	9.3
10 ml	11.4	1.6	1.7	1.2	11.8	8.1	4.6	3.1	11.8	10.1	6.9	3.8
15 ml	9.9	1.4	1.2	0.8	11.6	4.4	4	2.7	11.7	6.9	5.3	3.2
20 ml	5.4	1.6	0.8	0.4	11.6	4.0	2.9	2.1	11.6	5.9	3.4	2.6
25 ml	4.5	1.2	0.7	0.4	11.5	3.6	2.3	2.0	11.6	4.3	2.9	2.6

Table 3.3. Effect of various molarities of nitric acid on the pH of exposure solutions.

After adding acid to samples, the samples were capped to prevent evaporation and left for two weeks at room temperature until the pH reached an equilibrium. During this period, the evolution of the pH of each solution was monitored periodically. The concentration of free chlorides after chloride desorption was measured using an automatic chloride titrator (T5, Mettler Toledo), and the concentration of released bound chlorides due to the drop in the pH of the solution was calculated using Eq. (22):

$$c_{released} = \frac{\left(c_d - c_f\right) \times V_c \times 34.45}{m_{dry}}$$
(22)

where $_{released is}$ the released bound chloride concentration (mg Cl⁻/g paste); c_d is the measured free chloride concentration (M) 14 d after the addition of acid; c_f is the free chloride concentration (M) after the binding period; V_f is the corrected final volume of solution (ml), which accounts for the volume of added acid to 60 ml chloride solution; and m_{dry} is the sample's oven-dried weight (g).

Figures 3.3 and 3.4 summarize the proposed desorption testing procedure and its experimental setup.



Figure 3.3 Schematics of chloride desorption testing procedure.



Figure 3.4. The Experiment setup for chloride binding (left) and desorption tests (right).

In addition to testing the chloride desorption properties of blended cement pastes samples, we used a model system to test the chloride desorption properties of calcium hydroxide, which is one of the main hydration products of cement. For this purpose, first, 2 g pure Ca(OH)₂ was dissolved

in one liter of distilled water. The 116.88 g NaCl was dissolved in this solution to make a 2 M chloride solution with a pH of 12.16. Next, 60 ml of this solution was added to glass containers, and different volumes of 1-molar nitric acid (5, 10, 15, 20, 25 ml) were added to containers. The pH dropped significantly after adding the acid, ranging from 1.3 to 0.4. The pH change is shown in Figure 4.35. It should be noted that because there was no paste inside the containers to buffer the pH, no increase in the pH was observed.

The chloride concentration before and after acid addition was measured using an automatic titrator (T5, Mettler-Toledo), and the difference was used to quantify the chloride desorption of calcium hydroxide.

3.4 Analytical Measurements

X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were carried out on representative ground paste samples before and after exposure to 0.7 M and 2 M NaCl, CaCl₂, and MgCl₂ solutions. In addition, post-exposure reaction products and phase changes within the samples after adding 25 ml of 1 molar nitric acid were characterized using XRD and TGA. The XRD recording was performed using a Bruker D8 Discover DaVinci. The X-ray tube functioned at 40 kV with a current of 400 mA. The diffraction patterns were recorded in the 20 range of 10° – 70° and analyzed using the Bruker DIFFRAC EVA software (version 5.1.0.5) loaded with the Crystallography Open Database (COD) [90, 91].

TGA was performed using the Q500 Thermogravimetric Analyzer (TA Instruments), as shown in Figure 3.5. The TGA tests were carried out in a nitrogen gas atmosphere at temperatures of 50– 500°C and a heating rate of 20°C/min to monitor the mass loss owing to the dehydroxylation of Friedel's salt.

A digital microscope (DM9, Tomolov) was used to investigate the extent of damage owing to chloride attack and acidic corrosion after chloride binding and desorption tests, respectively.



Figure 3.5. The analytical tools used to characterize chloride binding and desorption products. XRD (left); TGA (middle); and a digital microscope (right).

3.5 Mass Change

All pastes were dried before exposure to salt solutions at 55°C to obtain a constant weight and marked as dried none-exposed mass. The same procedure was done on all specimens after the acid exposure, recorded as dried after acid exposure. The mass change was calculated as the difference between these two measurements.

4 CHLORIDE BINDING RESULTS

4.1 Hydration Characterization of Binary Blended Cement Pastes

Adding SCMs to an OPC system promotes pozzolanic reactions, in which portlandite is consumed to form C-S-H gel [92, 93]. Since SCMs' pozzolanic reactivity is not the same and is mainly governed by the chemical composition of the SCM and its amorphicity [92-94], they can alter the C–S–H and pore solution composition in different ways [93].

Figure 4.1 shows the XRD scans of 56 d cured samples. The results indicate that portlandite was the most dominant detected phase in all samples. Ettringite, C4AF, monocarbonate, ferrite, portlandite, calcite, and belite were also detected. The inclusion of SCMs reduced portlandite peaks' magnitude due to their pozzolanic reactivity.

In TGA tests and DTG analysis, two significant dips were found at around 100°C and 450°C, which can be attributed to ettringite and portlandite [95], as shown in Figure 4.2. The portlandite dips in binders differ, which means a lower mass loss associated with portlandite after replacing OPC with SCM and due to pozzolanic activity. TGA results also show that the mass loss percentage related to portlandite in OPC was 4.86% which dropped to 4.09, 3.42, and 4.15% in FA15, SG25, and SF5, respectively. The results show that increasing the SCMs replacement level reduced the portlandite content. For example, portlandite mass loss in FA30, SG50, and SF10 was 3.43, 2.51, and 3.61%, respectively, suggesting the consumption of portlandite by SCMs as a result of pozzolanic reactions [96].



Figure 4.1. The XRD scans of 56-d paste samples containing different SCMs (E: Ettringite, C: C4AF, M:





Figure 4.2. The DTG analysis of 56-d hydrated paste samples containing different SCM (E: Ettringite and

CH: portlandite).

4.2 Chloride Binding Isotherms of Binary Blended Cement Pastes

Figures 4.3–6 illustrate the relationship between the free and bound chlorides concentrations in seven cementitious systems. The results show a nonlinear relationship between free and bound chlorides in most cases. The Langmuir and Freundlich isotherms—which are given in Eqs. (1) and (2)—were fit to the results to identify the binding isotherm that best mimics the nonlinear binding behavior of the chlorides in these samples. Table 4.1 shows each fit's residual sum of squares (RSS) and the corresponding parameter estimates associated with each isotherm. The results show that the Langmuir isotherm was a better fit for chloride binding of paste samples in NaCl and MgCl₂ solutions, whereas the Freundlich isotherm was a better fit for CaCl₂ solutions.

	~ 1 1	Lan	gmuir Isoth	erm	Freu	Freundlich Isotherm		
System	Solutions	$lpha_L$	β_L	RSS	$lpha_F$	eta_L	RSS	
	NaCl	15.32	0.06	23.46	14.07	0.98	23.67	
OPC	CaCl ₂	21.60	0.10	10.96	19.43	0.91	11.01	
	MgCl ₂	65.98	0.60	58.94	69.60	0.64	22.86	
	NaCl	28.40	0.09	28.27	25.90	0.91	27.17	
FA15	CaCl ₂	46.63	0.28	95.65	35.00	0.82	117.39	
	MgCl ₂	87.16	0.78	53.24	46.64	0.64	99.87	
	NaCl	61.99	0.48	323.73	39.99	0.76	419.70	
FA30	CaCl ₂	84.09	0.65	419.63	48.20	0.69	572.24	
	MgCl ₂	114.39	0.88	389.67	57.38	0.62	626.58	
	NaCl	44 73	0 59	32.88	25 14	0 49	70.66	
SG25		38.16	0.26	9.29	29.47	0.78	5.29	
2010	MgCl ₂	92.19	0.95	98.72	45.38	0.54	73.98	
	N ₂ C1	37 54	0.24	15 82	20.23	0.82	55 16	
SG50		35.06	0.24	+3.82	34 41	1.06	17.40	
5050	MgCl ₂	59.57	0.18	52.55	49.17	0.85	51.54	

 Table 4.1. The Langmuir and Freundlich isotherms parameter estimates.

	0.1.1	Langmuir Isotherm			Freundlich Isotherm		
System	Solutions	α_L	eta_L	RSS	$lpha_F$	eta_L	RSS
	NaCl	91.07	2.64	40.27	22.36	0.45	91.09
SF5	CaCl ₂	50.24	1.27	4.37	20.67	0.51	0.35
	MgCl ₂	26.70	0.28	21.87	21.62	0.63	10.81
	NaCl	157.31	3.46	11.46	33.17	0.36	80.03
SF10	CaCl ₂	20.42	0	14.29	20.09	1.03	14.16
	MgCl ₂	54.41	0.70	1.25	30.16	0.62	1.84

Figure 4.3 shows that the cation of the salt type played a significant role in the chloride-binding capacity of the OPC pastes. The highest chloride binding was observed in MgCl₂, followed by the decreasing order of CaCl₂ and NaCl. This pattern can be explained by the role of cation type in altering the pH of the solution. NaCl solution resulted in a higher pH than CaCl₂ and MgCl₂, and the solubility of Friedel's salt is pH-dependent. As a result, an increase in pH due to exposure to NaCl solution intensifies Friedel's salt's solubility, reducing bound chlorides capacity. Another reason for a higher bound chloride content in CaCl₂ is the contribution of Ca²⁺ to the development of C-S-H, which can adsorb chloride ions. MgCl₂ causes a higher Ca/Si ratio in C-S-H [97], which increases its chloride uptake capacity. In MgCl₂ solution, the formation of magnesium silicate hydrate (M-S-H), which promotes porosity, would increase chloride ingress on paste.



Figure 4.3. The chloride binding isotherms of OPC pastes exposed to NaCl, CaCl₂, and MgCl₂.

Figure 4.4 shows that replacing a portion of OPC with fly ash improved the system's chloride binding and increased the number of bound chlorides. For example, at 2 M NaCl solution, replacing the OPC with 15 and 30% fly ash increased the number of bound chlorides by 176% and 216% compared to their OPC counterparts. The same trend was observed in CaCl₂ and MgCl₂ solutions. The increased chloride binding due to the inclusion of fly ash can be attributed to the higher Al₂O₃ content of fly ash, which is nearly 4.8 times greater than OPC (Table 3.1). In addition, the inclusion of fly ash in an OPC system triggers a pozzolanic reaction, which results in the consumption of portlandite to form C-S-H (with a low Ca/Si ratio), an increase of Al-rich phases and AFm content, and finally a reduction in ettringite [93]. In addition, the TGA and XRD records of none-exposed samples confirmed lower portlandite contents in FA15 and FA30 than in OPC. Portlandite is consumed by pozzolans such as fly ash to form C-S-H [93]. Therefore, more chlorides can physically or chemically react with hydration phases, leading to a higher bound chloride.



Figure 4.4. The chloride binding isotherms of OPC+ fly ash paste exposed to NaCl, CaCl₂, and MgCl₂ (a) FA15; (b) FA30.

The inclusion of slag in OPC pastes also led to more chloride binding than in the OPC system. For example, in samples exposed to 2 M NaCl, relacing OPC with 25% and 50% slag increased the number of bound chlorides by approximately 46% and 85%, respectively. The same trend was observed in CaCl₂ and MgCl₂ solutions. The higher chloride binding capacity of SG25 and SG50 is due to differences in the hydration mechanisms, which lead to a higher uptake of chloride ions replacing OPC with slag results in the formation of more C-S-H, a hydrotalcite-like phase, and AFm phases [93, 98]. Hydrotalcite can absorb a large number of chloride ions, giving slagcontaining binders superior chloride binding capacity [99]. In addition, slag contains a slightly higher Al₂O₃ than OPC, which can produce more AFm and Aft phases during hydration. Moreover, Al could bind with C-S-H and increase the Si/Al ratio, which increases the capability of the C-S-H phase to uptake chloride ions [93]





Figure 4.6 shows that while adding silica fume to OPC could increase the chloride binding capacity of the system if exposed to NaCl solution, a decline in chloride binding was observed when the OPC+SF pastes were exposed to CaCl₂ and MgCl₂ solutions. Silica fume is mainly composed of SiO₂ (95.40%) and has a significantly smaller particle size than other SCMS. The reported median particle size of portland cement, fly ash, slag, and silica fume is 14.1, 6.4, 20, and 0.418 μ m, respectively, and their specific surface area is 360, 510, 721, and 17102 [100, 101] m²/kg, respectively. Moreover, the Al₂O₃ content in silica fume is less than that in OPC and slag, which can negatively affect its chloride binding capacity [22, 23, 35, 39].

The inclusion of silica fume in OPC paste can create a number of changes in the system: first, it can produce more C-S-H gel with a lower Ca/Si ratio compared to OPC. As discussed earlier, a higher C-S-H gel in a cementitious system is beneficial because it can increase the possibility of physical chloride binding [22]. Due to its composition (more than 95% SiO₂), silica fume has

highly pozzolanic reactivity and can consume portlandite and form C-S-H, especially at high replacement levels discussed in Figure 4.1 SF10 had lower portlandite compared to SF5. Moreover, SF refines the pore distribution and alters the mineral proportion of the binder, causing dilute contents of C₃A and C₄A, leading to lowers chemical binding [22]. Compared to other SCMs, previous investigations show that physical binding does not considerably contribute to chloride binding when SF is included in the binder [39].



Figure 4.6. The chloride binding isotherms of OPC+ silica fume pastes exposed to NaCl, CaCl₂, and MgCl₂ (a) SF5; (b) SF10.

4.3 XRD Analysis of Chloride Binding Products

The XRD scans of OPC paste samples after exposure to selected solutions with molarities of 0.7 M and 2 M are shown in Figure 4.7. A qualitative comparison of XRD results shown in Figures 4.1 and 4.7 indicate that portlandite was the dominant detected phase before and after exposure to salt solutions. In OPC specimens not exposed to salt solutions (Figure 4.1), calcite (C_c) and belite (C_2S) peaks were also detected. The XRD scans indicate the formation of Friedel's salt at around

11.3 to 11.4 degrees when specimens were exposed to salt solutions. The presence of Friedel's salt is a clear sign of the chemical binding of chloride with AFm phases, which support the binding and TGA tests that will be shown later. In addition, at around 9 degrees, an ettringite peak can be seen in samples immersed in salt solutions. The presence of ettringite is attributed to the partial dissolution of AFm phases containing $SO_4^{2^\circ}$, such as monosulfoaluminate, which is metastable in salt solutions [102]. The peak between 40 and 60 degrees in specimens exposed to MgCl₂ was identified as Mg(OH)₂ (brucite), a product of the reaction between portlandite and MgCl₂. The presence of brucite formation in the surface layer is evident by visual inspection.



Figure 4.7. The XRD results for OPC samples after two weeks of exposure to salt solutions (FS: Friedel's salt, CH: Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, B: Brucite).

Figures 4.8 through 4.10 show the XRD results of binary blended-cement paste samples after exposure to chloride solutions. In general, Friedel's salt formation can be observed in all samples, and its intensity seems somewhat stronger in samples exposed to MgCl₂ solutions.



Figure 4.8. The XRD results for fly ash samples after two weeks of exposure to salt solutions (a) FA15; (b) FA30 (FS: Friedel's salt, CH: Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, B: Brucite).

The XRD results for fly ash-containing binders indicate stronger Friedel's salt humps which can be attributed to their considerably higher aluminum oxide than OPC, providing more chemically binding of chloride ions. In addition, specimens exposed to MgCl₂ show the presence of brucite in both FA15 and FA30 exposed to MgCl₂. Portlandite and brucite humps in FA30 have lower magnitudes than FA15 because portlandite consumed by fly ash and its available contents are reduced to react with MgCl₂ to form brucite. In addition, Friedel's salt humps were more substantial in 2 M salt solutions than in 0.7 M due to higher chloride binding when the free chloride concentration increased. XRD records support binding isotherms, demonstrating more intense Friedel's salt peaks in MgCl₂ than NaCl and CaCl₂, which means more bound chloride amounts.

In both SG25 and SG50 samples, Figure 4.9, stronger Friedel's salt peaks are observed compared to OPC. For example, 0.7 M and 2 M MgCl₂ have higher magnitude peaks than their counterpart NaCl and CaCl₂. For MgCl₂ scans, brucite is present, and calcite peak magnitude is

considerably higher than before exposure records (Figure 4.1). The presence of ettringite after exposure to the salt solution is also detected at around 9, 16, 23, and 35 degrees.



Figure 4.9. The XRD results for slag samples after two weeks of exposure to salt solutions. (a) SG25; (b) SG50) (FS: Friedel's salt, CH: Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, B: Brucite).

Figure 4.10 displays the XRD scans of silica-containing samples. Portlandite is the primary detected peak in both SF5 and SF10 paste, and the presence of Friedel's salt is also observed. The Friedel's salt peaks in 2 M solutions are stronger than their 0.7 M counterparts. In addition, the formation of brucite was also detected in samples exposed to MgCl₂ solution, as discussed earlier. The XRD scans of SF5 and SF10 results showed the presence of ettringite in the paste. In line with the results from other binders, the intensity of Friedel's salt peaks in MgCl₂ is higher compared to two other salt solutions.



Figure 4.10. The XRD results for silica fume samples after two weeks of exposure to salt solutions, (a) SF5; (b) SF10 (FS: Friedel's salt, CH: Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, B: Brucite).

4.4 TGA Analysis of Chloride Binding Products

Figures 4.11 to 4.14 show the first derivative thermogravimetric (DTG) analysis of paste samples after exposure to 0.7 and 2 molarity NaCl, CaCl₂, and MgCl₂ solutions. The DTG results show three significant mass losses, corresponding to ettringite at 85 to 210°C [95], Friedel's salt at 235 to 375°C [8, 103, 104], and portlandite at 385 to 490°C [95]. In some literature, the decomposition of Friedel's salt was also reported in the temperature ranges of 30°C to 180°C [38, 41], which was also observed in this study.

Figure 4.11 shows that regardless of the salt cation, after exposure to 0.7 M and 2 M chloride solutions, the presence of Friedel's salts is visible, which agrees with the XRD results and the previous findings [8, 30, 105].



Figure 4.11. The DTG results of OPC paste samples after exposure to chloride solutions.

The mass fraction of Friedel's salt in paste samples can be determined based on Eq. (23):

$$m_{Fs} = \frac{M_{Fs}}{6M_{H_2O}} m_{H_2O}$$
(23)

where m_{Fs} is the mass fraction of Friedel's salt, m_{H_2O} is the mass loss (wt. %) of the main layer of water obtained from the TGA test, and M_{FS} and M_{H_2O} are the molar mass of Friedel's salt (561.3 g/mol), and water (18.02 g/mol), respectively. The m_{H_2O} for Friedel's salt can be determined from TGA analysis by subtracting the none-exposed paste results from the paste after salt exposure, in the temperature range that Friedel's salt was observed. Table 4.2 shows the observed temperature range and the measured mass fraction of Friedel's salt (m_{FS}) in samples exposed to 0.7 M and 2 M salt solutions. The different reported temperature ranges associated with Friedel's salt decomposition in Table 4.2 suggests that the SCM type and the salt cation type can slightly shift this temperature; however, Friedel's salt decomposition was in the range of 240°C to 420°C. For MgCl₂ and CaCl₂, Friedel's salt peak shifted slightly to the right. The measured Friedel's salt shown in Table 4.2 indicates that the concentration of chlorides in the exposure plays a critical role in Friedel's salt formation, and regardless of salt cation type, increased free chloride concentrations led to the formation of more Friedel's salt. The results also showed that the mass fraction of Friedel's salt is the highest in MgCl₂, followed by CaCl₂ and NaCl solutions, which agree well with the chloride binding results and XRD scans.

Paste system	Salt type	Cl ⁻ concentration (M)	Temperature Range (°C)	m _{H2O} (%)	m _{Fs} (%)
		0.7	270-390	0.56	3.04
	NaCI	2	240-390	0.8	4.14
ODC	$C_{2}C_{1}$	0.7	270-380	0.6	3.1
OPC	CaCl ₂	2	270-380	0.66	3.41
	MaCl	0.7	355-410	0.84	4.39
	MgC1 ₂	2	340-400	1.6	5.89
		<u> </u>		0.7	0.65
	NaCl	0.7	260-390	0.7	3.65
		2	250-390	0.74	3.84
FA15	CaCl ₂	0.7	270-360	0.75	3.89
		2	260-360	0.8	4.15
	MgCla	0.7	250-370	1.24	6.43
	MgC12	2	340-410	1.38	7.14
		0.7	250-400	0.63	3 27
	NaCl	2	240-390	0.65	3.37
		0.7	260-400	0.66	3.44
FA30	CaCl ₂	2	250-390	0.82	4.25
		0.7	350-420	1.21	6.3
	MgCl ₂	2	250-410	1.69	8.79
	NaCl	0.7	270-390	0.77	4.01
	ituei	2	260-390	0.97	5.04
SG25	CoClo	0.7	270-390	0.77	4.01
		2	260-400	0.9	4.69
	MgCl ₂	0.7	350-410	1.71	8.88

Table 4.2. Measured mass fraction of Friedel's salt in different cementitious systems.

Paste system	Salt type	Cl ⁻ concentration (M)	Temperature Range (°C)	m _{H2O} (%)	m_{Fs} (%)
		2	-	-	-
	NaCl	0.7	280-410	0.67	3.49
	ituei	2	260-400	1.28	6.63
SG50	CaCla	0.7	270-400	0.81	4.23
5050	CaCI2	2	250-410	1.13	5.88
	MaCla	0.7	330-410	1.39	7.21
	lvigC12	2	260-410	2.48	12.89
	N ₀ C1	0.7	250-380	0.37	1.9
	NaCI	2	260-390	0.52	2.68
SE5	$C_{\alpha}C_{\alpha}$	0.7	250-370	0.39	2.04
313	CaCl ₂	2	250-380	0.4	2.08
	MaCl	0.7	360-400	1.02	5.31
	MgCI ₂	2	340-420	1.29	6.71
	NaCl	0.7	270-390	0.43	2.22
	NaCI	2	250-380	0.55	2.85
	$C_{\alpha}C_{\beta}$	0.7	260-370	0.39	2
SE10	CaC1 ₂	2	240-360	0.53	2.77
SF10		0.7	350-420	1.34	6.96
	MgCl ₂				
		2	340-410	1.16	6.04

Figure 4.12 shows that, similar to OPC, the salt cation and the concentration of chlorides influenced Friedel's salt content in samples containing fly ash. Compared to OPC, the calculated Friedel's salt in FA15 and FA30 was higher, except in 2 M NaCl. In both FA15 and FA30, more Friedel's salt was observed with an increase in the concentration of chlorides in the exposure solution. For example, the Friedel's salt content in FA15 specimens exposed to 0.7 M NaCl, CaCl₂, and MgCl₂ was 3.65, 3.89, and 6.43%, respectively, which increased to 3.84, 4.15, and 7.14% in

2 M solution. The results show that the formation of Friedel's salt depends on cation type in the order of $Mg^{2+} > Ca^{2+} > Na^+$, and samples exposed to $MgCl_2$ had a higher Friedel's salt content. While binding isotherms show higher binding capacity in FA30 than FA15, Figure 4.12 indicates that replacing a higher percentage of fly ash did not necessarily lead to forming more Friedel's salt when samples were exposed to the same salt solution except for 2-M MgCl₂. Therefore, it should be noted that Friedel's salt formation merely shows part of the chemical binding of chloride ions with AFm phases. Chlorides can also bind physically with C-S-H phases. Including a higher percentage of fly ash not only forms higher C-S-H gel but also reduces the pore solution's alkali and OH– concentration because alkalis in SCMs are released considerably slower during the hydration process [46]. The lower concentration of OH⁻ facilitates the binding of chloride ions in the C-S-H phase because Cl⁻ and OH⁻ ions compete for adsorption on hydrated cement. Therefore, reduced OH⁻ concentration due to a higher replacement level of fly ash can lead to a higher binding capacity in FA30 than in FA15.



Figure 4.12. The DTG results of fly ash paste samples after exposure to chloride solutions; (a) FA15 and (b)

FA30.

Figure 4.13 shows the main phases in DTG curves for SG25 and SG50. Due to data collection issues, the DTG result for SG50 exposed to 2 M MgCl₂ is not presented. Compared to OPC, slag inclusion increased Friedel's salt content, regardless of cation type. The calculated Friedel's salt mass for SG25 in 0.7 M NaCl, CaCl₂, and MgCl₂ increased roughly y 32, 29, and 102% compared to their OPC counterparts. In SG25 and SG50, the highest detected Friedel's salt dips were for samples exposed to MgCl₂. Like fly ash, increasing the slag replacement level from 25 to 50% did not facilitate the formation of more Friedel's salt. However, higher SCMs replacement, as discussed for FA15 and FA30, promotes C-S-H development which has considerable effects on physical chloride binding. A closer look at DTG results indicates the formation of Friedel's salt at around 120°C in a 2 M salt solution, which did not form in the molarity of 0.7 M. This shows a superior binding capacity with higher free chloride concentrations.



Figure 4.13. The DTG results for slag paste samples after exposure to chloride solutions; (a) SG25 and (b) SG50.

Figure 4.14 displays DTG results for SF5 and SF10 that only for MgCl₂ the Friedel's salt dips are considerable. Compared to OPC pastes, adding silica fume reduced the Friedel's salt content

in NaCl and CaCl₂, but a relatively slight increase in MgCl₂. SF5 and SF10 paste resulted in 38 and 27% reduction in Friedel's salt mass compared to OPC in the 0.7 M NaCl and CaCl₂ solutions and 35% reduction in 2 M NaCl and CaCl₂. However, the calculated Friedel's salt is higher in SF5 and SF10 immersed in MgCl₂ than OPC.



Figure 4.14. The DTG results of silica fume paste samples after exposure to chloride solutions; (a) SF5 and (b) SF10.

Figure 4.15 summarizes the measured mass fraction of Friedel's salt (%) in samples exposed to 2 M chloride solutions. Two conclusions can be drawn based on this figure: first, the incorporation of slag resulted in the highest amount of Friedel's salt among the seven tested cementitious systems. For example, replacing 50% of OPC with slag increased the Friedel's salt content by nearly 60, 72, and 119% compared to OPC paste in 2 M NaCl, CaCl₂, and MgCl₂ solutions, respectively. The increased chloride binding of slag-blended paste samples can be attributed to its higher Al₂O₃ content, which influences the hydration mechanism, particularly C-S-H gel. Second, among the three tested slats in this study, exposure to MgCl₂ solution led to forming the highest amount of Friedel's salt, regardless of binder type. For example, the Friedel's salt mass in OPC pastes exposed to MgCl2 solution was 42 and 73% higher than in NaCl and CaCl₂ solutions, respectively. In FA15 pastes, the increased Friedel's salt percentage in MgCl₂ compared to NaCl and CaCl₂ was approximately 86%.



Figure 4.15. The mass fraction of Friedel's salt in paste samples made with OPC, fly ash, slag, and silica fume

4.5 Discussion

4.5.1 The Role of pH of Exposure Solutions in Chloride Binding

The pH of the distilled water used in this study was 5.86, and the measured pH of the 2-molar NaCl, CaCl₂, and MgCl₂ solutions was 6.8, 9.4, and 8.7, respectively. When paste samples were immersed in 60 ml salt solutions, the pH gradually increased during the exposure period due to the leaching of portlandite and its buffering capacity. The results indicated that after two weeks of exposure to salt solutions, the pH increased to approximately 12.3, 11.4, and 8.8 for containers containing NaCl, CaCl₂, and MgCl₂ 2 M solutions. Table 4.1 lists the pH of salt solutions containing different paste samples, measured two weeks after exposure.

As shown in Eqs. (5, 6, and 8), NaCl, CaCl₂, and MgCl₂ react to portlandite and produce NaOH, Ca(OH)Cl, and Mg(OH)₂. NaOH is a strong base, increasing the OH⁻ concentration and can significantly increase the solution pH, as shown in Table 4.3.

After exposing the paste samples to MgCl2 solution, a whitish color substance was observed. This product is suspected to be Mg(OH)₂, also known as brucite, which is formed as a result of the reaction between MgCl₂ and Ca(OH)₂.

Table 4.3. Average measured pH of containers containing salt solutions and a paste after two weeks.

System	NaCl	CaCl ₂	MgCl ₂
OPC	12.38	11.48	8.58
SG25	12.35	11.54	8.80
SG50	12.17	11.40	8.77
SF5	12.18	11.40	8.76
SF10	12.09	11.45	8.79
FA15	12.19	11.37	8.55
FA30	12.16	11.30	8.70

4.5.2 The Role of The Salt Cation in Chloride Binding

The chloride binding results underline the influence of the cation type of the salt on chloride binding and demonstrate a higher chloride binding with increasing the concentrations of free chlorides. These results agree well with the previous finding in literature [13, 41, 106] that MgCl₂ followed by CaCl₂ have a higher affinity to bind with cement hydration products than NaCl. The same trend was observed in systems containing different replacement levels of SCMs.

The cation of the salt can influence the pH of the salt and pore concrete pore solution. Previous research reported that the pH of the concrete pore solution increases in the presence of NaCl and decreases in the presence of CaCl₂ and MgCl₂ [8, 13, 41]. When NaCl dissolves in water, aqueous

Na⁺ reacts with portlandite to produce calcium chloride and sodium hydroxide (NaOH), increasing the pH of the solution. Calcium chloride reacts later with tricalcium aluminate (C3A) to form Friedel's salt. An increase in the pH of the pore solution leads to a decrease in the number of bound chlorides [13, 55, 106]. This is attributed to the solubility of Friedel's salt, as the main AFm-type phase responsible for binding chloride anions in cement. The solubility of Friedel's salt is pHdependent, and it increases as the pH of the pore solution increases [55]. It is worth mentioning that the leaching of Na⁺ and K⁺ in the presence of CaCl₂ and leaching of Na⁺, K⁺, and Ca⁺ in the presence of MgCl₂ originate a pH reduction, leading to enhancement in chloride binding capacity [107].

Another underlying reason that MgCl₂ and CaCl₂ form more bound chlorides is the development of more C–S–H phases. Chloride ions can be physically adsorbed onto the surface of cement hydrates, especially C–S–H [55]. Ca²⁺ from calcium-bearing salts contributes to the development of more C–S–H, which can take up more chlorides from the solution. Mg²⁺ from magnesium-bearing salt makes four main changes. First, it reacts with portlandite; second, it forms brucite and CaCl2; third, it increases the Ca/Si ratio in the C–S–H gel; and fourth, it reacts with C-S-H and forms M-S-H, and forms magnesium oxychloride [41, 108]. Weerdt et al. [41] stated an influential role of the C-S-H phase and solution pH on the chloride binding capability of cement paste. Increasing pore solution pH can reduce the quantity of adsorbed chlorides on C-S-H [107]. Weerdt et al. [41] concluded that a higher Ca/Si ratio in C-S-H improves the chloride content of the C-S-H phase.

Table 4.4 summarizes the number of bound chlorides for different pastes when exposed to 2 M salt solutions. When exposed to NaCl and CaCl₂ solutions, the highest number of bound chlorides

was observed in FA30, followed by SG50, FA15, SF10, and SG25. In MgCl₂, SG50 showed higher bound chloride than FA30, followed by FA15 and SG25.

Deste type	Chloride binding at the molarity of 2 (mg Cl/ g paste)					
Paste type	NaCl	CaCl ₂	MgCl ₂			
OPC	25.35	33.72	59.00			
SG25	36.97	46.43	60.99			
SG50	47.03	64.12	80.56			
FA15	44.58	47.51	63.73			
FA30	54.70	65.28	72.99			
SF5	25.65	28.60	33.05			
SF10	38.72	39.69	43.63			

Table 4.4. Average measured bound chlorides in different paste samples when exposed to 2 M salt solutions.

Previous investigations on surface electrostatic properties of C-S-H and its interaction with chloride ions revealed that the physical adsorption of chloride ions is more dominant than the chemical chloride binding, such as Friedel's salt [109].
5 CHLORIDE DESORPTION RESULTS

5.1 Chloride Desorption of Ca(OH)₂ in a Model System

Figure 5.1 shows the effect of volumetric addition of nitric acid on pH and chloride binding in a saturated $Ca(OH)_2 + 2$ M NaCl solution. The chemical reaction between nitric acid and calcium hydroxide produces calcium nitrate and water. Figure 5.1a shows that adding nitric acid, even in low volumes, can significantly reduce the pH of the solution, which can be attributed to the reduced alkalinity of the solution and calcium nitrate precipitation. Figure 5.1a shows that the pH reduction rate slowed down after adding 10 ml nitric acid, and a further increase in the volume of acid did not change the pH significantly. One explanation for this could be the depletion of calcium and reaching an equilibrium state, which is very close to the pH of nitric acid.

Figure 5.1b shows a reduction in the concentration of bound chloride as the solution acidifies. The slight increase in bound chlorides at pH = 0.4 is explained by a series of chemical reactions, as shown in Eqs. (24–26), which results in the consumption of aqueous chlorides to produce hydrochloric acid.

$$Ca(OH)_{2} + 2HNO_{3} \rightarrow Ca(NO_{3})_{2} + 2H_{2}O$$
(24)

$$Ca(NO_3)_{2(aq)} + 2NaCl_{(aq)} \rightarrow CaCl_{2(aq)} + 2NaNO_{3(aq)}$$
⁽²⁵⁾

$$\operatorname{CaCl}_{2(aq)} + 2\operatorname{HNO}_{3(aq)} \to 2\operatorname{HCl}_{(aq)} + \operatorname{Ca}(\operatorname{NO3})_{2(aq)}$$
(26)



Figure 5.1. pH change and its effect on chloride binding in a model Ca(OH)₂ system. (a) pH change; (b) bound chlorides.

It is important to note that there is a distinct difference between chloride desorption in a model system and the one containing a paste sample. In a model system, calcium hydroxide concentration is finite and easily accessible to nitric acid. Therefore, the chemical reactions listed in Eqs. (24–26) take place fast, and the pH equilibrates quickly. In a system containing blended cement paste samples, however, calcium hydroxide leaches out from the sample to the exposure solution during the binding period, and some remain untouched inside the sample. With the addition of nitric acid, the same chemical reactions occur first with the leached calcium hydroxides. However, when the solution's acidity increases, the paste samples' outer layer starts corroding, providing access to an additional source of calcium hydroxide and other hydrated phases that can neutralize the solution's acidity. Therefore, the pattern shown in figure 5.1a does not apply to a system with paste samples.

5.2 Chloride Desorption of Binary Blended Cement Pastes

Figures 5.2 through 5-8 show the measured concentration of free chloride after adding acid to OPC and other blended systems. The results show a continuous reduction in the concentration of free chlorides in the exposure solution due to the dilution effect due to adding acid to the salt solution. Two replicate samples were tested for each system, and the results show a good agreement between the measurements.



Figure 5.2. Measured free chlorides after desorption in samples containing OPC. (a) NaCl; (b) CaCl₂; (c)



MgCl₂.

Figure 5.3. Measured free chlorides after desorption in samples containing FA15. (a) NaCl; (b) CaCl₂; (c)

MgCl₂.



Figure 5.4. Measured free chlorides after desorption in samples containing FA30. (a) NaCl; (b) CaCl₂; (c)

MgCl₂.



Figure 5.5. Measured free chlorides after desorption in samples containing SG25. (a) NaCl; (b) CaCl₂; (c)

MgCl₂.



Figure 5.6. Measured free chlorides after desorption in samples containing SG50. (a) NaCl; (b) CaCl₂; (c)

MgCl₂.



Figure 5.7. Measured free chlorides after desorption in samples containing SF5. (a) NaCl; (b) CaCl₂; (c) MgCl₂.



Figure 5.8. Measured free chlorides after desorption in samples containing SF10. (a) NaCl; (b) CaCl₂; (c)

MgCl₂.

Figures 5.9 through 5.15 compare the concentration of free chlorides before and after acid addition by accounting for the volume change due to adding acid. The results show that the concentration of free chloride content in the solution increased after adding acid regardless of salt and binder type. The increased concentration of free chlorides suggests releasing some of the bound ones. The results show that the magnitude of released chloride varied with the added acid volume, and in most cases, the highest release was observed when 5–10 ml of nitric acid was added to the solution. The main reason is that further acid addition completely alters the surface layer, leading to the formation of hydrogels, which can adsorb some of the free chlorides. This mechanism will be further articulated in the discussion section.



Figure 5.9. Measured free chlorides in OPC samples exposed to salt solutions before and after adding nitric

acid. (a) NaCl; (b) CaCl₂; (c) MgCl₂.



Figure 5.10. Measured free chlorides in FA15 samples exposed to salt solutions before and after adding nitric

acid. (a) NaCl; (b) CaCl₂; (c) MgCl₂.



Figure 5.11. Measured free chlorides in FA30 samples exposed to salt solutions before and after adding nitric

acid. (a) NaCl; (b) CaCl₂; (c) MgCl₂.



Figure 5.12. Measured free chlorides in SG25 samples exposed to salt solutions before and after adding nitric



acid. (a) NaCl; (b) CaCl₂; (c) MgCl₂.

Figure 5.13. Measured free chlorides in SG50 samples exposed to salt solutions before and after adding nitric

acid. (a) NaCl; (b) CaCl₂; (c) MgCl₂.



Figure 5.14. Measured free chlorides in SF5 samples exposed to salt solutions before and after adding nitric

acid. (a) NaCl; (b) CaCl₂; (c) MgCl₂.



Figure 5.15. Measured free chlorides in SF10 samples exposed to salt solutions before and after adding nitric acid. (a) NaCl; (b) CaCl₂; (c) MgCl₂.

The bound chloride content before acid addition (Table 4.4) was compared to those measured after adding nitric acid, and the percentage of released bound chloride was calculated and is shown in Figure 5.16. The results show that adding 5– 10 ml acid led to a significant release of bound chlorides, which increased the concentration of free chlorides in the solutions, as Figure 5.9 shows. Adding 5 ml nitric acid to the solutions nearly released 87%, 92%, and 86% of bound chlorides in NaCl, CaCl₂, and MgCl₂ solutions. The number of released chloride ions from the pastes after adding 10 ml nitric acid yielded somewhat similar results. Among various salt solutions, Figure 5.16 shows that released bound chlorides after 5– 10 ml acid in NaCl and MgCl₂ solutions were almost the same and lower than CaCl₂.

Nevertheless, with further acid addition, the released bound chloride in NaCl is lower than CaCl₂ and MgCl₂, except at 25 ml acid addition. The lower released bound chlorides in NaCl solution can be attributed to its higher initial pH value before acid addition and higher pH (ranging from 11 to 12) after two weeks. The lower percentage of released bound chlorides is favorable because it means a lower free chloride concentration.

In most cases, samples immersed in CaCl₂ solution experienced the most significant release of bound chlorides when nitric acid was added to the solution. However, a higher release of bound chlorides in MgCl₂ solution was only observed when 15 ml nitric acid was used.

Figure 5.16 also displays the pH of solutions, measured two weeks after adding nitric acid to the salt solutions. The results show that samples immersed in NaCl solution had a higher pH, followed by CaCl₂ and MgCl₂. The higher pH value in the NaCl solution is due to the reaction between nitric acid and Na⁺ ions, which produces sodium nitrate and sodium hydroxide, which increase the pH value.



Figure 5.16. The released bound chlorides and measured pH after two weeks of exposure to nitric acid in samples containing OPC.

The percentage of released bound chlorides and pH after two weeks of exposure to acid for the blended cement paste samples are shown in Figures 5.17 through 5.19. In FA15 pastes (Figure 5.17a), when 5–10 ml acid is added, the highest release of bound chlorides, with more than 90%, was observed in NaCl, followed by CaCl₂ (nearly 80%) and MgCl₂ (nearly 60%). Further acid

addition resulted in a higher release of bound chlorides in the NaCl solution compared to CaCl₂ and MgCl₂, except when adding 25 ml of acid. Similarly, in FA30 pastes (Figure 5.17b), the release of bound chlorides in NaCl was more than 87% at all acid levels, considerably higher than two other salt solutions. After adding 5 to 15 ml acid to the NaCl solution, the pH ranged from 11 to 12 and was higher than CaCl₂ and MgCl₂ solutions. Adding 20–25 ml acid led to a more significant reduction in pH, particularly in FA30 pastes (Figure 5.17b). A lower pH level in FA30 pastes than in FA15 is mainly due to its lower portlandite content which can buffer the pH. When fly ash replacement level increased from 15% to 30%, there were no noticeable changes in the percentage of released bound chlorides in NaCl and MgCl₂ solutions. However, the percentage of released bound chlorides in CaCl₂ reduced, especially in 5–10 ml acid. For example, in samples exposed to CaCl₂ by adding 5–10 ml acid, 81% released in bound chlorides in FA15 reduced to less than 67% in FA30.



Figure 5.17. The released bound chlorides and measured pH after two weeks of exposure to nitric acid in samples containing fly ash. (a) FA15; (b) FA30.

Figure 5.18a shows that in SG25 paste, by adding 5 to 15 ml acid, the lowest and highest release of bound chlorides were observed in samples exposed to MgCl₂ and NaCl solution. In both SG25 and SG50 binders, adding 5– 10 ml acid resulted in a higher pH in NaCl, followed by CaCl₂ and MgCl₂. However, further acid addition considerably reduced the pH level in NaCl and CaCl₂ solutions. SG50 paste showed a lower range than SG25, especially after 15 ml acid addition, which can be attributed to its lower portlandite content. Adding 20 ml acid brought the pH in SG50 under 8, and adding 25 ml acid caused the pH to drop below 6 in all salt solutions. Regarding the effect of slag replacement level on released chlorides and pH, Figure 5.18 indicates that SG50 outperformed SG25. Increasing the slag replacement level from 25 to 50% decreased the average percentage of released bound chloride in NaCl, CaCl₂, and MgCl₂ solutions by 7.8%, 28.2%, and 29.4%, respectively. Similarly, increasing the slag replacement reduced the pH by 19%, 16.8%, and 8.7% in NaCl, CaCl₂, and MgCl₂ solutions.



Figure 5.18. The released bound chlorides and measured pH after two weeks of exposure to nitric acid in samples containing slag. (a) SG25; (b) SG50.

The release of bound chlorides after acid addition for binders containing silica fume is shown in Figure 5.19. CaCl₂ solution resulted in lower released bound chlorides in both SF5 and SF10 pastes in all acid volumes compared to NaCl and MgCl₂. In SF5 paste (Figure 5.19a), the released bound chlorides for specimens immersed in CaCl₂ were less than 50% in all acid volumes, and the same trend was observed in SF10 samples, except for those exposed to 5 ml nitric acid, which was 59%.



Figure 5.19. The released bound chlorides and measured pH after two weeks of exposure to nitric acid in samples containing silica fume. (a) SF5; (b) SF10.

The pH measurements revealed that SF5 and SF10 samples immersed in NaCl solution had a higher pH after two weeks of exposure to acid, followed by CaCl₂ and MgCl₂. For SF5 paste, the pH at different acid volumes ranged from 10.2 to 11.9, 10.3 to 11.4, and 8.6 to 8.8 in NaCl, CaCl₂, and MgCl₂ solutions, respectively. SF10 samples had a similar pH range in NaCl and MgCl₂ solutions and a slightly lower pH in CaCl₂ after adding 25 ml acid, which reduced the pH to 9.6. The results indicate that an increase in silica fume content from 5 to 10% reduced the amount of released bound chloride in NaCl and MgCl₂ by, on average, 16.1 and 7.4%, enhancing the

capability of the binder to keep the bound chlorides in place after pH reduction. However, in the CaCl₂ solution, increasing the silica fume replacement level had no significant impact on the percentage of released chlorides.

5.3 Visual Inspection of Samples After Chloride Desorption Test

An acid attack can dissolve and leach acid-susceptible constituents, mainly calcium hydroxide, from the cement paste, resulting in increased capillary porosity, loss of cohesiveness, and eventually loss of strength [78]. Additionally, the decalcification of cement paste generates intense tensile stresses on the surfaces of paste samples, leading to the formation of cracks [110]. An analysis of images taken from OPC shows no sign of visible damage to OPC samples when exposed to 5 ml nitric acid for two weeks. However, as Figure 5.20 shows, the extent of the damage increased with an increase in the volume of added acid and was in the forms of decoloration, surface corrosion, and surface grazing/cracking. Based on visual observations of the surface cracks under a microscope, there were considerable amounts of crystalized salt and other residuals, potentially creating expansive pressure within the cracks during crystallization. In samples exposed to MgCl₂, a considerable amount of white precipitate was observed on the surface. Based on the previous investigation [108], this white layer can be a combination of CaCl₂, Mg(OH)₂, and Mg₃(OH)5Cl·4(H₂O).



Figure 5.20. Images of OPC samples after two weeks of exposure to nitric acid.

Table 5.1 shows the damage in samples exposed to 25 ml nitric acid for two weeks. The high volume of nitric acid damaged the exposed surface and formed a porous whitish/yellowish-colored layer on the surface of the samples. Under this layer, the remaining cement matrix seemed to be sound with a typical greyish color of cement paste. Images for other samples exposed to a lower volume of acid can be found in <u>Appendix A</u>.

Paste	NaCl	CaCl ₂	MgCl ₂
OPC			
SG25			
SG50			
FA15			
SF5			
SF10	J)		

Table 5.1. Samples after exposure to 25 ml nitric acid.

5.4 XRD Analysis of Chloride Desorption Products

An XRD analysis was performed to investigate the influence of acid exposure on the crystallographic structure and chemical changes in the composition of paste samples. Figure 5.21 compares the XRD scans of OPC pastes before and after exposure to 25 ml nitric acid. The results indicate that the intensity of portlandite peaks was weaker after acid addition due to the leaching of calcium hydroxide. It is evident from the XRD results that a considerable amount of ettringite, an expansive crystalline phase, was present after the acid attack. The main reason is attributed to the dissolution of AFm phases (such as monosulfate (C3A. CaSO₄. 12H₂O)) [85]. Friedel's salt peaks around 11.3 degrees after exposure to 25 ml can suggest that some tightly bound chlorides could not disassociate due to the drop in the pH or there were new chemical chloride binding on the pastes' subsurface layers. When acid attacks cementitious samples, it alters the surface layer and dissolves portlandite, which ultimately buffers the pH. Finally, with an increase in the pH of the solution, the available chloride ions in the solution can ingress into the paste sublayers and form physical or chemical bounds with the hydration products. As discussed in the visual inspection section (section 5.3), a considerable portion of a paste was still intact even after exposure to 25 ml of acid and, therefore, could form Friedel's salt. Another reason for the presence of Firediel's salt in Figure 5.21 is that before exposing the samples to acid, they were dried and then immersed in the salt solutions for two weeks. It is possible that a number of the chloride ions ingressed to the deeper layers and formed chemical bonds with the hydration products. Since the progression of acid attack is slow, it did not reach those inner layers. Therefore, the presence of Cl-AFm in paste after acid addition can be expected. Figure 5.21 shows calcium nitrate peaks after

acid exposure due to nitric acid and portlandite reactions. Quartz was also detected in acid-exposed pastes due to C-S-H dissolution.



Figure 5.21. The XRD results for OPC samples before and after exposure to 25 ml acid. Samples were first exposed to 2 M salt solutions (FS: Friedel's salt, CH: Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, B: Brucite).

Figure 5.22 displays the XRD results of fly ash samples before and after exposure to nitric acid. Similar to OPC results, the presence of ettringite and calcium nitrate after acid exposure is observed on XRD scans. In both FA15 and FA30 paste exposed to MgCl₂, the reduction in portlandite peak intensity, especially around 18 degrees, are apparent. Moreover, the portlandite peaks in FA30 had lower magnitudes than FA15 before and after exposure to acid, which is caused by more pozzolanic reactions due to a higher replacement level of fly ash. Another noticeable point in Figure 5.22 is the presence of brucite peaks in pastes immersed in MgCl₂ before acid addition at around 18.7, 38.1, and 58.8 degrees, and their attenuation after exposure to nitric acid for two weeks. The reaction between brucite and nitric acid forms a highly water-soluble salt, magnesium nitrate, and is the leading cause of this peak attenuation. The observed whitish color layer forming

on the surface of samples immersed in 2 M MgCl₂ and exposed to nitric acid in Table 5.1 can be explained by the precipitation of magnesium sulfate formation.



Figure 5.22. The XRD scans of fly ash samples before and after exposure to 25 ml acid. Samples were first exposed to 2 M salt solutions. (a) FA15; (b) FA30 (FS: Friedel's salt, CH: Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, B: Brucite).

The same portlandite and Friedel's salt peaks were also observed in SG25 and SG50 samples, as Figure 5.23 shows. The pH of SG25 exposed to MgCl₂ solution before adding acid was around 8.8, which dropped to 6.7 after one week of exposure to 25 ml of acid and bounced back to 8.4 during the second week. For SG50 samples, in which most of the portlandite was consumed during the hydration, the solution was more acidic, and the pH was around 5.9 after two weeks of exposure to acid. Prolonged exposure to a low pH environment can dissolve portlandite phases. Figure 5.23b shows that the portlandite peaks after acid addition to SG50 samples are weaker than their SG25 counterparts. Even before adding acid, the portlandite peaks of specimens exposed to MgCl2 were substantially weaker than other salt solutions.



Figure 5.23. The XRD scans of slag samples before and after exposure to 25 ml acid. Samples were first exposed to 2 M salt solutions. (a) SG25; (b) SG50 (FS: Friedel's salt, CH: Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, B: Brucite).

Figure 5.24 shows the XRD scans for SF5 and SF10. Like other binders, the dominant phase before acid addition was portlandite, and the presence of Friedel's salt was also observed. As explained earlier, acid addition caused the formation of ettringite and calcium nitrate. The results show that the portlandite peaks in pastes containing silica fume were not significantly changed after the addition of acid, which can be due to the higher pH of their exposure solution, which was above eight after two weeks of exposure to nitric acid.



Figure 5.24. XRD scans of silica fume samples before and after exposure to 25 ml acid. Samples were first exposed to 2 M salt solutions. (a) SF5; (b) SF10 (FS: Friedel's salt, CH: Portlandite, Cc: Calcite, C2S: Belite, E: Ettringite, B: Brucite).

Additional XRD tests and analysis were performed on the surface layer of three OPC paste samples exposed to 25 ml of nitric acid to determine its chemical composition and identify the phases formed on the altered layer, as shown in Figure 5.25. For this purpose, zero-diffraction plates were used because the number of removed materials from the corroded surface of the sample was only a few milligrams. Figure 5.26 shows the prominence of brucite peak in samples exposed to MgCl₂, which can be formed due to a reaction between portlandite and MgCl₂. In addition, quartz, gibbsite, gypsum, and calcium nitrate were also detected. The XRD scans indicated that the corroded layer in NaCl and CaCl₂ were amorphous and mainly composed of quartz. The authors suspect that the light-brown color of the corroded layer is due to the presence of iron in the altered layer, as previously reported in [85]. However, the XRD scans were unable to detect any iron-containing crystalline phase.



Figure 5.25. Sample preparation for testing the chemical composition of corroded layer (OPC paste exposed

to 25 ml acid addition).



Figure 5.26. The XRD results of the corroded layer of OPC paste exposed to 25 ml acid (Q: Quartz, Gi: Gibbsite, G: Gypsum B: Brucite, CN: calcium nitrate).

5.5 TGA Analysis of Chloride Desorption Products

Figures 5.27 through 5.30 compare the DTG results of paste samples exposed to salt solutions before and after acid exposure. The DTG results show three significant mass losses, corresponding to ettringite at 85 to 210°C [95], Friedel's salt at 235 to 375°C [8, 103, 104], and portlandite at 385 to 460°C. The results indicate considerably shallower dips for portlandite after acid exposure, which results from leaching. While the second dip in Figures 5.27 through 5.30 is labeled as Friedel's salt, it is essential to note that due to the formation of new phases after the addition of 25 ml nitric acid addition, other phases such as brucite may be formed that have a similar dehydroxylation temperature to Friedel's salt. The reported decomposition temperature ranges by Scrivener et al. [111] for Friedel's salt (250°C to 400°C), brucite (around 400°C), aluminum hydroxide (around 270°C), magnesium silicate hydrates (around 270°C and 400°C) all have an overlap, which makes it very challenging to distinguish between their mass losses on TGA curves. The presence of Friedel's salt in DTG curves supports XRD results and therefore is used in this study.



Figure 5.27. The DTG results for OPC sample before and after 25 ml acid addition.

Figure 5.28 displays the DTG curves for specimens containing fly ash. The Friedel's salt dips in NaCl and CaCl₂ before and after acid addition are similar and did not change noticeably. The explanation provided for Friedel's salt presence in OPC samples is valid for other binders, including FA15 and FA30. In the MgCl₂ solution, Friedel's salt dips after acid addition were observed but not as pronounced as before. The reason can be attributed to a lower pH level in the MgCl₂ solution compared to two other solutions before and after acid addition, leading to more portlandite leaching out of paste samples. The pH of FA15 and FA30 pastes immersed in the MgCl₂ solution before acid addition was around 9. Adding 25 ml of acid decreased this pH to approximately eight after two weeks. Friedel's salt dips were observed in Figure 5.28b (FA30 paste) at around 120°C, which disappeared after exposure to acid. These dips probably represented Friedel's salt on the surface layer, which was dissolved and released their chlorides into the solution.



Figure 5.28. The DTG results of fly ash-containing samples before and after exposure to 25 ml nitric acid (a) FA15 and (b) FA30.

Figure 5.29 displays DTG curves of SG25 and SG50 pastes. Similar to other binders, the results for specimens immersed in NaCl and CaCl₂ before and after acid exposure are similar, and Friedel's salt is still observed in paste even after exposure to acid. The results for SG25 pastes exposed to 2 M MgCl₂ before acid addition are unavailable due to data collection issues. Figure 5.29.b shows that after acid addition, the Friedel's salt dip became slightly shallower and shifted to the left.

Comparing the DTG results of SG25 and SG 50 with other SCMs show the magnitude of the third peak (portlandite) is noticeably lower even before the addition of acid, especially in the MgCl₂ solution. This can be attributed to two main reasons: First, MgCl₂ reacts to portlandite to form brucite and CaCl₂. Secondly, the consumption of portlandite due to pozzolanic reaction with slag particles and formation of C-S-H gel. As a result, the pH in slag-containing samples was lower, and after acid addition, part of the remaining portlandite leached out, contributing to the shallower portlandite dip in slag compared to other binders.



Figure 5.29. The DTG results of slag-containing samples before and after exposure to 25 ml nitric acid (a)

SG25 and (b) SG50.

Figure 5.30 illustrates DTG curves for binders containing silica fume. The result shows nitric acid exposure did not change the Friedel's salt dip considerably in NaCl and CaCl₂ solutions. However, there was a significant reduction in Friedel's salt content in samples exposed to MgCl₂ solution. Comparing before and after acid addition suggests that the replacement level of silica fume did not significantly influence Friedel's salt content. However, lower dips for portlandite are evident due to increased pozzolanic reaction and SF replacement level.



Figure 5.30. DTG results of silica fume-containing samples before and after exposure to 25 ml nitric acid (a) SF5 and (b) SF10.

Table 5.2 summarize the mass fraction of Friedel's salt in a temperature range of 240 to 420°C before and after acid exposure, calculated based on Eq. (23). The results show that except for SF5 and SF10, other pastes had a higher Friedel's salt compared to OPC. In NaCl solution, Friedel's salt mass sightly increased after acid addition, except for SG50, that 8.7% lower mass was detected. The increase in Friedel's salt mass after acid addition was also observed in samples exposed to CaCl₂ solution, except for SG50 and SF10, in which Friedel's salt was reduced.

However, in the MgCl₂ solution after 25 ml acid addition, the trend is reversed, and for all binders calculated, Friedel's salt is lowered compared to what it was before acid.

Deste	Exposure		Calculated		
Paste	condition	NaCl	CaCl ₂	MgCl ₂	
OPC	Before acid	4.14	3.41	5.89	
010	After acid	4.36	4.64	5.00	
FA15	Before acid		3.77	7.14	
	After acid	5.23	4.31	7.01	
FA30	Before acid After acid	3.37	4.25	8.79	
11130		4.45	4.78	5.90	
SG25	Before acid After acid	5.04	4.69	-	
5625		5.43	6.19	8.46	
SG50	Before acid After acid	6.63	5.88	12.89	
5650		6.05	5.38	7.09	
SF5	Before acid After acid	2.68	2.08	6.71	
515		3.30	2.50	4.67	
SE10	Before acid After acid	2.85	3.60	4.60	
51 10		3.58	2.51	2.27	

 Table 5.2. Measured mass fraction of Friedel's salt in a temperature range of 240 to 420 for before and after adding 25 ml acid.

5.6 Sample Mass Change After Chloride Desorption Test

The process of chloride binding and desorption results in the formation of new products or the dissolution of hydration products, which can affect the samples' mass. The primary new phase formed after exposure to the salt solution is Friedel's salt, and the analytical tests confirmed its formation after binding tests. For example, when pastes are immersed in NaCl solution, NaCl reacts with portlandite and then tricalcium aluminate (C_3A) to form Friedel's salt. The stoichiometry of a balanced chemical equation, as shown in Eq. (27), shows that 2 mol of NaCl reacts with one mole of portlandite and 3 moles of CaO·Al₂O₃ to form 3 moles of Friedel's salt.

The mass molar of portlandite, CaO·Al₂O₃, and Friedel's salt is 74.09, 270, and 561.3 g/mol, respectively. Thus, for instance, in a reaction between one ml of two-molar NaCl with portlandite and C₃A, 0.12 g NaCl reacts with 0.07 and 0.81 g portlandite and C₃A, respectively, and forms 1.68 g Friedel's salt. As a result, this reaction forms a product heavier than the reactants.

$$2\text{NaCl} + \text{Ca}(\text{OH})_2 + 3\text{CaO}.\text{Al}_2\text{O}_3 + 10\text{H}_2\text{O} \rightarrow 3\text{CaO}.\text{Al}_2\text{O}_3.\text{CaCl}_2.10\text{H}_2\text{O} + 2\text{NaOH}$$
(27)

The same is true for two other salt solutions. As mentioned in Eq. (7), $CaCl_2$ can react with portlandite and C_3A and produce Friedel's salt. MgCl₂ first reacts with portlandite, resulting in brucite and CaCl₂, which can react further with the hydration products to form Friedel's salt.

Salt crystallization within the sample pores after drying can be another possible causing an increase in the sample mass. Remember that those samples used in the desorption test were first exposed to 2molar salt solutions for two weeks before acid addition. Visual observation of samples after desorption showed a clear sign of salt crystallization. Figure 5.31 shows an example of salt crystallization within the surface cracks.



Figure 5.31. Salt crystallization within the cracks after drying of samples exposed to 2 M salt solutions.

After acid was introduced to the system, the reaction between nitric acid and portlandite produced calcium nitrate, which is highly soluble. This reaction can result in the decalcification of the sample, which manifests itself by discoloration and formation of surface cracks, as shown in Figure 5.32. As discussed in section 2.3.3, the formation of cracks, especially at high acid volumes on the corroded layer due to nitric acid attack, was expected and observed. More images of samples after the desorption test can be found in Appendix A.



Figure 5.32. Discoloration and corrosion of outer layer of samples as a result of exposure to 25 ml acid for two weeks.

According to Eq. (19), two moles of nitric acid can react with one mole of portlandite, forming one mole of calcium nitrate. The molar mass of calcium nitrate and portlandite is 164.09 and 74.09 g/mol, respectively. The number of moles in 5, 10, 15, 20, and 25 ml of one molar nitric acid is 0.005, 0.010, 0.0015, 0.0020, and 0.0025, respectively. Therefore, for example, adding 5 ml of 1-M nitric acid to the solution consumes 0.0025 moles of portlandite and produces 0.0025 moles of calcium nitrate, assuming that Eq. (19) is the only reaction taking place. Based on their molecular mass, 0.18 g portlandite reacts to 0.31 g acid and forms 0.41 gr calcium nitrate, which is highly soluble in water at room temperature. This means portlandite (in a solid form) is converted to a soluble phase with a higher mass than portlandite. The decalcification of paste as a result of this reaction continues as long as enough portlandite and nitric acid are available in the system. Based on TGA and XRD results for samples exposed to 25 ml acid, the presence of portlandite was

confirmed even after such a high volume of acid. Therefore, portlandite was not depleted, and nitric acid concentration was a limiting factor in the reaction discussed above. In addition, Taheri et al. [112] reported a solubility of 56% for calcium nitrate, so it can partially remain on the sample, very low intensity of calcium nitrate was observed in XRD scans after 25 ml acid addition.

It should be noted that when acid is added to a solution, several reactions happen. First, the added acid reacts with salt and produces bases such as NaOH. Then acid reacts with paste components such as C-S-H and portlandite. In the presence of brucite, nitric acid can form magnesium nitrate, which is highly soluble and can leach out to the solution. Thus, while the presented explanation is valid, one should remember that more than one reaction takes place concurrently.

Figure 5.33 displays the percent mass changes of OPC samples after exposure to different volumes of acid. The positive values of ordinate in this figure show the mass gain, and the negative ones represent mass loss. The mass change results for OPC paste in Figure 5.33 show that any increase in the added volume of nitric acid after 10 ml resulted in a mass loss in OPC samples, which can be attributed to the leaching of Ca-bearing phases such as portlandite and C-S-H from the paste. The results indicate a higher mass change rate in CaCl₂ followed by MgCl₂ and NaCl. The lower rate of mass change in NaCl can be related to its initial higher pH than two other solutions and a higher pH after two weeks of exposure. The results also show that the amount of mass loss at high acid volumes (>15 ml) in CaCl₂ was higher than in NaCl and MgCl₂.



Figure 5.33. Percent mass change in OPC samples after exposure to nitric acid at different volumes.

Figure 5.34 displays the mass change of binders containing fly ash. A descending pattern is observed for FA15 paste in the NaCl solution. However, FA30 pastes showed an ascending pattern in NaCl after adding 5 ml due to unknown reasons. In both FA15 and FA30 pastes immersed in MgCl₂, adding 5 ml acid led to a mass gain, and further acid volumes resulted in a mass loss. The same trend was observed in CaCl₂, except from 10 ml to 15 ml. As explained earlier, the mass loss with further acid addition is related to the formation of high soluble salts (magnesium nitrate and calcium nitrate) and the leaching of portlandite. Replacing OPC with fly ash led to a lower or similar mass loss in all solutions.



Figure 5.34. Percent mass change in samples containing fly ash after exposure to nitric acid at different volumes. (a) FA15; (b) FA30.

Figure 5.35 shows the mass change of binders containing slag. The results show that adding 5 to 20 ml acid resulted in a mass loss in most samples. Nevertheless, an ascending pattern at the end is observed due to an unknown reason. In NaCl solution, slag-containing pastes had a higher mass loss than specimens immersed in CaCl₂ and MgCl₂, except at 25 ml. The highest mass loss rate for SG25 and SG50 was observed in NaCl and CaCl₂, respectively. Compared to OPC paste, SG25 had a higher mass gain in MgCl₂ solution and higher mass loss in NaCl and CaCl₂ solutions.



Figure 5.35. Percent mass change in samples containing slag after exposure to nitric acid at different volumes. (a) SG25; (b) SG50.

Figure 5.36 displays the mass change in SF5 and SF10. Both pastes exposed to 5 ml acid gained mass relative to their none-exposed counterparts. However, after adding 10 ml acid to SF5 and 15 ml acid to SF10, sample mass was considerably reduced compared to their non-exposed counterpart. The mass gain in 5 ml acid can be attributed to chemical binding, and the mass loss can be attributed to severe leaching of the calcium-bearing components of pastes. SF5 and SF10 have similar mass losses compared to OPC paste, except for SF10 immersed in NaCl solution, which resulted in higher mass loss.



Figure 5.36. Percent mass change in samples containing silica fume after exposure to nitric acid at different volumes. (a) SF5; (b) SF10.

5.7 Discussion

5.7.1 The Role of pH in Chloride Desorption

In section 5.1, we discussed the difference between a model system and the one containing a paste sample. To recap, in a system containing blended cement paste samples, nitric acid cannot attack all the portlandite in the paste, and as more calcium hydroxide, alkalis, and free lime leach out from the paste's inner layers, the potency of acid reduces, and the pH increases in return. Therefore, unlike a model system where pH never recovers after the addition of acid, the results of desorption tests showed an increase in the pH after two weeks of exposure to acid.

The pH measurements in this study indicated that after adding nitric acid, even at low volumes, the pH of the exposure solution dropped significantly for a few minutes but slowly rose. Figure 5.37 shows the pH measurements measured right after the adding acid and then at 7 and 14 days following the addition of different volumes of nitric acid to different samples. The results show an increase in the pH with time, which confirms the buffering capacity of paste samples because of the reaction between portlandite and nitric acid. Comparing the subplots in Figure 5.37 suggests that the rate of pH increase is closely related to the added volumes of acid, and the exposure solution could reach an equilibrium much faster when a smaller volume of nitric acid was added. For example, in 5 ml acid addition to a salt solution, all binders reach to plateau after a week. In a higher acid volume, binders containing higher percentages of SCMs such as SG50 and FA30 had lower pH than OPC pastes due to their lower portlandite contents. The results showed that when 20 and 25 ml acid was introduced to samples, the binder containing SCMs had lower pH than OPC pastes (black line on Figure 5.37) after one week and two weeks. Among all binders, SG50 and FA30 had FA30 had the lowest pH at high acid volumes (> 15 ml).

Nitric acid attack on paste samples can have several effects; First, nitric acid can react with aqueous Na^{+} , Ca^{2+} , and Mg^{2+} ions in the salt solution to produce highly water-soluble NaNO₃, $Ca(NO_3)_2$, or $Mg(NO_3)_2$. These soluble salts can react with water, producing NaOH, $Ca(OH)_2$, and $Mg(OH)_2$, which can slightly increase the pH of the exposure solution. Then, as discussed in section 5.6, acid attacks hydration products, producing soluble salts and forming an altered porous layer that evident cracks on the surface. The number of observed cracks (Appendix A) and corroded layer thickness increased by increasing acid volume, which equals a lower pH.



Figure 5.37. The evolution of pH in containers after adding different volumes of acid.

Second, the layer-wise progression of acid attack on paste samples can result in the dissolution of hydrated phases and exposure of the underlying neat layers to the salt solution. At this point, if the pH of the solution is still low, the dissolution of the paste continues. Otherwise, the neat, exposed layer can provide sites for further chloride binding.

In addition, the leaching of portlandite and silicates and their reaction with nitric acid can produce hydrogels of silica, aluminum, and ferric oxide [113]. The authors hypothesized that these precipitated calcium salts and hydrogels could absorb some of the free chlorides from the exposure solution. Previous studies reported forming similar gel-like products during chloride extraction by nitric acid. For example, Lolivier [114] reported the formation of gelatinous silica during chloride extraction from hardened concrete. At the same time, Ahmed and Trejo [115] found whitish gypsum-like products rich in calcium, sulfur, and alumina during chloride extraction from calcium aluminate and calcium sulfoaluminate paste samples containing admixed chlorides. Figure 5.38 schematically shows the mechanisms of acid attack and chloride desorption.



Figure 5.38. An illustration showing the mechanisms of chloride desorption. (a) neat sample exposed to chlorides for two weeks; (b) an instantaneous drop in the pH of the solution after adding nitric acid, which
results in the corrosion of the outer paste layer; (c) formation of porous calcium nitrate layer and hydrogels after two weeks, which buffers the pH.

5.7.2 The Role of The Salt Cation in Chloride Desorption

This study showed that the cation of the chloride salt plays an essential role in releasing bound chloride. For example, more than 90% of bound chlorides were released after adding 5 ml of nitric acid to samples immersed in NaCl solution. In the CaCl₂ solution, regardless of the binder type, the amount of released bound chloride was relatively lower than that of in NaCl solution, especially for SF5 and SF10, which released less than 50% and 60% of bound chlorides, respectively. In addition, the results indicate that disassociation percentages declined when the replacement level for fly ash and slag increased (for fly ash from 15 to 30% and slag from 25 to 50%). In the MgCl₂ solution, when 5 ml acid was introduced to the different solutions, almost 60% of the bound chlorides were released, except for SG 25 and SG50, which had a release rate of 89 and 33%, respectively.

It should be emphasized that the visual observation of containers containing 15 ml of acid and more, as shown in Figure 5.39, showed an apparent change in the color of exposure solution due to acid attack and leaching of Ca-bearing phases. This study focused on the chloride desorption mechanism of blended cement pastes. When high volumes (≥ 15 ml) of acid are introduced to the system due to the complex nature of the acid attack on cement paste, it is hard to differentiate the impacts of acid attack on the released bound chloride mechanism. As a result of carbonation in real life, the pH falls to around 8 to 9. Therefore, a more detailed discussion is provided within this pH range.



Figure 5.39. Discoloration in the exposure solution of samples after two weeks of exposure to different volumes of acid. (a) NaCl; (b) CaCl₂; and (c) MgCl₂ (from left to right 5, 10, 15, 20, 25 ml acid added).

It is critical to note that there is a difference between the percentage of released bound chloride and the content (mg cl/g paste) of available free chloride after pH reduction. The binding section presented the quantity of total bound chlorides after exposure to 2 M salt solutions. As a rule of thumb, if two pastes have the same percentage of released bound chlorides, the one with a higher chloride binding content releases more chlorides after desorption. For example, the amount of binding for OPC paste in NaCl, CaCl₂, and MgCl₂ is 25.35, 33.72, and 59 mg Cl/ g paste. The percentage of released bound chlorides after adding 5 ml acid in these solutions is nearly 87%, 92%, and 86%. While the disassociation percentage in NaCl and MgCl₂ is very close, due to the differences in total binding in these two solutions, the amount of released bound chloride would be 22.10 mg Cl/ g in NaCl and 50.79 mg Cl/ g in MgCl₂ solutions. Therefore, considering the number of bound chlorides and the percentage of released bound chlorides, one can calculate the available amount of free chlorides after pH reduction. Figures 5.39 and 5.40 display the chloride content after adding 5- and 10-ml nitric acid, respectively. Each rectangular bar consists of two parts: released and bound chloride contents, the sum of which equals the total bound chloride before acid addiction. The results show that chloride desorption is influenced by the binder composition, cation type, and pH. The inclusion of SCMs has a trade-off between achieving higher binding and releasing higher chloride content and lowering the system's buffering capacity due to the consumption of portlandite. Regarding pH levels in binders, while instant pH after adding 5 ml acid was very low (pH= 1 to 2), after a few days, due to buffering capacity of calcium phases, pH rose, and therefore, the solution showed a minimal change in pH after two weeks compared to other acid volumes. For example, the measured pH of seven cementitious systems exposed to NaCl before adding acid was 12.1 to 12.4, dropping to 11.5 to 12.1 after a week of exposure to 5 ml acid.

Figure 5.40a displays that almost all of the bound chlorides were released from adding 5 ml nitric acid to the NaCl solutions. Since blended pastes contained less portlandite due to the pozzolanic reaction, they showed a lower pH during the exposure to acid, leading to a higher release of bound chlorides.

Figure 5.40b shows that the number of bound chlorides remaining in the sample was higher than that in the NaCl solution. This result confirms the importance of cation type on the chloride binding and desorption capacity. The presence of Ca^{2+} can contribute to C-S-H development, impacting chloride adsorption. Likewise, Mg^{2+} impacts the C-S-H structure (increased Ca/Si) and provides more $CaCl_2$ after reaction to portlandite.

In the MgCl₂ solution, all binders showed a higher or equal bound chloride portion compared to NaCl and CaCl₂. Figure 5.40c shows that chloride binding capacity for binders exposed to MgCl₂ is higher than the other two salt solutions, and the bound chlorides are more resistant to the pH drop in the solution– in contrary to other salt solutions, a higher portion of bound chlorides remained bounded when exposed to 5 ml nitric acid.

Figure 5.40 shows that increased SCM replacement levels positively influenced the chloride desorption mechanism. In other words, based on the results of three salt solutions, a higher replacement level led to maintaining a higher portion of bound chlorides in place when pH dropped to a lower range. For example, Figure 5.40 shows that the portion of bound chlorides that were not released (i.e., the pink shaded area) after exposure to 5 ml acid was higher in FA30 than in FA15. This finding suggests that increasing the SCM replacement level increases the system's resistance against chloride desorption, reducing the risk of corrosion in reinforced concrete structures exposed to low-pH environments.



Figure 5.40. The amount of total bound and released chloride (mg Cl/ g paste) in different pastes the addition of 5 ml nitric acid (a) NaCl; (b) CaCl₂; (c) MgCl₂.

Figure 5.41a shows that by adding 10 ml acid to NaCl solution, more chlorides remained bound in samples containing high replacement levels of SCMs. As discussed earlier, this phenomenon can be explained by the corrosion of the samples' surface layer and the rebinding mechanism with the neat layers underneath the surface.

In CaCl₂, while the amount of unreleased chlorides in OPC is slightly lower than NaCl, for the rest of the samples, a higher portion of chlorides remained bound when 10ml acid was added to the solution. Similar to NaCl, binders that contained a higher percentage of SCMs performed better. Overall, samples exposed to MgCl₂ showed the best performance in keeping the bound chlorides after adding 10 ml. Even before adding acid, the pH level in the MgCl₂ solution (pH~9) was lower than in the other solutions. Therefore, it is suspected that adding more acid to the MgCl₂ solution and the resulting significant drop in the pH leads to the dissolution of the surface and higher SCMs replacement level positively impacted the chloride desorption mechanism. FA30, SG50, and SF10 kept more chloride in bound form compared to FA15, SG25, and SF5, respectively.



Figure 5.41. The amount of total bound and released chloride (mg Cl/ g paste) in different pastes the addition of 10 ml nitric acid (a) NaCl; (b) CaCl₂; (c) MgCl₂.

6 CONCLUSION

This study investigated the chloride binding and desorption mechanism of paste samples containing OPC and three commonly used SCM, fly ash, slag, and silica fume, in a low pH environment. The paste sample was cured for 56 days and 14 days immersed in three salt solutions, including NaCl, CaCl₂, and MgCl₂ at six molarities (0.1, 0.3, 0.5, 0.7, 1, and 2 M). Then chloride binding isotherms were developed for seven binders. In the second phase of this study, different volumes of 1 M HNO₃ (5, 10, 15, 20, and 25 ml) were added to containers containing a paste and two molar salt solutions to investigate chloride desorption in a low pH environment. The following conclusions can be drawn from the results:

- For OPC samples, MgCl₂ and CaCl₂ resulted in more chloride binding than the NaCl solution. The same trend was observed when SCMs were included in the samples.
- Incorporating 15 and 30% of fly ash increased the chloride binding at 2 M NaCl solution by 1.76 and 2.16 times compared to OPC. The same trend was observed for CaCl₂ and MgCl₂ solutions.
- Replacing OPC with 25 and 50% slag enhanced chloride binding at 2 M NaCl solution by approximately 46 and 85% compared to OPC. The same trend was observed for CaCl₂ and MgCl₂ solutions.
- TGA results after the binding test revealed that in terms of Friedel's salt formation, the inclusion of silica fume was the least favorable, and slag was the most promising.
- The amount of measured free chloride after acid addition increased compared to the samples without acid, regardless of binder and cation types.

- In FA15 and FA30 pastes, a higher chloride disassociation was observed in NaCl solutions than in CaCl₂ and MgCl₂.
- The results for SG25 and SG50 revealed that regardless of cation type, the inclusion of higher slag increased the chloride binding and reduced the percentages of released bound chlorides.
- The desorption results revealed that an increased silica fume content from 5 to 10% enhanced the chloride binding capacity and dissociation behavior.
- The inclusion of SCMs is a trade-off between achieving higher binding and releasing higher chloride content and lowering the system's buffer capacity due to the consumption of a considerable amount of portlandite.
- Chloride disassociation is influenced by the binder composition, cation type, and pH.

6.1 Recommendations for Future Works

In future works, the authors recommend using different test setups for desorption. For example, instead of adding different volumes of acid to a container containing a salt solution and a paste, it would be better to remove the pastes from the container, wash the surface to clean the crystallized salts, and then immerse the sample in a new solution with a predefined pH. Because the pH of DI water (~6) is relatively low, it is highly recommended to use dilute NaOH solution to make a solution with a desirable pH.

One of the disadvantages of acid addition is bringing the solution pH to a specific level. For example, a significant ph drop using acid is unavoidable, thus making inferences about the influence of pH on chloride desorption complex. While the new proposed changes would prevent sudden changes in the pH of the exposure solution, it should be noted that due to the buffering capacity of the paste sample, it is almost impossible to maintain the pH at the same level during the entire experiment.

This study investigated the performance of paste samples on chloride binding and desorption. However, there is still a knowledge gap regarding the impact of sample type (paste, mortar, and concrete), sample shape (powder vs. uncrushed samples), and sample saturation state on chloride binding and desorption mechanism.

Another limitation of the current study is the application of pure salt solutions. In reality, State and local departments use a blended mixture of NaCl, MgCl₂, and other chemical solutions in winter to minimize the risk of freezing. The chloride binding results of commonly used salt solutions in cities and comparing them with pure salt solutions used in most laboratories can help maintain the infrastructure for a more extended period.

The final suggestion is to investigate the influence of wet–dry or freeze and thaw cycles on chloride binding and desorption of samples exposed to salt solutions to simulate an actual concrete specimen in service. While the test setup for this purpose seems challenging, the results can be very beneficial and provide significant insights into the mechanisms of concrete deterioration after the cyclic application of road salts.

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APPENDIX A

Images of Samples Taken after Two Weeks of Exposure to Acid

OPC Paste Samples

Acid volume	NaCl	CaCl ₂	MgCl ₂
5			
10		140	
15			
20			
25			

FA15 Paste Samples

Acid volume	NaCl	$CaCl_2$	MgCl ₂
5			
10			
15		FIS	
20			
25			

FA30 Paste Samples

Acid volume	NaCl	$CaCl_2$	$MgCl_2$
5			
10	R.		
15			
20			

SG25 Paste Samples

Acid volume	NaCl	$CaCl_2$	MgCl ₂
5			
10			
15			
20			
25	C C C C C C C C C C C C C C C C C C C		Mes

SG50 Paste Samples

Acid volume	NaCl	CaCl ₂	MgCl ₂
5			
10			
15			
20	Ó		
25			

SF5 Paste Samples

Acid volume	NaCl	$CaCl_2$	MgCl ₂
5			
10			
15			
20			
25			

SF10 Paste Samples

Acid volume	NaCl	CaCl ₂	MgCl ₂
5	-		
10			
15			
20			
25			

APPENDIX B

Proposed Test Method to Measure the Chloride Desorption Capacity

of Cementitious Systems

1. Scope

This test method provides procedures for the sampling, testing, and analysis of the release of bound chlorides in paste samples made of ordinary portland cement (OPC), fly ash, and slag under the conditions of the test.

2. Reference Documents

ASTM C305 Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency.

ASTM D1193-99 Standard Specification for Reagent Water.

ASTM C1152-20 Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete.

3. Significance and Use

The disassociation of bound chlorides in cementitious systems is an unfavorable mechanism. It increases the free chloride concentration in concrete pore solution, leading to chloride inducedcorrosion initiation. The concrete industry is currently using blended cement containing OPC and many other cementitious materials such as fly ash, slag, and silica fume. There is no standard method for measuring the disassociation of bound chlorides as a result of exposure to low-pH environments. This proposed test method outlines the procedure and steps needed to quantify the amount of released bound chlorides due to exposure to acidic environments.

4. Apparatus

4.1 Balance: Capable of reproducing results within 0.0002 g with an accuracy of \pm 0.0002 g.

4.2 Mixer: Mortar mixer, a 5-liter mortar mixer is preferred for small batches.

4.3 Stirrer: Magnetic stirrer with variable speed or a metal spatula of convenient size.

4.4 Pipette: Adjustable pipette 1 to 10 ml with increments of $100 \,\mu$ L.

4.5 Potentiometric Titrator: Potentiometer meeting requirements of ASTM C1152-20 section 5.3.4 or automatic titrator. For the former, follow ASTM C1152-20 sections 9.3 to 9.8 to perform titration.

4.6 pH meter and electrode: A digital pH meter with a high alkali sensing glass electrode suitable for high pH applications electrode is preferable.

4.7 Oven: An oven capable of maintaining the temperature at 55 ± 2 °C.

4.8 Glass container: 200 ml containers with a lid, preferably made of glass, capable of resisting an acidic environment without the risk of spilling.

5. Reagents

5.1 Water: Distilled or deionized water meeting ASTM D1193-99 for Type III reagent water.

5.2 Calcium chloride (NaCl): ACS grade solid NaCl with a purity of >99.9 %.

5.3 Nitric acid (HNO₃): Nitric acid (70%) with a density of 1.400 g/mL and a molar mass of 63.01 g/mol.

5.4 Silver nitrate (AgNO₃): ACS grade AgNO₃ with a purity of >99.9%.

5.5 Moisture-absorbent silica gel.

5.6. Buffer solutions: National Institute of Standards and Technology (NIST) buffer solutions (Required for accurate pH measurements)

6. Paste Sample Preparation

Prepare paste samples with a water-to-binder ratio of 0.4 in a mortar mixer according to ASTM C305 mixing procedure. After mixing, cast samples into circular disc-shaped molds with a diameter of 33 mm and depth of 15 mm. Seal the samples and store them in an environmental chamber maintained at 25°C and RH of 95%. Demold specimens after 24 hours and keep them inside Ziplock bags in an environmental chamber, maintained at 25°C and RH of 95%, for 56 days. Then, dry the cured samples in an oven at 55°C to obtain a constant weight. During the drying process, place soda lime and moisture-absorbent silica gel inside the oven to prevent carbonation and moisture buildup.

7. Solution Preparation

7.1 Salt Solutions: To make a 2 M NaCl solution, dissolve 116.88 gr NaCl in 500 ml water and adjust the volume to 1 L.

7.2 Acid: To make a 1 M nitric acid solution, slowly add 64.296 mL of your stock solution to 250 mL of water. Then, adjust the final volume of the solution to 1 L with water.

8. Procedure

8.1 Chloride Binding

8.1.1 Immerse the paste samples in 60 ml of prepared salt solutions in capped containers to prevent evaporation for 14 days at ambient temperatures of $23^{\circ}C \pm 2^{\circ}C$. At least three replicates are needed for each salt solution.

- 8.1.2 Measure the free chloride concentration of prepared salt solutions in section 7.1 using a potentiometric titration using a 0.05 M AgNO₃ titrator. Record it as **A**, the initial chloride concentration.
- 8.1.3 Measure the free chloride concentration in the exposure solutions using a potentiometric titration using a 0.05 M AgNO₃ titrator. Record it as **B** the measured free chloride concentration after 14 days.

8.2 Chloride Desorption

8.2.1 Test the accuracy of the pH meter using a buffer solution with a known pH. Then, record the pH of salt solution inside thee containers at the room temperature of $23^{\circ}C \pm 2^{\circ}C$.

8.2.2 Add 10 mL 1-molar nitric acid to the containers. After adding the acid, cap the containers to prevent evaporation and leave them for 14 days at ambient temperatures of $23^{\circ}C \pm 2^{\circ}C$ until the

pH reaches an equilibrium. If the pH did not reach an equilibrium point, leave the solution until the pH measured on two consecutive days showed no more than 3% difference.

8.2.3 Measure the concentration of free chlorides in the equilibrated solution and record it asC.

9. Calculation

9.1 Calculate the bound chloride concentration using Eq. (1):

$$c_b = \frac{\left(A - B\right) \times V \times 34.45}{m_{dry}} \tag{1}$$

where:

 c_b = bound chloride concentration, mg Cl⁻/g paste,

A= initial chloride concentration of the exposure solution, M,

B = measured free chloride concentration after 14 days, M,

V = volume of the exposure solution, ml, (i.e., 60 ml),

 m_{dry} = sample's oven-dried weight, g, and

34.45 = molar mass of chlorine, g/mol.

9.2 Calculate the released bound chlorides using Eq. (2):

$$c_r = \frac{\left(C - B\right) \times V_c \times 34.45}{m_{dry}} \tag{2}$$

where:

 c_r = released bound chloride concentration, mg Cl⁻/g paste,

C = measured free chloride concentration 14 days after the addition of acid, M,

B = measured free chloride concentration after the binding period, M,

 V_c = corrected final volume of solution, ml (i.e., 60 ml plus added acid volume), and

 m_{dry} = oven-dried weight of samples, g.

10. Precision and Bias

10.1 Precision: Neither ruggedness test results nor an interlaboratory study of this test method has been performed.

10.2 Bias: Since there is no accepted reference material suitable for determining the bias of this test method, no statement on bias is made.