



Effect of Combined Sulfate-Chloride Attack on Concrete Durability-A Review

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ABSTRACT: Chloride and sulfate ions damage the reinforced concrete in marine environment due to the corrosion and formation of expansive products, respectively. Interaction of chloride-sulfate ions on concrete deterioration is very complicated. Little research has been conducted in this respect.

In this study, the effect of chloride ions on sulfate attack and effect of sulfate ions on chloride attack were reviewed. According to the results, contradictory reports were observed in studies. However, most of the researchers believed that chloride ions mitigate the sulfate attack in combined chloride- sulfate solutions. On the other hand, regarding the influence of sulfate ions on chloride attack, some of the researchers reported the mitigating effect, but others referred to the accelerating effect. Tricalcium aluminate (C_3A) content, water to cement ratio (w/c), duration of submerging, corrosive ions concentrations, cation type, type of pozzolan and its replacement are important parameters that could affect the concrete performance against combined chloride-sulfate solution.

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1- Introduction

Almost all the researchers in the field believe that chloride/sulfate deterioration is the most serious problem for serviceability of concrete structures especially in marine environments [1]. Regarding the mechanism of sulfate attack, it should be noted that in the presence of the calcium hydroxide, when the latter comes in contact with sulfate ions, the alumina containing hydrates are converted to the high sulfate form of ettringite. Ettringite crystals grow, expand, or swell by mechanisms, which are still the subject of controversy among researchers. While there is an agreement that most ettringites will expand in this formation, the exact causes are not agreed. The excessive expansion, cracking, delamination and loss of strength can be the results of sulfate attack.

About the mechanism of chloride attack, when chloride ions reach the steel, they depassivate the area surrounding the steel and in the presence of water/air, the steel commences to corrode. The products of corrosion are greater in volume (up to 600%) than the original steel resulting in an expansion and later spalling of the concrete [2].

In the combined attack, the mechanism which leads to the deterioration is so complicated. Stroh et al. [3] summarized the mechanism of the combined sulfate-chloride attack: i) Fast ingress and binding of chloride ions by alumina, resulting in Friedel's salt formation ii) Sulfate ions from the solution react partly with portlandite forming gypsum and lowering the pH; iii) A lower pH value leads to the depletion of Friedel's salt, and iv) Excess sulfate ions form ettringite.

Therefore, it is necessary to study the combined effect of these two phenomena. In this study, the effect of chloride ions on sulfate attack and vice-versa, the effect of sulfate on chloride attack on concrete durability were studied.

The degree to which this combined attack can occur depends on water penetration of specimens, the kind of chloride and sulfate salts and their concentrations, the cation type, the chemistry of the binder present, the exposure time and the type of pozzolan and its replacement. These effective parameters discussed during the article.

2- Effect of chloride ions on sulfate attack

Song et al. [4] believed that the chloride binding capacity of concrete in natural diffusion process is a complicated function concerning many factors, among which the cation type and the contact duration are significantly important. Al-amoudi et al. [5] reported that the increase in solubility of calcium aluminate hydrate led to the formation of non-expansive crystals in sulfate attack process. They also concluded that transformation of aluminate hydrate phase to calcium chloroaluminate such as Friedel's salt reduced ettringite formation. Harrison [6] believed that monosulfate reaction due to ettringite formation is slow and this might be due to substitution of sulfate by chloride ions in the structure of monosulfate which leads to a modification of the morphology of ettringite.

Due to different ionic mobility's and ion valences, chloride ions penetrate into cement matrix faster than sulfate ions. For this higher penetration, chloride ions could react with tricalcium aluminate of cement paste to make Friedel's salt

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which leads to the reduction of products formed, including ettringite, gypsum and thaumasite [1].

Moon et al. [7] performed long-term experiments to evaluate the resistance of Ordinary Portland Cement (OPC) with different C_3A contents and silicate ratios against chloride solutions. They reported that the structure of cement matrix would be maintained safely against Friedel's salt.

Al-amoudi et al. [8] believed that the effect of chloride ions on magnesium sulfate attack was not significant and it might be due to the conversion of cementitious C-S-H gel to non-cementitious M-S-H form not affected by chloride ions. Al-amoudi et al. [9] investigated the effect of sulfate and combined chloride-sulfate solutions on expansion and strength reduction of mortar specimens. They reported that the presence of chloride ions in sulfate solution mitigated the sulfate attack on OPC and blended cement specimens. They observed that sulfate destruction in cement specimens with 3.5% C_3A content (Type V cement) did not significantly differ from specimens contained 8.5% C_3A content (Type I cement).

Partial cement replacement with fly ash performed better than OPC, silica fume and slag to delay sulfate attack. In this investigation, OPC generally performed better than the blended cement against magnesium sulfate attack. Authors represented that more destruction observed in silica fume and slag specimens could be related to the reaction between Mg^{2+} and C-S-H phase. They believed that in the absence of calcium hydroxide, magnesium cation directly reacts with cementitious C-S-H gel and converts it to non-cementitious M-S-H gel. However, the blended cement performance depends on the type of pozzolan used.

They evaluated the effect of water to cement ratio on sulfate attack of mortar specimens in both sulfate and combined sulfate-chloride solutions. They observed that strength reduction and expansion of 0.5 w/c mortar specimens prepared with Type I and Type V cements were 42 and 48% and 0.106 and 0.093%, respectively. These values increased to 48 and 54%, 0.114 and 0.096% when the water to cement ratio reduced to 0.35. Figure 1 shows the details for type I cement with 0.5 w/c mortar specimens.

They indicated that the performance of lower w/c ratio (w/c = 0.35) was observed to be inferior to the performance of the same cement made with a higher w/c ratio (w/c = 0.5). In type I and V cements for both w/c of 0.35 and 0.5, the presence of chloride ions in sulfate solution mitigated the results of expansion and strength reduction. Ben-Yair [10] also reported the same results; He subjected mortar specimens with w/c of 0.35 to combined solution of 3.5% sodium chloride and 0.4% sodium sulfate for more than eight years and observed that its expansion was more than that in specimens with w/c of 0.5. This might be due to the fact that expanded products formed from the reaction between cement and sulfate salts, do not accommodate with finer pore structure, while a mixture of coarser pore structure has a better compatibility with expanded products. Chiker et al. [11] reported that the influence of chloride on increasing sulfate attack is more significant for high and middle w/c concretes, while it is negligible for low w/c ratio concretes.

Maes et al. [12] investigated the effect of combined sulfate-chloride solutions on four mix designs (OPC, sulfate resistance and slag cements with 50 and 70% replacement) by monitoring mass and length changes. Water cement ratio

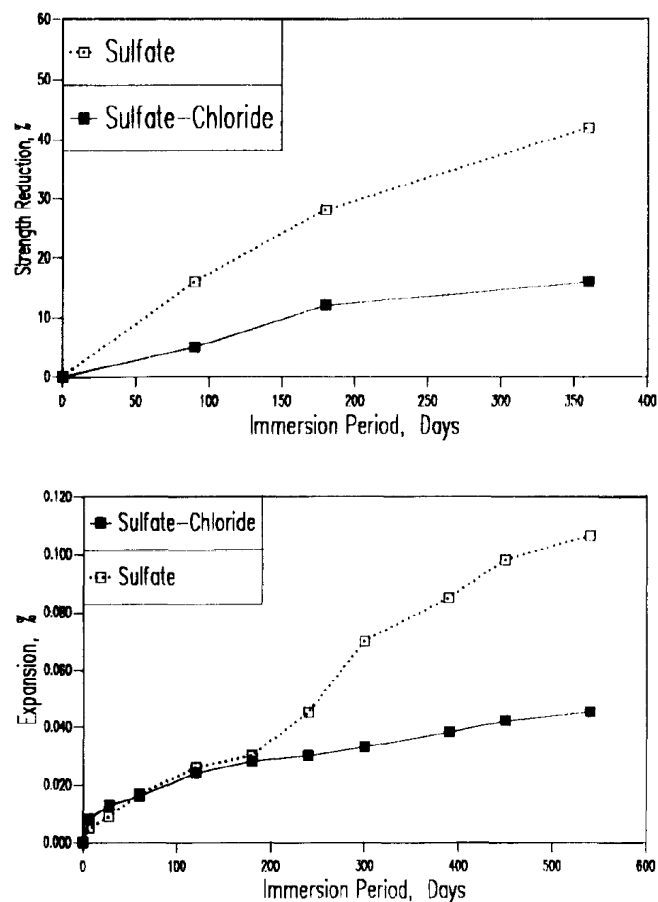


Fig. 1. Strength reduction (up) and Expansion (down) of mortar specimens (with type I cement and 0.5 w/c) subjected to sulfate and combined sulfate-chloride solutions [9]

of 0.45 was selected for all specimens. They prepared 50 g/l Na_2SO_4 as a reference and 50 g/l Na_2SO_4 + 50 g/l NaCl as a combined chloride-sulfate solution to evaluate the effect of chloride ions on sulfate attack. They reported that chloride ions mitigated the sulfate attack in the combined solution. Sulfate deterioration in presence of chloride ions was delayed. Both chloride and sulfate ions were bounded to form ettringite, gypsum and Friedel's salt. But the production of chloride reaction; Friedel's salt, was not stable in the presence of sodium sulfate [13]. Therefore, it is assumed that when Friedel's salt vanished and this mitigating effect disappeared, more ettringite and gypsum formatted and destruction started. They reported that when mortar specimens subjected to combined sodium sulfate-sodium chloride solution, although more ettringite existed, no deterioration observed. This might be for the less content of gypsum. They believed that destruction under sulfate attack occurred when both ettringite and gypsum existed together. Therefore, the observation of a destruction in specimens subjected to just sodium sulfate solution could be for the existence of the mentioned material together. Kunther et al. [14] approved this issue. Maes et al. [12] believed that chloride ions had neither positive nor negative impact on sodium sulfate attack in slag mortar specimens. Slag mortar had a high resistance against sodium sulfate attack. They observed no significant changes in mass or expansion of specimens subjected to sodium sulfate solution.

Lee et al. [1] subjected mortar specimens to sodium sulfate

and combined sodium sulfate-sodium chloride solutions for 510 days. Sulfate ions concentration was 33800 ppm and sodium chloride content was 3.5%. Effect of silica fume and water to cement ratio was studied. The visual investigation, compressive strength, expansion measurement, X-ray diffraction (XRD) and also mercury intrusion porosimetry (MIP) were used for better identification. Results indicated that the presence of chloride ions in sulfate solutions mitigated the destruction of OPC mortar specimens caused by sulfate attack especially for high water to cement ratios. In this respect, they represented the following objectives:

- Increase in solubility of ettringite and gypsum in combined chloride-sulfate solution led to the reduction of sulfate products in cement paste.

- Formed ettringite in combined chloride-sulfate solution had less expansion.

- More diffusion rate of chloride ions in comparison to sulfate ions, led to the reduction of common sulfate attack due to the reaction of chloride ions with C₃A in cement paste and formation of Friedel's salt.

Results indicated the appropriate performance of silica fume. They reported that usage of silica fume (even low dosage), had a beneficial effect on prevention the surface destruction and compressive strength reduction and also a high mortar expansion. Strong pozzolanic reaction and less calcium hydroxide formation caused silica fume performed well. They reported that after 510 days submerging to the corrosive solution, in sulfate solution, high water to cement ratio caused a severe destruction. In specimens subjected to combined chloride-sulfate solution, destruction was lower than that in a sulfate solution. In specimens containing silica fume, destruction was not sensible.

Zhang et al. [15] studied the expansion of concrete against sulfate-chloride solutions. They believed that the higher concentration of sulfate ions led to the greater expansion and the more severe damage in the concrete. They also reported that the presence of chloride ions can reduce sulfate attack. They finally proposed a theoretical expansion model on the assumption that concrete may be treated as a porous visco-elastic material. Delayed ettringite and gypsum are considered as main causes of internal expansion in this research.

Mavropoulou et al. [16] studied the durability evaluation of cement exposed to combined chloride-sulfate ions. They represented that in all cases the chloride ions mitigated the external sulfate attack, a fact that was mainly attributed to the Friedel's salt formation. They also believed that the addition of limestone filler led to the durability increment.

3- Effect of sulfate ions on chloride attack

The accurate roll of sulfate ions on reinforcement corrosion caused by chloride ions is unknown yet. The presence of both sulfate-chloride ions would have a significant effect on reinforcement corrosion [17]. Dehwah et al. [17] subjected the OPC (type A with 8.5% C₃A and type B with 9.65% C₃A) and Sulfate Resistance (with 3.6% C₃A) specimens to combined corrosive solutions (5% NaCl by adding 1, 2.5 and 4% Na₂SO₄) for 1200 days. They reported that time of initiation of chloride-induced reinforcement corrosion is affected by cement type and its C₃A content. They observed that time of initiation of corrosion in OPC was longer than that in SR specimens. Corrosion current density decreased by increasing C₃A content. Higher surface resistivity observed

in OPC in comparison to SR may be attributed to high C₃A content which led to the increase of chloride binding. To evaluate the effect of cation type, similar solutions were made with magnesium sulfate salt. Results showed that the presence of sulfate ions in chloride solution and the cation type did not have a significant effect on the time of initiation of chloride-induced reinforcement corrosion. However, by increasing sulfate concentration, corrosion rate increased, as well. Magnesium-based sulfate in combined solution led to a higher corrosion rate caused by chloride in comparison to sodium based sulfate. In this investigation, corrosion current density in specimens subjected to combined sodium chloride- sodium sulfate was 1.1 to 2 times more than that in just sodium chloride solution. Corrosion current density increased with the increase of magnesium concentration to 2.5% SO₄⁻². This increase was 1.1 to 2.2 times more than that in specimens subjected to just sodium chloride. 4% SO₄⁻² in magnesium sulfate devoted less corrosion current density in comparison to 2.5% SO₄⁻². Corrosion current density also increased with time developing. About corrosion potential, all specimens had more negative potential at earlier times. Time developing led to the reduction of corrosion potential. In general, all specimens after 150 to 180 days submerging in solutions, had almost a constant corrosion potential. For example, corrosion potential in OPC specimens (type A with 8.5% C₃A) which submerged in sodium chloride and sodium sulfate had a similar trend such as SR specimens (with 3.6% C₃A). Long-term performance in corrosion potential test devoted more stability to specimens subjected to sodium based in comparison to magnesium-based sulfate.

Little investigation was carried out about the effect of sulfate attack on the stability of bound chlorides [18]. Brown and Badger [13] investigated the distribution of chloride and sulfate binding on the specimens subjected to magnesium sulfate, sodium sulfate and sodium chloride attack. They reported that in some concrete specimens, secondary ettringite was extensively observed in absence of gypsum.

Geng et al. [18] investigated the stability of bound chlorides in cement paste against sulfate attack. They prepared cement paste with/without pozzolan (30% fly ash, 30% slag, combined 15% fly ash plus 15% slag and 21% fly ash plus 9% slag) replacement and subjected them to 5% sodium sulfate and 5% magnesium sulfate solutions. Due to the reduction of experiment time, chloride binding was made with usage of 0.5 mol/l sodium chloride as the mixing water. The w/c of 0.5 was selected for all specimens. In this investigation, mechanisms of the release of bound chlorides obtained based on X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and differential thermo gravimetric analysis (DTG). Results showed that the stability of bound chlorides was significantly susceptible to sodium sulfate attack. Before 28 days of submerging, most of the bound chlorides released due to the sodium sulfate attack. They reported that magnesium sulfate attack could induce the release of bound chlorides, but the stability of bound chlorides was less susceptible to magnesium sulfate in comparison to sodium sulfate attack. This is relatively due to the low pH in pore solution and also the blocking effect of brucite on ionic transport. Friedel's salt dissection procedures in which chloride ions are substituted for sulfate ions, has a key role in releasing bound chlorides not only under the attack of sodium sulfate but also in magnesium sulfate attack. The final product originated

from Friedel's salt is secondary ettringite. Stability of bound chlorides caused by C-S-H gel was not susceptible to sodium sulfate attack. In magnesium sulfate attack, bound chlorides released from cementitious C-S-H gel due to the convert to non-cementitious M-S-H form. Whereas bound chlorides caused by C-S-H gel was less than that in Friedel's salt, the effect of C-S-H gel on the stability of chloride binding was not significant. At the same standard curing condition, the mass ratio of bound chlorides to initial total chlorides (RCI) increased with the decreased proportion of fly ash to slag. This parameter in blended cement was higher than that in OPC. On the other hand, as curing time developing, bound chlorides content increased, but, the rate of that reduced with time. Although the usage of fly ash and slag could promote the concrete ability in the aspect of chloride binding, the stability of Friedel's salt in pozzolanic specimens (slag and especially fly ash) was more susceptible to sodium sulfate attack. This might be for a drop in alkalinity of pore solution because of pozzolanic reaction. However, the usage of these pozzolans in concrete can resist the penetration of sodium sulfate and therefore, reduce the attack of sodium sulfate on the stability of bound chlorides. Other researchers also reported that the usage of fly ash and slag in concrete not only promotes the capacity of chloride binding but also leads to the resistance of the concrete against sulfate attack [19, 20].

Weerdt et al. [21] evaluated the effect of sulfate and magnesium on chloride binding. Hydrated cement paste subjected to magnesium chloride, sodium chloride, combined sodium chloride-magnesium chloride, combined magnesium sulfate-magnesium chloride and also artificial seawater solutions at 20°C. Isotherms of bound chlorides and pH content were measured in this investigation. Chloride binding behavior of OPC pastes in different solutions was the same as each other except for specimens subjected to magnesium chloride solution. In these solutions, bound chlorides remained constant (0.0005 g chlorides in a gram of hydrated cement paste) by increasing chloride ions concentration. However, in specimens subjected to magnesium chloride solution, by increasing chloride ions concentration, bound chlorides continuously increased until 0.02 g chlorides in a gram of hydrated cement paste for an added solution with 2.5 M chloride.

The sodium chloride, combined sodium chloride-magnesium chloride and also artificial sea water solutions resulted in a slight increase of the pH content for chloride concentrations of the added solutions of 0.5 M. In the higher concentration added solutions, a gradual decrease of the pH content was observed. The presence of magnesium chloride in combined sodium chloride-magnesium chloride caused a higher decrease in the pH content in comparison to sodium chloride solution. pH obtained for artificial seawater solution classified between sodium chloride and combined sodium chloride-magnesium chloride. Magnesium chloride and combined magnesium chloride-magnesium sulfate led to a notable pH decrease in all specimens (see Figure 2).

Magnesium content in seawater solution led to the reduction of pH content and consequent increase in the chloride binding by augmenting the chloride uptake in the C-S-H. But magnesium content in seawater is limited. Therefore, a slight decrease in pH does not result in a significant increase of the chloride binding in comparison to, for example, sodium chloride exposure. It seems that the presence of sulfate

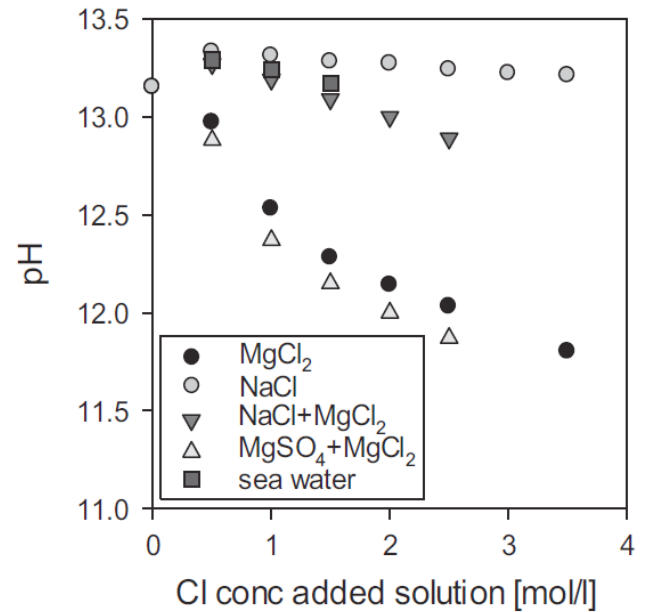


Fig. 2. pH of the supernatants as a function of the chloride concentration of the added solutions [21]

in seawater could reduce bound chlorides and C-S-H in hydrated cement paste incorporate more sulfate ions instead of chloride ions when subjected to combined magnesium sulfate- magnesium chloride.

Xu et al. [22] investigated the release of bound chlorides on OPC and blended cement. They used silica fume, fly ash and slag with 10, 30 and 50% replacement with cement, respectively. 0.22, 0.32 and 0.42 were the water to cement ratios which sodium chloride in 0.5, 1, 1.5 and 3% cement weight was used as mixing water. They prepared solutions with 5% sodium sulfate, potassium sulfate and magnesium sulfate as corrosive solutions. They concluded that chloride binding increased with the increase of both w/c and total chloride content. They observed that silica fume led to decrease and fly ash and slag led to the increase of chloride binding. Chloride binding pretty released with sulfate attack. Released chlorides were affected by w/c, total chloride content, pozzolan and type of cation. The release of bound chlorides generally decreased by increasing w/c and increased by increasing total chloride content. Replacement of cement by silica fume, fly ash and slag reduced the release of bound chlorides. In this respect, silica fume devoted the best performance to prevent the release of bound chlorides. Magnesium sulfate led to the less release of bound chlorides in comparison to sodium sulfate and potassium sulfate. In sulfate attack procedures, conversion of Friedel's salt to ettringite caused the release of bound chlorides. They presented the corrosion risk with Cl-/OH- indicator. The ultimate corrosion risk in sodium sulfate attack was sequenced as: reference < 50% slag < 30% fly ash < 10% silica fume specimens. Potassium sulfate < sodium sulfate < reference < magnesium sulfate, signed the sequence of corrosion risk related to the subjected solution type.

Maes et al. [12] investigated the effect of sulfate ions on chloride attack. They prepared four mix designs (OPC, sulfate resistance (SR) and slag cements with 50 and 70% replacement) with constant w/c of 0.45. The reference solution was 165 g/l NaCl. Adding 27.5 and 55 g/l Na₂SO₄ to reference made the first (Comb 1) and the second (Comb 2) combined

solutions. They reported that free chloride penetration in OPC concrete increased with the increase of sodium sulfate content for 7 to 14 weeks subjected to corrosive solutions. In SR concrete, chloride penetration depth in combined solution stayed stable or slightly decreased. After 7 weeks submerging in Comb 2 solutions, chloride penetration depth in SR was lower than OPC, but this condition vanished with the longer time exposure (about 14 weeks). In general, cement replacement by slag promoted the resistance of mortar/concrete against chloride penetration and sulfate attack. In slag cement specimens similar results observed; chloride penetration depth increased with the presence of sodium sulfate.

Tumidajski et al. [23] investigated the effect of sulfate on chloride penetration and diffusion in OPC and specimens with pozzolan (5% slag and a slight silica fume) replacement for about 60-month exposure. 4.95 g/l NaCl used as a reference and 4.95 g/l + 22.19 g/l Na₂SO₄ used as a combined solution. According to the results, sulfate ions led to the decrease of chloride penetration and diffusion in OPC. However, in slag cement, these parameters were slightly increased. Table 1 shows the penetration results until 60 month submerging.

Table 1. Chloride ions penetration of type 1 cement (concrete 1) and pozzolanic cement (concrete 2) specimens subjected to Na₂SO₄+NaCl (bath 1) and NaCl (bath 3) solutions [23]

| Time (Months) | Bath 1 | | Bath 3 | |
|---------------|------------|------------|------------|------------|
| | Concrete 1 | Concrete 2 | Concrete 1 | Concrete 2 |
| 3 | 0.18 | 0.34 | 1.50 | 0.32 |
| 6 | 0.81 | 0.26 | 1.75 | 0.18 |
| 9 | - | 0.37 | 1.67 | 0.19 |
| 12 | 1.02 | 0.42 | 1.42 | 0.15 |
| 16 | 1.15 | 0.65 | 1.62 | 0.17 |
| 20 | 0.95 | 0.44 | 1.32 | 0.15 |
| 24 | 1.10 | 0.40 | 1.62 | 0.15 |
| 28 | 1.45 | 0.50 | 1.94 | 0.11 |
| 34 | 1.53 | 0.63 | 1.98 | 0.21 |
| 46 | 2.05 | 0.54 | 2.10 | 0.42 |
| 60 | 2.03 | 0.64 | 2.30 | 0.52 |

unit: centimeter

Shaheen et al. [24] investigated the effects of sulfate ions and associated cation type on reinforcement corrosion in the presence of chloride ions. They observed that Na₂SO₄ mitigated the chloride attack whereas MgSO₄ stimulated this effect. They also reported a better performance of OPC against magnesium oriented sulfate attack than the pozzolanic cement whereas contrary results were reported for sodium oriented.

Shaheen et al. [25] investigated the effect of chloride and combined chloride-sulfate ions on corrosion of reinforcing steel in electrolytic concrete powder solution. They prepared the powder solution with OPC and PPC. Sodium chloride and sodium sulfate were used as corrosive ions. Results showed that PPC specimens had a more compressive strength than OPC in both chloride and combined chloride-sulfate contaminated concrete. In all specimens, more compressive

strength was devoted to chloride contaminated concrete as compared to that in combined chloride-sulfate contaminated concrete. According to the polarization results, the passivity range of steel reinforcement decreased with the increase in free chloride ion concentration. Sulfate ions mitigated the effect of chloride ions in reducing the passivity range of steel. The range of passive zone was less in PPC as compared to that in OPC which is attributed to a lower chemical chloride binding in PPC than that in OPC.

Liu et al. [26] used electromechanical measurements to investigate the corrosion behavior and determine chloride threshold value (CTV) of reinforcement subjected to chloride and sulfate attack in simulated concrete pure solution. They represented that electrochemical measurements were effective in detecting corrosion behavior of steels. The concomitant presence of chloride and sulfate ions led to higher corrosion current density which indicated sulfate ions accelerated the corrosion of reinforcing steels.

Kato et al. [27] investigated the effect of reaction between sulfate ions and cement hydrate on changes in chloride ions penetration. According to the results, sulfate ions mitigated the chloride penetration depth in mortar specimens with w/c of 0.5 until 476 days submerging. But chloride penetration increased at 476 to 792 days submerging. Filling the pores by deposition of calcium sulfate dihydrate (resulted in reaction of cement hydrate and sulfate ions) was the probable reason reported for the mitigating effect and increase in released chloride ions (by observing a gradual decrease in Friedel's salt and therefore decrease in chloride binding) was the probable reason reported for the mentioned destructive effect of combined chloride-sulfate solution. They also represented that the presence of magnesium in combined chloride-sulfate solution led to a higher chloride penetration depth after 476 and 792 days submerging in comparison to sodium. Figure 3 shows the results of this investigation.

Zuquan et al. [28] investigated the interaction between sulfate and chloride attack. 3.5% NaCl, 5% Na₂SO₄, and a combined solution of 3.5% NaCl and 5% Na₂SO₄ used as a corrosion solution. Naturally, immersion (stored in corrosion solution for long duration) and drying-immersion cycles were the corrosion regimes employed in this study. They used fly ash as cement replacement (20 and 30%). They reported that a presence of sulfate in the combined solution increased the resistance to chloride ingress into concretes at early exposure period, but the opposition was observed at latter exposure period. They also represented that addition of fly ash may significantly improve the resistance to chloride ingress into concretes and the resistance to sulfate erosion when a suitable amount of fly ash addition and low water to cement was employed.

Merida et al. [29] also evaluated the chloride permeability of the pozzolanic concrete cured in sulfate solutions. They resulted that the use of natural volcanic replacing 5% by the weight of cement in the mixture of high-performance concrete influences positively the durability specimens concrete cured in sulfate environment.

Ramezani pour et al. [30] investigated the effect of sulfate ions on chloride attack with the preparation of standard mortar with cement replacement of 7.5% silica fume and 17.5% trass a natural pozzolan. They used penetration profile, rapid chloride migration, and half-cell potential tests until 180 days submerging to corrosive solutions. They finally reported that

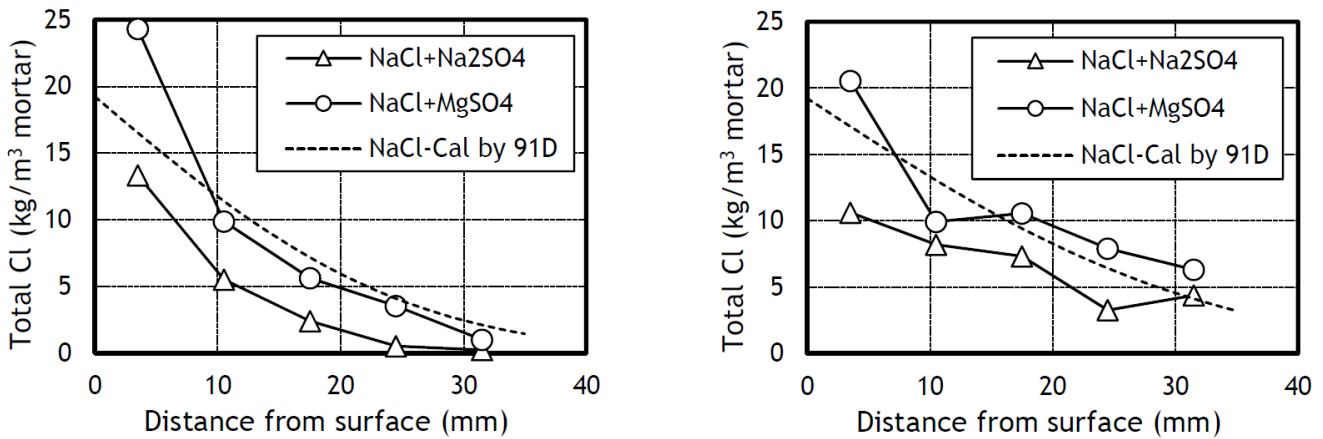


Fig. 3. Chloride ions concentration distribution (up: 476 days, down: 792 days) [27]

chloride ions penetration in the presence of sulfate decreased in the control samples. However, in silica fume samples a slight increase in chloride penetration was observed. For trass samples, a lower concentration of sodium sulfate (27.5 g/l) reduced the chloride penetration while the higher concentration (55 g/l) led to the increase of chloride penetration in these specimens. Due to the investigation of the effect of cation type associated with sulfate salt, magnesium and sodium were

products in combined solution and eventually reduction of ettringite and also the reduction in accessibility of sulfate ions to C_3A by chemical binding to Friedel's salt formation are the mentioned causes.

- In respect to the effect of sulfate ions on chloride attack, some researchers believed that the presence of sulfate accelerates the chloride attack. Less chloride binding and the release of bound chlorides in the presence of sulfate would

Table 2. General summarization of the reports

evaluated. According to the results, more negative of half-cell potential and higher chloride penetration devoted to samples submerged in combined solution with magnesium-based sulfate salt. The surface electrical resistivity of specimens was measured until 200 days curing in lime water. According to the results, the surface electrical resistivity of silica fume samples was about 5 times more than the control. For trass samples, results were better than the control. According to AASHTO [31], chloride penetrability of these specimens was classified in very low, low and moderate for silica fume, trass and the control specimens, respectively. They reported that chloride penetration profiles represented a regular behavior despite the probable irregular shape of the capillary voids.

4- Discussion

Although the coupled effect of sulfate-chloride attack has been investigated under laboratory condition, field conditions are more complicated [32], However, regarding the combined effect of chloride-sulfate ions on the durability of concrete, reports of researchers are summarized in Table 2.

5- Conclusion

- In general, C_3A content in cement has a key role in the mechanism of sulfate attack on chloride binding behavior. Increase in C_3A content could be effective in reducing reinforcement corrosion due to binding the chloride ions in form of Friedel's salt. On the other hand, increase in C_3A accelerates the sulfate attack as well. Therefore, it seems that cement used in specimens subjected to combined chloride-sulfate solutions should have an optimum content of C_3A to be effective in mitigating sulfate attack and also resist against reinforcement corrosion.

- Generally, most of the researchers believed that chloride ions mitigate the sulfate attack. Increase in solubility of sulfate

be the causes. However, others reported the mitigating effect. Contradictory results indicate that some parameters such as exposure time, cement composition, type of pozzolan and its replacement, corrosive ions concentrations, cation type, etc. would affect the results.

- As mentioned, chloride ions mitigate the sulfate attack and sulfate ions would accelerate or mitigate the chloride attack. It should be noted that deterioration of concrete caused by the interaction of these destructive ions. Therefore, investigating the effect of each salt on the other one separately, could not represent the performance of concrete subjected to combined solutions. In this respect, both chloride and sulfate experimental evaluation should be considered together to ensure that concrete structures perform well in combined corrosive environments.

- Cation type associated with salts is another parameter that affects the behavior of combined solution. Most of the researchers believed that magnesium cation is more corrosive than the sodium due to low alkalinity and loss of cohesion in samples.

- Pozzolanic materials with the formation of secondary silicate gel and reducing permeability would be appropriate to produce a resisting concrete mixes. Results showed that although the usage of some pozzolanic materials would increase chloride penetration in combined chloride-sulfate solutions, the concentration of chloride in those specimens was generally lower than the control specimens. Therefore, the usage of appropriate pozzolanic material with suitable dosage replacement is suggested in the combined solutions.

| Objects | Results | Description |
|---|--|--|
| Effect of chloride ions on sulfate attack | Mitigating effect [1, 5-6, 8-9, 12, 15, 33-34] | - Less accessibility of sulfate ions to hydrated C3A due to the higher penetration rate of chloride ions and reaction with C3A to bound chlorides in form of Friedel's salt reduces sulfate attack, - Increase in solubility of ettringite in chloride solutions causes less ettringite formation. - Less strength reduction and less expansion observed in combined chloride-sulfate solutions. - Substitution of chloride ions for sulfates in monosulfate structure modifies the morphology of ettringite. |
| Effect of sulfate ions on chloride attack | Accelerating effect [12, 16-18, 21, 26-28] | - Some authors believed that sulfate ions lead to the increase of chloride attack due to reduction in chloride binding and the increase in the release of bound chlorides in the presence of sulfate. |
| | Mitigating effect [23-24, 27-28, 30] | - Other researchers reported the mitigating effect of sulfate on chloride attack. Filling the pores with the deposition of products of sulfate reactions is reason reported. - Exposure time, the composition of the cementitious material and cation type are important parameters in this respect. |
| Effect of cation type | More corrosive effect of magnesium [17, 27, 30, 35] | - Magnesium cation associated with sulfate leads to the convert of cementitious C-S-H gel to non-cementitious M-S-H form. The low alkalinity of solution contained magnesium and loss of cohesion in concrete would be the reasons for the more corrosive effect of magnesium in comparison to sodium. Higher corrosion density and more negative half-cell potential observed in NaCl+MgSO ₄ in comparison to NaCl+Na ₂ SO ₄ solution. |
| | Different results [18, 22] | - A few researchers reported different results: stability of bound chlorides was less susceptible to magnesium in comparison to sodium or less release of bound chlorides in presence of magnesium cation due to the low pH in the pore solution and the blocking effect of the brucite on ionic transport. |
| Effect of pozzolans | Inconsistent results: - Generally, satisfactory results - Other results [9, 18, 22-23, 30] | - In general, adding pozzolanic material to cement leads to the reduction of permeability of specimens. Most of the investigations indicated the satisfactory results of blended cement specimens against combined chloride-sulfate environments. In this respect, contradictory results in the performance of blended cement were reported. However, kind of pozzolan and its replacement is so important in this respect. - More susceptible of Friedel's salt to sodium sulfate attack, alkalinity reduction, weaker performance in magnesium sulfate, high corrosion risk or increase the chloride ions penetration in combined solution are the issues indicated that blended cement would be performed weaker than the control. But there is no consensus on this matter. |

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