Review

Resistance of Concretes to External Chlorides in the Presence and Absence of Sulphates: A Review

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Abstract: Corrosion of steel reinforcement due to chloride attack remains a major reinforced concrete durability concern. The problem is prevalent for concrete structures located within marine environments or frost-prone locations where chlorides containing de-icing salts are used. This paper is a state-of-the-art review into chloride binding in Portland cement concrete, with consideration of the differences induced by the presence of sulphates, such as found in seawater. The review also considers the use of supplementary cementitious materials (SCMs), the use of which has increased because of their potential to enhance durability and reduce the carbon footprint of concrete production. Such materials impact on phase assemblage and microstructure, affecting chloride binding and transport properties. Therefore, field and laboratory studies are critically reviewed to understand how these could help in the design of more durable concretes. The contributions of chloride binding, hydrate compositions and microstructures of the binding materials affecting chloride transport in concretes are also evaluated to suggest a more robust approach for controlling the problem of chloride attack.

1. Introduction

One of the greatest challenges facing the construction industry is how to ensure the longevity of reinforced concrete structures. A key concern is the ingress of chlorides, which are known to cause the initiation of embedded steel bar corrosion by de-passivating the protective film provided by the high alkalinity of concrete pore solution around the steel bar [1]. Aggressive, chloride-rich environments can arise through, for example, the application of de-icing salts or the presence of aggressive marine environments. In the latter situation, the principal agents of attack are a combination of chlorides and sulphates from seawater [2–4]. These problems have continued to exist, despite extensive research to understand and proffer solutions to them. Furthermore, changes in binder composition, with increasing use of supplementary cementitious materials and cement-replacement materials (here considered as ground granulated blast furnace (GGBS), fly ash, silica fume, metakaolin, calcined clays and limestone), can lead to a reduction in the pH of concrete pore solutions in fresh, hardened concrete [5], while changes in pore structure and phase assemblages can also affect the susceptibility to carbonation, thus, affecting the local alkalinity over the long term. However, these binders also offer increased aluminate levels, which can bind both sulphates and chlorides [6–8]. A number of studies investigated the attack of concrete structures by external chlorides [9–14], with others looking at the combined attacks of chloride and sulphate [4,8,15–17]. The increasingly wide palette of cementitious binder available to civil engineers [18] has made these problems even more complex. Hence, there is a need for a comprehensive overview, which brings together key developments concerning the combined attack of concrete by chlorides and sulphates. The present study draws from published research in academic and professional journals

and databases to review how different factors affect the resistance of concrete to external chlorides, with or without the presence of sulphate ions.

2. Resistance of Concrete to External Chlorides

Chloride-induced corrosion of steel reinforcement has been identified as one of the primary causes of early deterioration and failure of marine concrete structures, bridges, viaducts, tunnels on roads and highways where de-icing salts are applied during the winter period. This corrosion is a serious problem, not only because of the reduction in the effective area of the steel reinforcement and the corresponding reduction in the load-bearing capacity of the structure, but also due to the expansive formation of the rust products, whose volume can be 3–6-times more than the volume of steel. These rust products cause internal stresses and consequently result in the cracking and spalling of the concrete surrounding the reinforcement [19,20].

Chloride attack can be considered as either internal or external. Internal sources of attack are thankfully rare, but can arise due to inappropriate admixtures, chloride-contaminated aggregates or chloride-bearing mix water. External chloride attack is more prevalent and arises through the application of de-icing salts or through the ingress of brackish water or seawater. Studies have shown that exposure conditions have significant effects on the rate of chloride ingress. The requirement for water as a transport medium means that airborne chlorides pose little danger, while cyclic wetting and drying allows for the accumulation of salts through crystallization during drying periods and more severe attack [21–24]. Chloride ingress into permanently wet concrete lies somewhere between these extremes. For this reason, most national and international standards incorporate exposure classes in their specifications for concretes. For example, BS EN 206 [25] sets out minimum requirements for concretes to resist chlorides, other than from seawater (XD classes) and chlorides from seawater (XS classes). Each of these are sub-divided into three, with XD/XS1 for exposure to airborne chlorides, XD/XS2 for chlorides ingressing into permanently submerged concrete and XD/XS3 for structures exposed to cyclic wetting and drying, such as tidal, splash and spray zones.

The rate at which external chlorides permeate into concrete is often used as an indicator of the concrete's durability. Lower rates indicate more durable structures and vice versa. The chloride diffusion coefficient (D_c) is a term mostly used to describe the rate of chloride ingress. The value of D_c can be obtained by fitting laboratory or field chloride ingress data into chloride diffusion models. Table 1 shows examples of such models, including the theory upon which they are based and their areas of application. The choice of the most appropriate model will depend on knowledge of the exposure condition, i.e., whether saturated or unsaturated. For saturated concrete (i.e., concrete continuously submerged in seawater), chloride ingress is assumed to be governed by pure diffusion [26], while for unsaturated concrete (i.e., concrete partially submerged in seawater or exposed to alternate wetting and drying cycles of seawater), chloride ingress is governed by a combination of diffusion and convection [27–29].

2.1. Factors Influencing the Rate of Chloride Ingress into Concrete

In addition to the chloride binding potential, the rate of chloride ingress into concrete depends on the pore structure of the hardened cement paste. In turn, there are many factors that affect the pore structure of the hardened cement paste, such as curing conditions, w/b ratio, binder composition, including the use of supplementary cementitious materials (SCMs), and the chloride binding ability of the cementitious materials in the concrete matrix [13]. The influence of some of these factors on chloride ingress is summarized in Table 2, while the role of chloride binding is discussed in the next section.

Table 1. Typical chloride diffusion models used in chloride ingress studies.

S/N	Model	Law Based On	Suitable Areas of Application	Ref.
1.	$J = -D\frac{dc}{dx}$	Fick's 1st law	Steady state conditions where there are no changes in flow of ions.	[30]
2.	$C(x,t) = C_s\left[1 - erf\left(\frac{x}{2\sqrt{D_c t}}\right)\right]$	Fick's 2nd law	Non-steady state conditions, usually suitable for saturated conditions such as laboratory ponding tests and field conditions where the samples are continuously immersed in seawater.	[26]
3.	$J(x) = -D\left[\frac{\partial c(x)}{\partial x} + \frac{ZFE}{RT}c\right]$	Nernst-Planck	Electrical accelerated tests.	[1,30]
4.	$\frac{\partial C_{tc}}{\partial t} = \underbrace{\mathrm{div}\left(D_c w_e \overrightarrow{\triangledown}\left(C_{fc}\right)\right)}_{\text{diffusion}} +$ $\underbrace{\mathrm{div}\left(D_h w_e C_{fc} \overrightarrow{\triangledown}(h)\right)}_{\text{convection}}$	Fick's 2nd law	Unsaturated conditions.	[27]

J is the flux, $C(x,t)$ is the chloride concentration at a given time and position, C_s is the surface chloride concentration, D_c is the chloride diffusion coefficient, t is the time, x is the depth in the diffusion direction, *erf* is the error function, Z is the valence of the ion (-1 for Cl^-), F is Faraday's constant, E is the electrical field, R is the universal gas constant, T is the temperature, C_{tc} is the total chloride concentration, w_e is the evaporable water content, C_{fc} is the concentration of chlorides dissolved in the pore solution (free chlorides), D_h is the effective humidity diffusion coefficient and h is the relative humidity.

Table 2. Factors influencing the rate of chloride ingress into concrete.

Factor	Effect	References
Porosity	The finer the pore structure, the greater the resistance to ingress of aggressive species, including chlorides.	[31–33]
Curing conditions	Prolonged curing reduces porosity and hence permeability, so enhances resistance to chloride ingress. Elevated temperatures, e.g., 40 °C and above, while increasing the degree of hydration, lead to a more porous network for a given degree of hydration. This leads to higher rates of chloride ingress.	[13,32,34,35]
w/b ratio	At any given temperature, higher values of w/b will result in higher rates of chloride ingress	[29,36,37]
SCMs	SCMs such as fly ash and GGBS, when used as partial replacement materials for PC lead to reduced porosity, and hence can reduce the rate of chloride ingress	[38–42]

2.2. The Role of Chloride Binding

When external chlorides permeate into concrete, they can exist as free ions dissolved in the pore water, can be bound chemically in the form of Friedel's or Kuzel's salt or bound physically to the surface of the hydration products (e.g., C-S-H). Since it is free chlorides that can induce reinforcement corrosion, chloride binding is beneficial to the durability of a concrete structure. Furthermore, the formation of Friedel's salt can also lead to pore blocking, slowing down the rate of chloride ingress [1,43,44]. Hence, the higher the chloride binding ability of cement, the less likely it is for chlorides to migrate through the concrete cover to the embedded steel reinforcement.

2.3. Factors Affecting Chloride Binding

Several factors have been reported to affect the formation of bound chlorides, such as the cement type, alkalinity of the pore solution, cation type of the salt, chloride concentration, temperature, presence of other anions, e.g., sulphates and carbonates, and the presence of SCMs in the mix. These factors are discussed here as follows.

1. Cement type:

The C_3A phase plays an important role in chloride binding. Sulphate-resisting Portland cements (Type V cements according to ASTM or CEM 1-SR in EN 197-1) have lower C_3A contents so as to inhibit expansive ettringite formation. Thus, these cements have lower chloride binding capacities and, thus, allow for greater free chloride penetration for a given permeability than ASTM Type I cements [45,46]. Hussain [47] observed that an increase in the C_3A content from 2.43 to 14% resulted in approximate 2.65- and 2.85-fold increases in the chloride binding capacity and chloride threshold, respectively. Meanwhile, Rasheeduzzafar [48] reported that Type I cements with C_3A contents of 9.5%, bound about 1.6-times more chloride than those with C_3A contents of 2.8%. Therefore, while increasing C_3A contents do increase chloride binding, other factors are also an influence. In a study by Kim et al. [49], an increased C_3A content resulted in increased chloride ingress at every depth (Figure 1), presumably implying that increased chloride binding capacity may accelerate the rate of chloride transport at a given exposure condition. This phenomenon can be attributed to the chemical balance of chlorides in the vicinity of the interfacial region between concrete and water-based media (salt solution). As the higher C_3A content imposes the increased binding of chloride ions on the surface of concrete, more chlorides percolate to meet the equilibrium of the chloride gradient. Thus, the mobility of chlorides would increase with the chloride binding capacity so that more free chlorides could be accumulated on the surface of concrete, thereby substantially increasing both the free and bound chlorides.
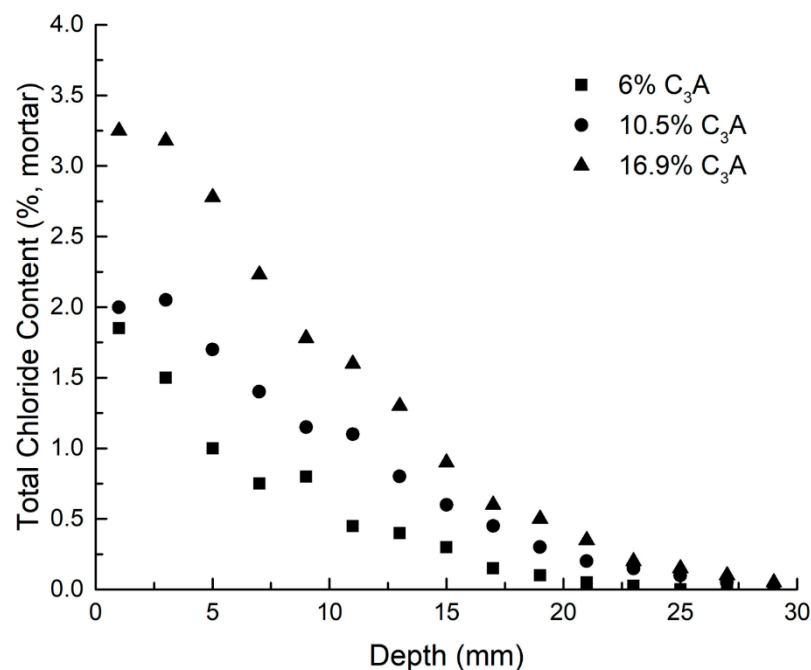

Figure 1. Chloride profiles for mortar samples with different C_3A contents after exposure to a 4.0 M NaCl solution for 100 days [49].

2. Alkalinity of the pore solution:

The free chloride to hydroxide ratio is an indicator of susceptibility to reinforcement corrosion, with a higher ratio leading to increased risk of corrosion. However, also, the pH of the pore solution can influence the stability of bound chlorides. Several studies [47,50–52] have shown that chloride binding capacity decreases with increasing pore solution pH (as shown in Figure 2). Meanwhile, Friedel's salt solubility increases at pH > 12, thereby releasing chloride to the pore solution and reducing the amount of chemically bound chloride [53].
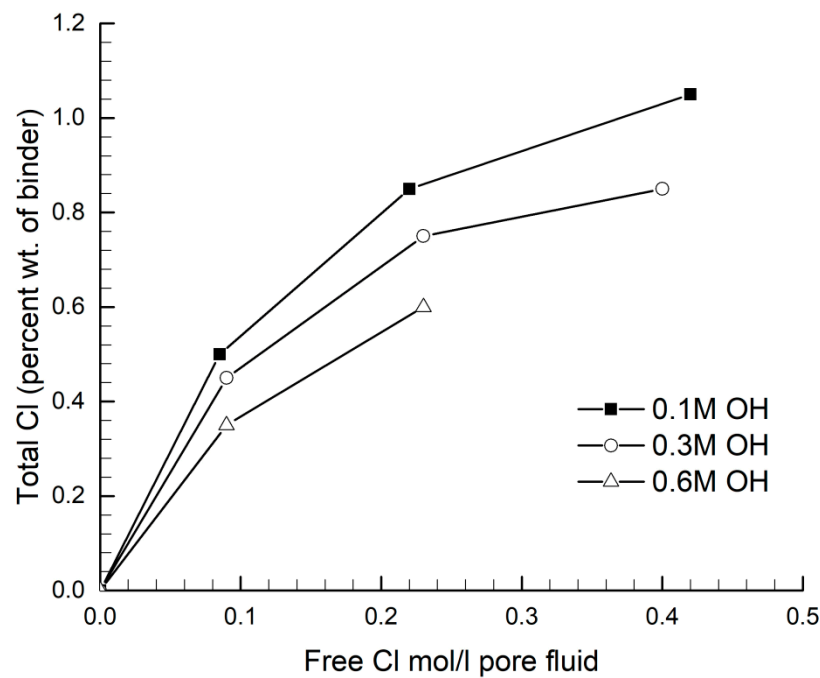
Figure 2. Effect of hydroxyl ion concentration on chloride binding for OPC pastes with water–cement ratio of 0.40 [54].

3.   Cation type of the salt:

The source of the chloride ions or the associated cation affects the amount of bound chlorides [55–57]. Arya et al. [56] observed greater chloride binding when samples were exposed to calcium and magnesium chlorides, compared to sodium chloride (see Table 3). This has been attributed to the cation's influence on chloroaluminate solubility, the accessibility of the chloride ions to the adsorption sites and the influence of the cation on the pH of the pore solution [53]. Na^+ ions raise the pH more effectively than Ca^{2+} or Mg^{2+}, and since chloride binding reduces with increasing pH, chlorides associated with Na^+ will experience lower binding rates than those associated with Ca^{2+} or Mg^{2+}.

Table 3. Influence of cation type on chloride binding for 2-day-old PC paste samples (w/c = 0.5) immersed in 20 g Cl/L solution for 28 days [56].

Cl Content (% by wt. of Cement)	NaCl	CaCl$_2$	MgCl$_2$
Free	0.831	0.765	1.480
Bound	0.804	1.408	2.347
Total	1.635	2.173	3.827
Bound/Total (%)	50	65	61

4.   Concentration of chloride solution:

Dhir [58] and others [9,40,55,59] observed that the chloride binding capacity of cement pastes increased with increasing chloride concentration (see Figure 3). This was attributed to the sensitivity of the chloride binding capacity on the Cl^-/OH^- ratio in the pore fluid.
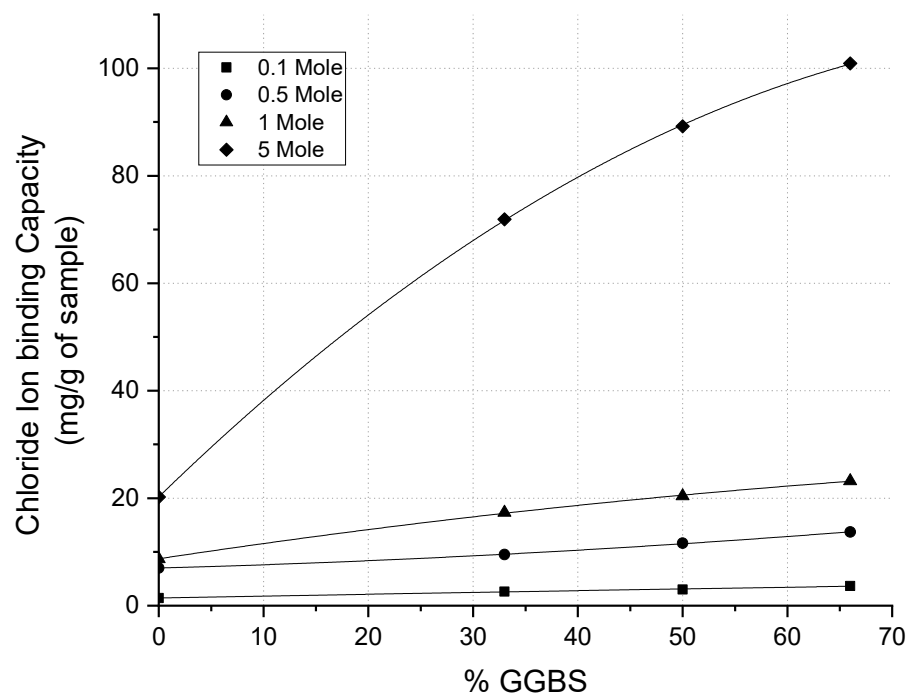
Figure 3. Effect of varying concentrations of chloride ions on chloride binding capacity [58].

5. Temperature:

There is some controversy on the effect of increasing temperature on chloride binding, especially at temperatures above 0 °C. Some studies [9,56,60,61] have reported increased chloride binding with increasing temperature, while others [62–65] have reported the opposite. Panesar [61] observed an increase in the amount of bound chlorides as the temperature was increased from 5 to 22 °C, for neat pastes and pastes containing 25, 50 and 60 wt% GGBS. Wowra [60] observed increased chloride binding from 0 to 40 °C. In both studies, increased chloride binding was attributed to faster reaction rates. Zibara [9] also observed increased binding with increased temperature upon exposure to 3 M chloride solution, but observed decreased chloride binding with increasing temperature at lower chloride concentrations (0.1 and 1.0 M). Ogirigbo and Black [13], meanwhile, attributed increased chloride binding at higher temperature (38 °C as opposed to 20 °C) to greater degrees of slag hydration.

Conversely, Hussain [62] observed that the amount of unbound chlorides was significantly higher at 70 °C than at 20 °C. Similar trends were reported by Maslehuddin [63] over a temperature range of 25 to 70 °C for admixed chlorides. This may be due to a partial release of the bound chlorides occurring at the higher temperature, as observed elsewhere [66]. In a study by Jensen [64], the bound chloride content calculated from the equilibrium solution decreased with increasing temperature. However, the impact of temperature was minor compared to that of the cement composition. Meanwhile, Qiao [67] did not observe any significant difference in the chloride binding capacity of cement pastes exposed to calcium chloride solutions at 5 °C and 23 °C.

6. Presence of other anions:

The presence of other anions, e.g., sulphates and carbonates, may affect the chloride binding capacity of the cements. This has been attributed mainly to reactions between the various anions in the pore solution.

In the case of sulphates, reduced chloride binding has been attributed to the preferential reaction of C_3A with sulphates [68]. In the presence of additional sulphates, the C_3A reacts with the sulphates to form ettringite [69,70], which is more thermodynamically stable than Friedel's salt. This reduces the amount of residual C_3A to bind the chlorides.

This has been reported by several researchers [68,71–76]; for example, Figure 4 shows the bound chloride content vs. free chloride content for slag blends, with or without anhydrite ($). For the slag blends with anhydrite (i.e., C2S1$ and C2S2$), additional anhydrite ($) was blended with the original slag blends (i.e., C2S1 and C2S2) so as to bring the sulphate contents of the slag blends to that of the plain cement. The presence of this additional sulphate lowered the bound chloride content.
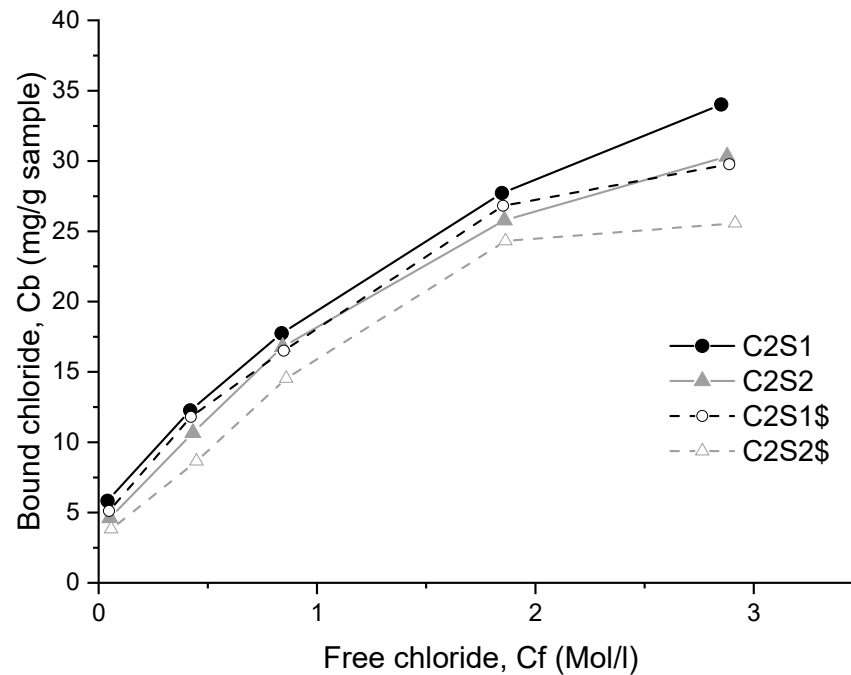

Figure 4. Bound chloride content vs. free chloride content for different slag blends [76].

On the other hand, carbonation changes the nature of the hydration products, e.g., portlandite $Ca(OH)_2$ is converted to $CaCO_3$ and so reduces the pH of the pore solution. This reduction in pH can result in a destabilization of Friedel's salt [77,78] and eventually a decrease in chloride binding.

7. Presence of SCMs:

As mentioned earlier, SCMs primarily affect resistance to chloride ingress by modifying the pore structure, hence, reducing permeability. However, SCMs, such as fly ash, GGBS, metakaolin, silica fume, etc., also affect chloride binding, the extent of which depends on the type of SCM.

- GGBS:

The addition of GGBS to PC increases the chloride binding capacity. This has been attributed to several factors, such as: (1) the high alumina content of GGBS [13,40,58,68,79], (2) an increase in the amount of hydrotalcite (Ht) formed, especially when greater proportions of GGBS are used [80,81], (3) a lower sulphate content of PC-GGBS blends [68,72,74] and (4) the formation of a C-A-S-H phase that is responsible for the binding, through physical adsorption, of about two-thirds of the chloride [82].

The chloride binding capacity of PC–slag blends is also dependent on several factors, such as the level of slag replacement, w/b ratio, chemical composition of the slag and the curing temperature. For example, Ogirigbo [13] found that slags with higher alumina contents had greater chloride binding capacities, while Dhir [58] found that chloride binding capacity increased with the level of slag replacement. They established a model relating chloride binding capacity and GGBS content, as shown below:

$$C_b = \left(-22.21G^2 + 39.45G + 3.36\right)X + \left(6.84G^2 - 6.40G + 3.64\right) \tag{1}$$

where C_b is the chloride binding capacity in mg/g of sample, G is the GGBS/total binder ratio and X is the chloride exposure concentration in mol/liter. However, their model considered just a single source of GGBS, excluding any impact of GGBS composition.

- Fly ash:

As with GGBS, the inclusion of fly ash in PC increases the chloride binding capacity [67,83,84]. Again, this is attributed primarily to fly ash's high alumina content, which facilitates the formation of more Friedel's salt. However, at very high replacement levels, fly ash has been found to reduce the chloride binding capacity [39].

The chloride binding ability of PC–fly ash mixes seems to also be influenced by other factors, such as the curing technique, presence of carbonates (carbonation), source of chloride (whether internal or external), pretreatment of the fly ash and class of fly ash [56,85–88]. Kayyali [85] observed that the chloride binding capacity of PC–fly ash pastes increased when the pastes were cured for longer duration, presumably due to the increased presence of chloride binding to C-S-H. They also observed significantly decreased chloride binding when pastes were subjected to environments containing carbonates. Arya [56] found that more chlorides were bound by PC pastes containing fly ash, when the chlorides were from internal sources as compared to when they were from external sources. Ma [87] observed that pretreating the fly ash with alkali solution before usage increased the chloride binding capacity of PC–fly ash pastes. Pretreatment with the alkali solution helped in depolymerizing the surface structure of the fly ash particles, thereby hastening the dissolution of ions and accelerating the pozzolanic reaction at an early age. As regards the influence of the class of the fly ash, Uysal [89] compared the durability performances of concretes incorporating Class C and Class F fly ash. They observed that the mixtures containing Class C fly ash performed better than those containing Class F fly ash, in terms of resistance to chloride ion permeability, and they attributed this to the higher chloride binding capacity of the Class C fly ash mixtures.

- Metakaolin:

Metakaolin has been widely reported to increase chloride binding [40,90,91] and its use is widespread in concrete exposed to chloride-rich environments. The addition of metakaolin to PC can also increase the rate of binding of internal chlorides [90]. Just like in GGBS and fly ash, the high chloride binding capacity is attributed mainly to metakaolin's high alumina content.

- Silica fume:

The impact of silica fume on chloride binding capacity is unclear. Most studies [38,55,56,92,93] report that chloride binding capacity decreases with increased replacement levels, but some [94,95] have reported increased chloride binding capacity. According to Nilsson [10], the addition of silica fume to concrete can affect chloride binding in three ways. The reduced portlandite content should reduce pore solution pH and dilution of the clinker should reduce the C_3A content. Both of these factors decrease chloride binding. Conversely, the pozzolanic reaction leads to C-S-H formation and increased chloride binding. The significance of each of these three factors seems to be dependent on the replacement level. At higher levels (10% and above), the reduction in C_3A appears to dominate and chloride binding is reduced, whereas, at lower replacement levels (5% and below), the addition of silica fume may increase chloride binding [96].

- Limestone:

While not strictly cementitious, limestone is also increasingly used as a cement-replacement material in cements, with many standards allowing for an up to 20% clinker replacement [97]. Such systems offer a considerable reduction in carbon footprint. However, they also alter the hydration and microstructure of the hardened cement paste.

The replacement of up to about 15% clinker with limestone leads to pore structure refinement due to the filler effect, limestone providing nucleation sites for the formation of C-S-H and encouraging hydration by increasing the effective water/cement ratio at the

early ages. Thus, chloride ingress has been found to be hindered in limestone cements [98]. However, at higher replacement levels, these changes are insufficient to overcome pore coarsening due to clinker dilution. The addition of limestone also leads to the formation of carboaluminates via the reaction with C_3A. It has been postulated that hemi- and monocarboaluminate formation could inhibit chloride binding in Friedel's salt.

Sui et al. [99] examined changes in phase assemblage and chloride binding in Portland cement systems blended with between 5 and 55% limestone. Paste samples with a water/solid ratio of 0.5 were cured for 28 days before immersion in 0.5 M NaCl for 1 year. Increasing limestone contents led to decreasing total chloride contents, from 13.52 mg/g in OPC to 8.89 mg/g in the sample prepared with 55% limestone. There was, however, an increase in free chloride content with increasing limestone content and this was attributed by the authors to the greater porosity and permeability enabling greater chloride ingress. However, they also reported a reduction in bound chloride contents with increasing limestone content, both in terms of that adsorbed onto C-S-H and that chemically bound as Friedel's salt. Thus, the increased free chloride content is likely a result of reduced chloride binding capacity.

- Calcined clay:

With increasing awareness of climate change and the need to decarbonize the cement industry, coupled with decreasing global availability of the aforementioned traditional SCMs [100,101], there are increasing moves to identify alternative SCMs [100,101]. Calcined clays offer great potential in this regard.

Work on binary Portland cement–calcined clay systems is limited. However, such systems are possible, so long as the clays have appreciable kaolin contents. As such, binary Portland cement–calcined clay systems are expected to show performance akin to Portland cement–metakaolin blends, albeit without the significant pore refinement and improved chloride binding capacity. However, low-grade calcined clays have shown significant potential in recent years in limestone calcined clay (LC3) cements.

- Limestone Ternary Cements:

Binary calcined clay Portland cements really only offer the potential for clinker replacement to ~35%. However, 50% clinker replacement is possible without loss of performance by blending clinker with a mixture of limestone and an SCM [100]. The early-age improvement in performance induced by the addition of limestone is complemented by its subsequent reaction with aluminates in the SCMs to produce carboaluminate phases. Again, a combination of pore structure refinement and modified phase assemblages can have an impact on chloride binding [102].

A number of various ternary blends has been investigated, with common combinations being limestone–fly ash cements, limestone–slag cements and LC3 cements. The performance of each of these is influenced by the reactivity of the SCM and the replacement level. There is a general reduction in porosity and, hence, transport properties over time, the extent of which is dependent on aluminosilicate hydration. For example, even after 6 months, greater capillary porosity was reported in limestone–FA blends than ordinary Portland cement specimens [103]. However, while de Weerdt et al. [104] reported similar behavior for limestone cements, they observed a significant reduction in capillary porosity by 90 days in the limestone–fly ash blend as the fly ash hydrated [104]. Reductions in capillary porosity were observed much earlier by Kim et al., but in fly ash limestone blends containing 80% clinker [105].

More reactive SCMs (e.g., slag and calcined clay) exhibit more refined pore structures than pure Portland cement systems, even at clinker contents of 50% and below. Among others, Zajac et al. observed smaller critical pore sizes and, hence, threshold pore access radii, in limestone–slag cements than in pure Portland cement after 28 days [106], while refined microstructures were observed within 3 days in LC3 systems [107]. Meanwhile, Aguayo et al. reported a halving of the chloride migration coefficient in a 1:1 metakaolin–

limestone mix at 20% total replacement compared to an equivalent 1:1 fly ash–limestone mix [108].

In addition to the reduction in chloride transport, ternary cements also offer potential for chloride binding. Generally, ternary limestone cements show higher chloride binding potential than limestone cements, but slightly lower than binary cements containing SCMs. The chloride binding capacity is related to the degree of SCM hydration and the aluminum content in the SCM [52]. Thus, at early ages, blends containing metakaolin, slag and natural pozzolans greatly outperform those containing fly ash and silica fume [109,110]. LC3 systems have generally been found to perform well and show good chloride binding potential, primarily due to the high clay reactivity and aluminum content [111]. Exposure to high chloride concentrations may lead to destabilization of monocarboaluminate [57] with the formation of Friedel's salt. However, in such situations, the chlorides are bound.

There have been very few studies of chloride-induced reinforcement corrosion in ternary cement systems, but the results are inconclusive. The addition of up to 20% limestone was found to increase the time taken for the corrosion potential to cross the -350 mV threshold (rendering the steel susceptible to corrosion) [112]. However, others have reported increased corrosion susceptibility in LC3 cements [113]. Densification increases the time taken for chlorides to reach the reinforcement, but the addition of limestone can reduce the pH and so increase chloride susceptibility. In summary, with the growing interest in ternary cements, there is a need for a better understanding of their curability performance.

2.4. Chloride Binding Isotherms

Chloride binding isotherms are mathematical models devised to relate free chlorides to bound chlorides. These may be grouped mainly into two sets, namely:

- Linear
- Non-linear—Freundlich, Langmuir and Brunauer Emmett Teller (BET)

2.4.1. Linear Chloride Binding Isotherm

The linear chloride binding isotherm assumes a linear relationship between the bound and free chlorides. It is usually expressed in the following form:

$$C_b = kC_f \tag{2}$$

where C_b is the bound chloride content, C_f is the free chloride content and k is a constant of proportionality. This early model was proposed by Tuutti [114] and seems to be only valid for free chloride concentrations less than 20 g/L. Neither Tang [59] nor Ramachandran et al. [115] could subsequently find any linear relationship between bound and free chloride contents. According to Tang [59], the linear chloride binding isotherm gives an oversimplification of the bound chloride content, generating very high bound chloride contents at high chloride concentrations. However, linear relationships have been reported in non-marine field conditions [54,116], where chloride levels are typically below the limit proposed by Tuutti.

2.4.2. Non-Linear Chloride Binding Isotherm

Due to the limitations and inaccuracies of the linear isotherm (as seen in Figure 5), most researchers now use non-linear chloride binding isotherms. The two most commonly used non-linear isotherms are the Freundlich and Langmuir isotherms. These isotherms were originally derived to describe gas adsorption on solid surfaces, where the Langmuir isotherm assumed monolayer coverage on a homogeneous surface and the Freundlich isotherm assumed multilayer coverage. In solid-solution systems, the situation is much more complicated and the underlying assumptions may no longer be valid. Therefore, the isotherms should be considered merely as empirical models and may be expressed in the forms given below:
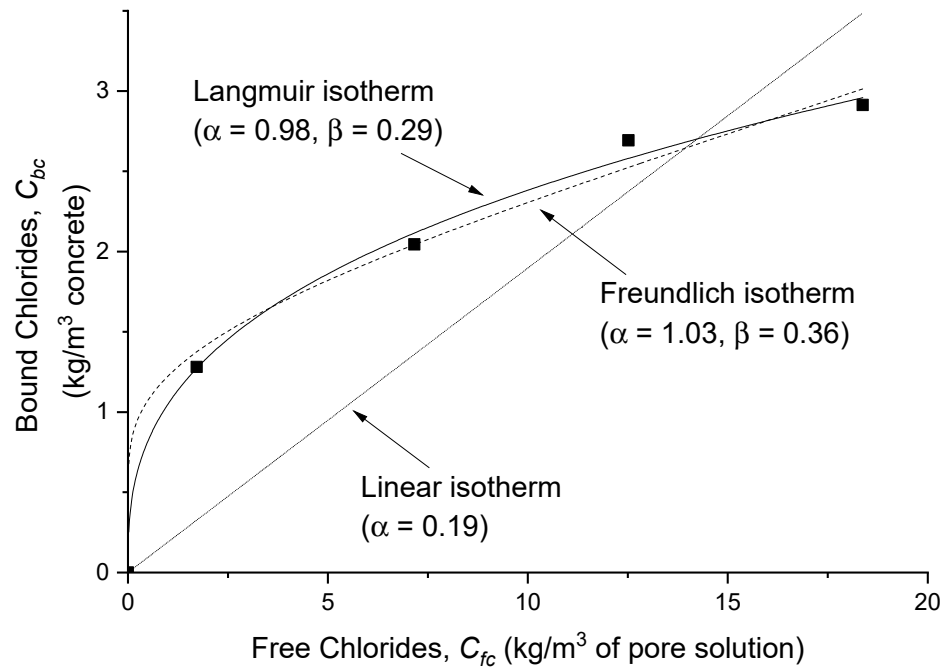
Figure 5. Plots showing linear and non-linear chloride binding isotherms [76].

Freundlich isotherm:

$$C_b = \alpha \cdot C_f^{\beta} \tag{3}$$

Langmuir isotherm:

$$C_b = \frac{\alpha \cdot C_f}{(1 + \beta \cdot C_f)} \tag{4}$$

where α and β are adsorption constants, which vary for different cement types. These constants do not have any physical meaning as they are not material properties but can be used to give an indication of the chloride binding capacities of the cementitious materials [13,40].

The Freundlich isotherm is more applicable at free chloride concentrations higher than 0.01 mol/L, while the Langmuir isotherm is more suitable for free chloride concentrations lower than 0.05 mol/L [59].

The third type of non-linear chloride binding isotherm, the BET isotherm, is usually used in gas adsorption. However, Tang [117] used it to model the relationship between free and bound chlorides, finding a good correlation when the free chloride concentrations were less than 1 mol/L. A modified form of this model (shown in Equation (5)) was also used by Xu [118] (cited in [53]) to describe chloride binding.

$$\frac{c_b}{c_{bm}} = \frac{\alpha \frac{c}{c_s}\left[1 - (1 - \beta)\left(1 - \beta \frac{c}{c_s}\right)^2\right]}{\beta\left(1 - \beta \frac{c}{c_s}\right)\left(1 - \beta \frac{c}{c_s} + \alpha \frac{c}{c_s}\left(1 - \beta \frac{c}{c_s} + \frac{c}{c_s}\right)\right)} \tag{5}$$

2.5. Methods for Determining Bound Chloride Content

There are several methods that can be used for determining the bound chloride content. The choice of a particular method depends mainly on the source of the chloride, i.e., whether internal or external. The methods commonly used are the equilibrium method, pore expression method and leaching method.

2.5.1. Equilibrium Method

This method is based on the principle of equilibrium and is used for determining the binding of external sources of chlorides. It involves immersing cement paste or mortar

samples into chloride solutions of known concentrations, allowing the system to reach equilibrium and then determining the chloride concentration of the solution by potentiometric titration using a silver-nitrate electrode. The bound chloride content is then determined by difference. This method has been used by several researchers [13,22,40,55,59].

The major drawback of this method is the length of time taken for the solution to reach equilibrium, which depends on the nature of the sample. Tang [59] found that it took 10 to 14 days to reach equilibrium for ground paste/mortar samples, with particle sizes ranging from 0.25 to 2 mm, while Tritthart [50] found that it took 1 year for 10 mm-thick paste samples to reach equilibrium. Grinding the samples to smaller sizes can significantly reduce the time it takes to reach equilibrium. However, the grinding process can subject the samples to carbonation or further hydration, which can itself influence the chloride binding capacity. Further, it is important that the homogeneity of the samples is ensured while using this approach, especially for ground samples.

2.5.2. Pore Expression Method

This method can be applied for both internal and external sources of chlorides and involves placing cylindrical specimens on a pore press and applying a load to express the pore solution [56]. Analysis of the pore fluids then reveals the chloride concentration, which is taken as the free chloride concentration. With the free water in the pore solution known, the bound chloride content can be determined. The drawbacks with this method are: (1) pore presses are not readily available and often have to be specially constructed; (2) the quantities of pore solution obtained are sometimes very low, especially for mixes with low w/b [53]; (3) the free chloride content is often overestimated, as some of the bound chlorides are released upon exposure to the high pressure [119].

2.5.3. Leaching Method

This method involves leaching out chlorides from paste or mortar samples. The samples are ground to a powder and mixed with a solvent, after which the chloride content of the mixture is determined. Several variants of this method have been used by researchers [120–122] to determine the free chloride content of paste or mortar samples, and the accuracy of each technique tends to depend on several factors, such as the solvent type, exposure time, temperature, cement type and total chloride content. Arya [122] used ethyl alcohol as a solvent and found it to be inefficient in leaching out the free chlorides. They also used various leaching methods, e.g., 48 h standing at 20 °C, 72 h standing at 20 °C, 6 h continuous stirring and 5 min boiling and allowing to stand for 55 min, and saw that each method was best suited for particular ranges of total chloride content.

3. Resistance of Concrete to External Chloride in the Presence of Sulphate

While the majority of work has focused on understanding chloride binding in isolation from other anions, this is unrealistic in natural environments. Of key importance is the co-existence of chlorides and sulphates, such as found in sea water. Some studies have investigated the effects of the concomitant attack of chlorides and sulphates on cement systems [123–125], with mixed findings. Both chlorides and sulphates react with hydrated aluminate phases to form Friedel's salt and ettringite, respectively. However, in combination, sulphates are preferentially bound to aluminates, leading to reduced chloride binding [71,126,127]. Yet, many factors, including ion concentrations [128,129], cation type [5,73,130], supplementary cementitious materials (SCMs) or type of cement [17,127,131], temperature [132,133], exposure conditions (wetting and drying versus static submersion) [134,135], etc., can affect the dynamics of chloride and sulphate interactions. These factors are discussed further below.

3.1. Effect of Chloride on Sulphate Deterioration

The effects of chloride on sulphate attack of cementitious materials are inconclusive, with various studies suggesting that chlorides may mitigate or accelerate sulphate attack or

have no significant effect [131]. The general consensus is that chlorides mitigate sulphate attack. However, differences in material compositions between different studies have made comparisons difficult. As early as 1956, Kind, as cited in [124], reported that chlorides reduce the rate of sulphate attack in Portland cement systems. However, this was countered by Ben-Yair, as also cited in [124], who argued that chlorides aggravate sulphate attack. A few other studies are highlighted below:

Sotiriadis et al. [131] investigated the effect of mineral admixtures, including natural pozzolana, fly ash and GGBS, on the deterioration of concrete due to thaumasite sulphate attack (TSA) and concluded that the presence of chloride reduced the deterioration of concrete due to sulphate attack when the binder was only limestone cement but was aggravated when limestone cement was combined with mineral admixtures.

Meanwhile, Harrison [125] studied the effect of chlorides present in Portland cement mortar and concrete mixes on their sulphate resistance. Sodium chloride did not have any substantial effect on sulphate attack, while calcium chloride increased the rate of sulphate attack. However, recent findings [15], indicated by Figure 6, showed that sulphate expansion was significantly reduced in the presence of sodium chloride. This discrepancy can be explained by the duration of exposure, with the more recent study showing that the effects of chlorides on reducing sulphate-induced expansion were only visible beyond 65 weeks. This agrees with Hossain [136], in that the concomitant presence of chloride ions in a sulphate environment mitigates sulphate attack of plain and blended cements, attributed to increased solubility of ettringite and gypsum in chloride solutions [132]. This was slightly refined by Al-Amoudi et al. [123], who reported that chlorides mitigated sulphate deterioration in plain cements, but the effect was not great for blended cements incorporating GGBS, fly ash and silica fume.
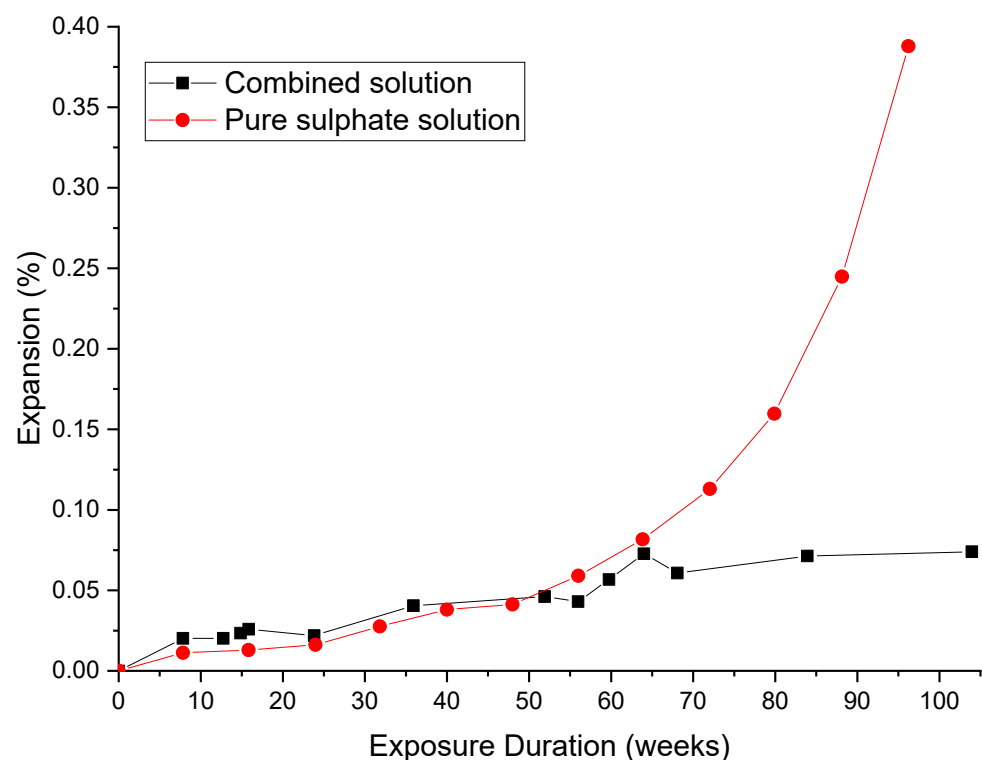

Figure 6. Comparison between expansion of CEM I mortar prisms exposed to pure sulphate [137] and combined chloride–sulphate solution [15].

Further, Abdalkader et al. [128] studied the effect of chloride on CEM I and CEM I blended with limestone filler exposed to sulphate at low temperature (5 ± 0.5 °C) for 630 days and showed that 0.5% chloride in sulphate solution increased damage but that the damage reduced when the chloride concentration was increased to 2%.

Figure 7 shows the changes in compressive strengths between exposure for 1 and 12 months to different combined chloride and sulphate solutions, as extracted from [18]. The chloride solution was kept constant at 3%, while the concentration of sodium sulphate was increased from 3% to 10%. Exposure for 1 month led to no discernable change in compressive strength. However, there was a clear trend, with increasing loss of strength with increasing sulphate concentration. This agrees with [129], where samples exposed to lower concentrations of combined solutions suffered less diminution in compressive strength than specimens exposed to higher concentrations.
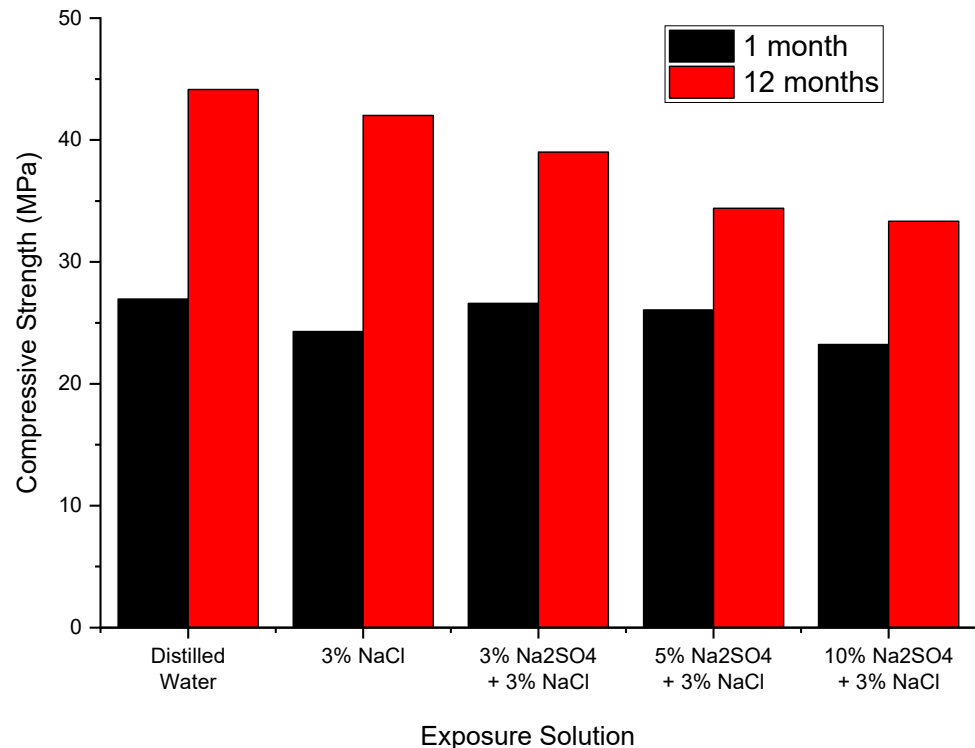

Figure 7. Effects of combined chloride–sulphate exposure on compressive strength of concrete [18].

3.2. Effect of Sulphate on Chloride Binding Capacity

The effect of sulphate on chloride resistance is less controversial than the converse situation discussed above. Sulphates affect the ingress of chloride into concrete at early-age exposure due to the preferential formation of ettringite crystals over Friedel's salt, leading to a compacted microstructure, thereby decreasing chloride ingress [126]. However, at later ages, the trend is reversed, possibly due to excessive formation of expansive ettringite crystals, resulting in cracks that provide channels for rapid ingress of chlorides into concretes [128,138]. It has also been reported that chloride ions penetrate cement matrices faster than sulphate ions do. However, Friedel's salt formation is depleted by incoming sulphates, thereby increasing free chloride levels [139].

The impact of magnesium sulphate on chloride binding in Portland cement paste was also investigated by De Weerdt et al. [140]. They found similar chloride binding in sea water and a NaCl solution, with chloride binding by both C-S-H and AFm phases reducing due to the presence of sulphate in sea water. Similar findings were reported by Xu [72]. However, chloride binding capacity increased with partial replacement of Portland cement by GGBS.

Combined sulphate–chloride exposure has been found to exacerbate reinforcement corrosion. Al-Amoudi and Maslehuddin [141] showed that steel corrosion was greater in combined chloride–sulphate solutions than in either pure chloride or sulphate solutions.

Similarly, Dewah et al. [142] concluded that long-term corrosion current density in chloride solutions increased in the presence of sulphate.

However, although there appears to be a consensus on the effect of sulphate on chloride attack of reinforced concrete, more work must be conducted to better understand the effects of changes in binder composition, effects of SCMs, temperature and exposure to solutions containing multiple compounds.

3.3. Effect of Sulphate on Chloride Diffusion

Table 4 shows data from different studies [15,76] using pure sodium chloride solution and a combined sodium chloride–sulphate solution. Non-steady-state chloride diffusion in plain CEM I and slag-blended mortars decreased due to the presence of sulphate in the attacking solution. As discussed earlier, chloride penetration is reduced due to the preferential reaction of sulphate ions with the aluminates in hydrated cements to form ettringite, thus, filling pores. This condition may not hold for longer-term exposure, as more ettringite formation may lead to expansion and possibly cracking, which, in turn, can increase chloride penetration at later periods [15]. This finding is supported in other studies, which showed lower chloride diffusion in combined solutions than pure chloride solutions [16,143]. The slag-blended cement in [16] contained 50% slag compared to 30% slags used in Ukpata and Ogirigbo. Nevertheless, the trends of chloride diffusion from pure to combined salt solutions remained similar.

Table 4. Comparisons between chloride diffusion in mortars exposed by submersion to pure chloride and combined chloride–sulphate solutions from different authors [15,16,76].

Curing Duration (Days)	20 °C Ogirigbo [76] & Ukpata [15]			20 °C Maes & De Belie [16]			38 °C Ogirigbo [76] & Ukpata [15]		
		D_a (m²/S)		D_a (m²/S)				D_a (m²/S)	
	Binder/Temperature	Pure Cl	Combined	Pure Cl	Combined	Binder/Temperature	Pure Cl	Combined
		($\times 10^{-12}$)	($\times 10^{-12}$)	($\times 10^{-12}$)	($\times 10^{-12}$)		($\times 10^{-12}$)	($\times 10^{-12}$)
7	C1-20 °C	51.50	1.40	-	-	C1-38 °C	44.10	2.03
7	30S1-20 °C	5.41	0.76	-	-	30S1-38 °C	3.56	0.67
28	C1-20 °C	17.50	1.43	5.27	3.72	C1-38 °C	7.92	2.01
28	30S1-20 °C	3.87	0.64	2.94	2.55	30S1-38 °C	2.47	0.94

Note: C1-20 °C = CEM I 42.5R samples cured at 20 °C; 30S1-20 °C = samples with 30% GGBS in CEM I cured at 20 °C, etc.

On the contrary, Cao [144] reported that the presence of sulphate in a combined solution of chloride and sulphate accelerated chloride diffusion in the short term but inhibited chloride diffusion in the long term. These changes may be explained by hydration dynamics and the resultant pore filling, which may inhibit diffusion in the long term [145]. This filling effect was confirmed by Wang [146]. Chen [147] also concluded that the corrosion of iron was aggravated in the presence of sulphate. Still, there are a number of recent studies concerning simultaneous attacks on concretes or mortars by combined chloride and sulphate solution, which did not consider the impacts of chloride and sulphate on each other [148–151].

3.4. Effect of Exposure Conditions

A number of previous studies showed that exposure conditions have significant effects on the deteriorations caused by chloride and sulphate attacks, whether in combination or in isolation. Most studies concluded that cyclic wetting and drying conditions are more devastating than permanent submersion due to the build-up of salts during drying stages [22,134,152,153]. These exposure conditions are well-noted and classified accordingly in the European Specification for concrete EN 206 [25]. However, inconsistencies in compositions of the combined chloride–sulphate solutions, as highlighted in Table 5, make comparisons across different findings difficult. Future studies may consider how this may be resolved.

3.5. Effect of Cation Type

Studies have shown that the resistance of concrete may vary depending on the nature of cation in the attacking compound. For instance, magnesium sulphate in seawater and other sources is more destructive to cements than sodium sulphate, due to the formation of $Mg(OH)_2$ with relatively low solubility and pH. The C-S-H phase becomes destabilized as Ca is substituted for Mg, leading to a lack of cohesion [142,154–156]. Similarly, studies have shown that exposure to $MgCl_2$ and $CaCl_2$ tends to bind more chlorides than exposure to NaCl. This may be attributed to changes in pH of the exposure solution and the chloride binding capacity of the C-S-H phase [55,157].

Table 5. Selected recent studies to highlight differences in binder compositions and methodologies.

Binder Compositions	Methods Employed to Study Chloride Attack	Methods Employed to Study Sulphate Attack	Compositions of Exposure Solutions	References
PC, LS, NP, FA, MK. GGBS		Visual inspection, mass measurements, Compressive strengths, XRD	21.14 g/L Cl + 20 g/L SO$_4$	[131]
PC, SF, FA, GGBS	XRD, Titration		5% Na$_2$SO$_4$, KSO$_4$, MgSO$_4$	[5]
PC, APS, FA		Flexural strength, SEM, XRD, MIP	24,530 ppm-NaCl, 4090 ppm-Na$_2$SO$_4$	[126]
PC	XRF, degree of hydration, chloride binding isotherms, titration, SEM-EDX		MgCl$_2$, NaCl, NaCl + MgCl$_2$, MgSO$_4$ + MgCl$_2$	[73]
PC, GGBS, HSR	Cl diffusion, Cl colour boundary,	mass change, length change, XRD	165 g/L NaCl, 27.5 g/L Na$_2$SO$_4$	[16]
PC, LS filler		Infra-red spectroscopy, XRD, SEM, Mass change	5–20 g/L NaCl, 6 g/L MgSO$_4$7H$_2$O	[128]
PC, 50% GGBS, 30% FA		DME, mass change, XRD, TCC, TGA/DSC, MIP wetting/drying	5% NaCl, 5, 10% Na$_2$SO$_4$	[143]
PC, Portland pozzolana cement	XRD, FTIR, EDX, potentiodynamic polarization		3–7% NaCl, 3–12% MgSO$_4$, Na$_2$SO$_4$	[129]
PC, CAC, GGBS	MIP, XRD, TCC	mass-change, compressive strength,	5% NaCl + 5% Na$_2$SO$_4$	[158]
PC, FA	Titration, TCC, coupled chloride-sulphate diffusion models	Titration, coupled chloride-sulphate diffusion models	10% NaCl + 5% Na$_2$SO$_4$	[145]
PC		Compressive strength, length change, mass change, SEM, EDX, TG(DTG/DSC) and XRD	3–10% Na$_2$SO$_4$ + 3% NaCl	[8]
PC		TCC, XRD, SEM, EDX, MIP	25% NaCl + 5% Na$_2$SO$_4$	[144]
PC	Diffusion, Numerical Model	Diffusion, Numerical Model	0.5% Na$_2$SO$_4$ + 0.4–0.8% NaCl	[159]

Notes: PC—Portland cement; LS—Limestone; NP—Natural pozzolana; FA—Fly ash; MK—Metakaolin; GGBS—Ground granulated blast-furnace slag; SF—Silica fume; APS—Activated paper sludge; HSR—High-sulphate-resistant cement; CAC—Calcium aluminate cement; TCC—Total chloride content; DME—Dynamic modulus of elasticity; FTIR—Fourier-Transform Infrared Spectroscopy; MIP—Mercury Intrusion Porosimetry; XRD—X-ray diffraction; SEM-EDX—Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy; TGA—Thermogravimetric analysis.

4. Concluding Remarks

- The rate of ingress of external chlorides into concrete is dependent on several factors, such as the pore structure of the concrete matrix, curing conditions, w/b ratio, use of supplementary cementitious materials (SCMs) and the chloride binding ability of the cementitious materials in the concrete matrix.
- Chloride binding is beneficial to the durability of a concrete structure in that it removes chloride ions from the pore solution that would have been available to initiate chloride-induced corrosion of the steel reinforcements. Hence, higher chloride binding capacity

of cement leads to reduced risk of chloride-induced reinforcement corrosion. Chloride binding also improves freeze–thaw resistance of concrete in cold weather.

- Chloride binding is influenced by several factors, such as the cement type, alkalinity of the pore solution, cation type of the salt, concentration of chloride solution, temperature, presence of other anions, e.g., sulphates and carbonates, and presence of SCMs in the mix. The increased aluminate contents of SCMs are beneficial to chloride binding. Similarly, increasing C_3A contents in cements improve chloride binding.
- Environmental factors also affect chloride binding, it being reduced at higher pH, in the presence of sodium ions or other anions. Meanwhile, chloride binding increases with the concentration of the chloride solution. The influence of temperature on chloride binding was not clear.
- In exposure to combined chloride–sulphate solutions, the sulphates reduce chloride binding, thus, ultimately leaving reinforcement more susceptible to corrosion. However, in the short term, sulphate ions can hinder chloride penetration due to ettringite formation. Conversely, the presence of sodium chloride tends to mitigate sodium sulphate attack. However, the presence of chloride may worsen $MgSO_4$ attack, especially at low temperatures (around 5 °C).

5. Future Perspectives

- This review focused on chloride binding in the presence of chlorides and combinations of chlorides and sulphates. In reality, other anions may also be present and this is worthy of further investigation.
- With a widening pallet of cementitious binder available to concrete technologists, there is a need to better understand both chloride permeation and chloride binding in these new binders. This need can and should extend to non-Portland cement binders, which were excluded from this review.
- There is a remarkable lack of consistency between simulated accelerated exposure conditions. Harmonization of accelerated exposure standards would be of benefit. These conditions should also take account of the effect of chloride concentration and additional ions on chloride binding.

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