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Mechanism of sulfate attack: a fresh look
Part 2. Proposed mechanisms

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Abstract

The first paper in this two-part series [Cem. Concr. Res. 32 (2002) 915] summarized the experimental results from a comprehensive research study on sulfate attack. The current paper utilizes these results to develop models for the mechanism of attack resulting from sodium and magnesium sulfate solutions. Implications of changing the binder constituents or the experimental variables, such as concentration and temperature of the solution on the proposed mechanism, are also discussed. The potential of these mechanistic models for use in service life prediction models has also been identified.

According to the proposed mechanism, the attack due to sodium sulfate solution progresses in stages. The expansion of an outer skin of the specimen leads to the formation of cracks in the interior region, which is chemically unaltered. With continued immersion, the surface skin disintegrates, and the sulfate solution is able to react with the hydration products in the cracked interior zone leading to the deposition of attack products in this zone. Now, this zone becomes the expanding zone, leading to further cracking of the interior of the mortar.

In the case of magnesium sulfate solution, a layer of brucite (magnesium hydroxide) forms on the surface of the mortar specimen. The penetration of the sulfate solution then occurs by diffusion across this surface layer. As the attack progresses, the formation of attack products such as gypsum and ettringite in the paste under the surface leads to expansion and strength loss. The expansion also causes cracking in the surface brucite layer, and this leaves the mortar susceptible to direct attack by the magnesium sulfate solution. Conditions favorable for the decalcification of calcium silicate hydrate (C-S-H) are thus created, and the ultimate destruction of the mortar occurs as a result of the conversion of C-S-H to the noncementitious magnesium silicate hydrate (M-S-H).

Keywords: Microstructure; Durability; Sulfate attack; Modeling; Mechanism

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1. Introduction

The ASTM E 632-82 [2], or the “Standard Practice for Developing Accelerated Tests to Aid Prediction of the Service Life of Building Components and Materials”, outlines a systematic approach to service life prediction. The standard calls for the identification of needed information, development of accelerated tests, interpretation of data, and the reporting of results. The standard was developed primarily to stipulate the requirements of accelerated tests for building materials. One of the basic assumptions involved in this standard is that the mechanisms involved should be similar in the laboratory and the field. However, this is not always the case with concrete durability problems, especially in the case of sulfate attack. The aspect of modeling the phenomenon of sulfate attack thus becomes complicated.

Researchers have attempted to study sulfate attack effects using diffusion-based models. However, the rates of damage associated with sulfate attack defy the predictions made from such models. Atkinson and Hearne [3] incorporated expansion data from sulfate attack experiments into an overall mechanistic model for sulfate degradation in which the criterion for disruption was the accumulation of a critical amount of stored elastic energy in the reaction zone. According to these investigators, the mechanistic model was more reliable compared to the diffusion-based models, which omit mechanical effects. Moreover, the observed

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degradation in the experiments was found to be linear with time. Thus, diffusion-based models, which predict a degradation that is proportional to the square root of time, would tend to underestimate the expansion.

Ouyang [4] proposed a model for sulfate attack on cement mortars based on the concept of progressive fracturing. An initial damage of the mortar was assumed to be a function of the gel–space ratio. The expansion of the matrix due to sulfate attack was incorporated as additional nucleated voids, which increase the existing initial damage prior to loading of the specimens. This model was able to predict the mechanical properties of cement mortars subjected to compression while undergoing sulfate attack.

Few models base the analysis of the problem of sulfate attack on a wide database of experimental results. Kurtis et al. [5] performed a statistical analysis of expansion data collected from a long-term experiment, and they were able to arrive at a predictive model that could suggest the damage (in terms of expansion) due to sulfate attack based on the chemistry of the cement (C_3A content) and the characteristics of the mixture (w/c).

In his study of sulfate resistance of blended cements, Irassar [6] described a new criterion for evaluation of sulfate resistance, which he called the ‘crack-time’. Flexural strength development was used as the test parameter to evaluate the different phases of sulfate attack including the following: filling of pores, cracking, strength loss, and deterioration of the structure. With time, the flexural strength of mortar bars in sulfate solution was found to increase up to a maximum, and then decrease rapidly. The evolution of the flexural strength was modeled as a second-degree parabola. The crack-time was defined as the time at which the flexural strength of mortar bars was a maximum. Using this parameter, successful predictions could be made for performance of concrete containing various blended cements in sulfate solutions.

Ferraris et al. [7] investigated the effects of the pH and concentration of the sulfate solution, as well as the size and shape of the specimen, on the expansion of mortar bars subjected to sodium sulfate attack. A finite-element modeling approach was proposed for creating predictive models.

Modeling the microstructural alterations is a challenging task due to the complicated mechanism of sulfate attack. However, without understanding the microstructural changes that accompany sulfate attack processes, it is not possible to accurately predict the damage using mechanistic models. The mechanism of sulfate attack proposed in this paper has been constructed through the analysis of experimental results for both physical and microstructural changes that occur during sulfate attack.

2. Summary of Part 1 of the paper [1]

In Part 1 of the paper [1], salient results from length change measurements and SEM investigations have been reported. The detailed results regarding all physical properties, chemical analyses, and microstructural studies on all the various types of mortars have been reported elsewhere by Santhanam [8].

Expansion of mortar specimens in sodium sulfate solution follows a two-stage process. During the initial stage (Stage 1), the expansion is very low. This period of low expansion is followed by a sudden increase in the expansion (Stage 2). In this second stage, the rate of expansion is nearly constant until failure. On the other hand, expansion in magnesium sulfate solution occurs at a continuously increasing rate and the characteristic two stages associated with sodium sulfate solution are not present.

Observations from SEM studies indicate the formation of various zones within the attacked mortar. In sodium sulfate solution, three distinct zones are formed. A cracked and highly deteriorated surface zone (Zone 1) is followed by a zone of deposition of attack products (Zone 2), primarily gypsum around aggregates and in pores, and ettringite within the paste. This is followed by the interior chemically unaltered zone (Zone 3), which is cracked. In magnesium sulfate solution, a surface double layer of brucite and gypsum provide a barrier to the free passage of the external solution to the interior of the mortar. Gypsum and ettringite are deposited just under this surface layer of brucite. In highly deteriorated areas, where the brucite layer is cracked, the conversion of calcium silicate hydrate (C-S-H) to magnesium silicate hydrate (M-S-H) takes place.

3. Proposed mechanism for sodium sulfate attack

The proposed mechanism for attack by sodium sulfate solution is shown in the schematic diagram in Fig. 1.

Step 1 depicts the initial state of the process. The mortar specimen is just introduced into the Na_2SO_4 solution that has a pH of 6–8. The pH of the surrounding solution changes to 11–12 just a few minutes after the specimen is introduced. If the water surrounding the mortar is stagnant, as is the case in a laboratory test, the pH will remain in the range of 11–12. However, in the case of a flowing sulfate solution, such as that in groundwater, the pH may stay at a low level (6–8). At low pH levels, the time for initiation of expansion, i.e., the length of Stage 1 as described in Part 1 of the paper, is reduced [7,9]. However, the rate of expansion after this initiation, i.e., during Stage 2, is not significantly different when the pH of the solution is low [9]. Thus, it can be assumed that the attack will proceed in a manner described by this model.

In Step 2, gypsum and ettringite start forming in the regions close to the surface. The surface zone of the mortar, where expansive gypsum and ettringite have formed, behaves like a skin that is trying to expand. However, the bulk of the mortar underneath, which is chemically unaltered, tries to resist this expansion. Thus, as described in Step 3, a resultant compressive force is generated in the surface

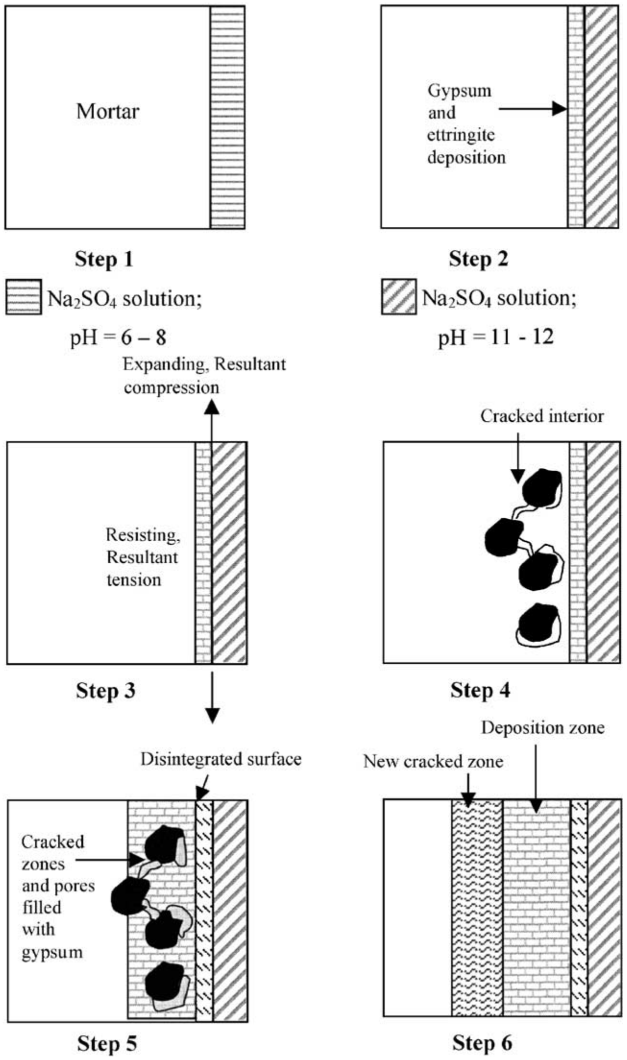

Fig. 1. Proposed mechanism of sodium sulfate attack.

region, while the bulk of the mortar is subjected to tensile forces. This causes cracks to appear in the interior of the mortar, as shown in Step 4.

Over time, the surface zone deteriorates due to continued penetration of the solution. When the solution is able to reach the cracked interior zones, it reacts with the hydration products and leads to deposition of attack products inside the cracks, as well as in the paste. Gypsum primarily deposits in the cracks and in voids, because these provide the best sites for nucleation. Hence, as shown in Step 5, a new region inside the mortar becomes the zone of deposition. This region then tries to expand, causing resultant tensile forces in the interior of the mortar. New cracks then appear in the interior zones. At this stage (Step 6), there are three distinct zones within the mortar —the disintegrated surface, the zone of deposition of attack products, and the interior cracked zone that is chemically unaltered. The disintegrated surface zone is also prone to the formation of thaumasite, because the sulfate solution has a direct access to the decalcified C-S-H and ettringite in this region. The attack thus progresses at a steady rate until a complete disintegration of the specimen occurs.

3.1. Implications of using admixtures upon the proposed mechanism

Analysis of the test data indicates that the disintegration of air-entrained mortars was delayed compared to the non-air-entrained (PC) mortars, although in terms of the physical properties and chemical analyses (amount of attack products forming), the two mortars were not much different. The entrained air voids provide sites for nucleation for the attack products, which leads to a reduced distress in the paste. Air voids can also help in arresting the growth of cracks due to their spherical shape. In terms of the proposed mechanism, it can be said that the cracking observed in Step 4 is reduced. In other words, although the air-entrained mortar undergoes expansion similar to that of the PC mortar, it is able to withstand the expansive stresses better than the PC mortar.

Sodium citrate is an effective retarding admixture for concrete. By slowing down the dissolution of calcium from the unhydrated cement compounds, it causes a retardation of the set and the early strength gain of concrete. When sodium citrate was used as an admixture, in an effort to modify the crystal growth habit of gypsum, the damage to mortars subjected to sulfate attack was reduced. Microstructural investigations using secondary electron imaging [8] did not show any obvious differences in the morphology of gypsum in the mortars with and without sodium citrate. However, the results from DSC analysis [8] suggest that the consumption of CH was slowed in the presence of sodium citrate. This can be attributed to the retarding effect of sodium citrate. Since gypsum forms by a through solution process from CH and the attacking sulfate solution, the formation of gypsum itself was slowed. Thus, any admixture that causes set retardation by slowing down the dissolution of calcium can be effective in slowing the rate of sulfate attack. In terms of the proposed mechanism, the formation of gypsum and ettringite in the surface zone in Step 2 is slowed down in the presence of sodium citrate. Microstructural studies indicated that the extent of gypsum and ettringite deposition was indeed smaller compared to PC mortars without sodium citrate.

Mineral admixtures affect the reaction in two ways. First, due to their ability to lower the permeability of the mortar system, the penetration of the sulfate solution into the mortar is also reduced. Second, due to consumption of CH by the pozzolanic reaction, the formation of gypsum itself is reduced (in Step 2 of the mechanism). Although these results reflect what is already known about using mineral admixtures in an attempt to reduce the negative effects of sodium sulfate attack, it is essential to see their effects with the perspective of the proposed mechanism.

3.2. Effects of temperature and solution concentration on the proposed mechanism

The main effect of increasing the temperature was to reduce the induction period before the onset of the rapid expansion in Stage 2 (as described in Part 1 of the paper [1]). In terms of the proposed mechanism, the formation of gypsum and ettringite in Step 2 was accelerated by increasing the temperature. The rate of expansion beyond the induction period was independent of the temperature.

An additional effect of the temperature was the change in the chemical nature of the attack. The conditions during the attack at 40°F are conducive to formation of thaumasite. Large regions near the surface of the mortar at 40°F were converted to thaumasite as a result of the direct attack on the C-S-H. However, the formation of thaumasite was not detected until after 21 weeks of immersion. This implies that the attack had proceeded to quite an extent before thaumasite was formed. Hence, it is possible that the formation of thaumasite took place, in the context of the proposed mechanism, after the disintegration of the surface zone occurred in Step 5. This was confirmed by the occurrence of substantial amounts of gypsum and ettringite, as well as expansion of the mortars before 21 weeks of immersion [8].

The main effect of increasing the solution concentration was an increase in the rate of expansion after the induction period, i.e., in Stage 2 as described in Part 1 of the paper [1]. The length of the initial period was not changed. This implies that the initial product deposition for all the concentrations occurred in a similar fashion. The rate of expansion should be related to the process in Step 5, where the cracked zones in the interior of the mortar get filled up by attack products, primarily gypsum. However, almost no gypsum formation was observed for the solutions with low concentrations. This indicates that the primary products deposited should be ettringite. The deposition of ettringite within the paste and voids was confirmed by SEM [8]. The solutions with low concentration did not cause much disintegration of the surface zones. In the context of the proposed mechanism, this could probably be due to a reduced rate of damage in Step 5.

4. Proposed mechanism of magnesium sulfate attack

The proposed mechanism for magnesium sulfate attack has been presented in the schematic diagram in Fig. 2. Step 1 represents the initial state of the process, when the mortar specimen in just introduced into a magnesium sulfate solution that has a pH of 7–8. Within a few minutes of the introduction of the specimen, the pH changes to between 9 and 10. A layer of brucite (magnesium hydroxide—$Mg(OH)_2$, or MH) rapidly forms on the surface of the specimen due to the reaction of CH with the solution. The layer of brucite is often complimented by a layer of gypsum that forms as a result of the same reaction on the inside of the brucite layer. This is depicted in Step 2. After the formation of these surface layers, the sulfate solutions penetrate the interior of the mortar by diffusion. This is the reason for the steady increase in the rate of deterioration observed in magnesium sulfate and absence of a sharp increase in the expansion rate, as shown in Fig. 2 in Part 1 of the paper [1].

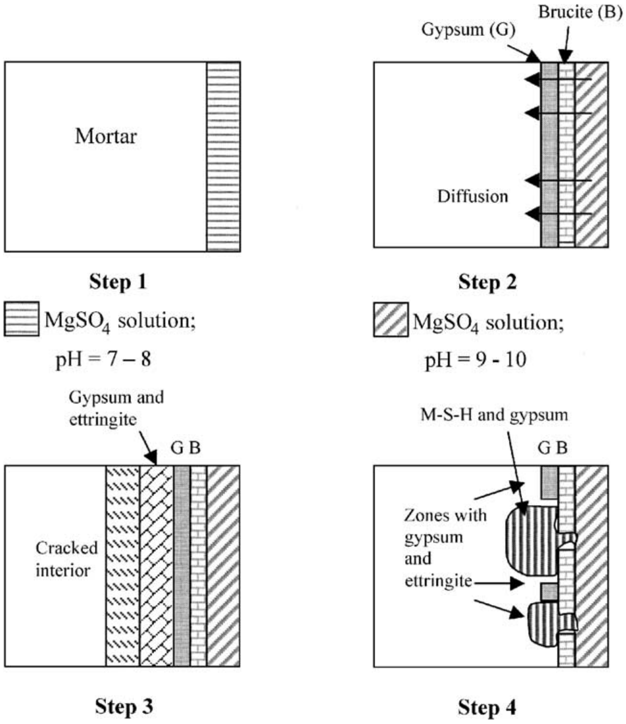

Fig. 2. Proposed mechanism of magnesium sulfate attack.

Formation of gypsum and ettringite (which decomposes to secondary gypsum at a later stage) in the regions close to the surface leads to expansion. Once again, using the same analogy of the expanding skin as in the case of sodium sulfate, cracks are created in the interior unaltered zones of the mortar, as depicted in Step 3.

The level of deterioration observed in magnesium sulfate, in terms of the visually observed physical deterioration and the measured expansion, is not as high as in sodium sulfate. The presence of the relatively impermeable surface layer of brucite accounts for the decreased penetration of the sulfate solution into the mortars. However, the layer of brucite can ultimately break down in several places due to expansion of the mortar and continued diffusion of the solution. Once channels of flow are established through the surface brucite layer, a direct attack of the C-S-H can occur. As a result of the attack on C-S-H, the formation of M-S-H and secondary gypsum takes place. This process is shown in Step 4. The ultimate failure of the mortar occurs as a result of the loss of strength and integrity due to the transformation of the paste to M-S-H.

4.1. Implications of using admixtures upon the proposed mechanism of expansion in magnesium sulfate solutions

The use of entrained air does not affect the performance of the cement mortar exposed to magnesium sulfate attack. The mechanism that has been proposed in the previous section does not suggest that there would be any improvement by using entrained air. However, the presence of entrained air near the surface of the mortars causes some brucite deposition in these voids. This could explain the additional degree of integrity observed in the air-entrained mortars. Once again, as in the case with sodium sulfate, the air voids could act as crack-arresting features.

The use of sodium citrate produced effects similar to those observed in samples exposed to sodium sulfate. The dissolution of Ca^{2+} was retarded, and, as a result, the formation of brucite and gypsum occurred over a longer period. Since the thickness of the brucite layer keeps increasing as a result of the continued brucite formation, the diffusion of the sulfates becomes more and more difficult. Thus, the deterioration observed in mortars with sodium citrate was much lower than deterioration observed in the normal (no admixture) mortars.

When mineral admixtures are used, the pozzolanic reaction leads to consumption of CH. Thus, the amount of brucite forming in these mortars is much smaller than in PC mortars. Since the thickness of the brucite layer governs the ease of diffusion of the sulfate ions, the reaction can proceed faster when mineral admixtures are used. The diffusion of sulfate ions across the brucite layer (in Step 2) is quicker. The easier diffusion leads to a quicker direct attack of the C-S-H (or Step 4) and an accelerated deterioration due to the formation of M-S-H and secondary gypsum. The negative effect of mineral admixtures during magnesium sulfate attack is often offset by the reduced permeability and densification caused by their use. This necessitates the determination of the optimum dosage of these mineral admixtures.

4.2. Effects of temperature and concentration on the proposed mechanism

An increase in the temperature or concentration of the attacking solution causes the rate of diffusion to increase. Hence, deposition of attack products under the brucite–gypsum double layer (as per Step 3) would be accelerated when the temperature or the concentration is increased. Thus, the overall deterioration of the mortar, due to the conversion of C-S-H to noncementitious M-S-H, is also accelerated. The increased rate of formation of attack products and the extensive conversion of surface paste into M-S-H were indeed observed by scanning electron microscopy [8].

The quantity of brucite forming at the surface was found to be dependent on the temperature of storage. An increase in the temperature of storage was accompanied by a higher amount of brucite forming. However, the increase in the amount of brucite was not significant enough to cause any alterations in the deterioration, in terms of the rate of expansion, and the observed damage in SEM.

5. Research significance

The results from this investigation suggest a quantifiable link between the physical properties and microstructural alterations. In the case of attack by sodium sulfate solutions, with some additional analysis of the depths of the three zones forming at any given stage of attack, accurate modeling of the attack can be performed. For this purpose, microstructural studies should be conducted in addition to measurements of physical properties at progressive ages, starting from a time just after immersion of the specimens. Using the information about the depths of various zones, repair strategies can be determined.

In order to create a reliable model for failure during sulfate attack, some more criteria need to be evaluated. For example, when the mortar or concrete is subjected to drying and wetting cycles, salt crystallization can add to the distress in the surface zones. Localized expansion caused by salt crystallization can lead to a quicker disintegration of the surface zone. Situations of partial submersion can also be tricky to model, since concentration gradients may be created at the solution–air interface.

These models have been created based on experiments with mortar specimens. The presence of large coarse aggregates can have a restraining effect on the expansion that has to be quantified. The rate of deterioration would possibly be reduced in the presence of the restraint offered by the coarse aggregates. Specimen size effect also needs to be addressed to successfully model the process of sulfate attack.

6. Summary

Data from expansion and scanning electron microscopy studies for mortars subjected to attack by sodium and magnesium sulfate were analyzed to propose mechanisms of attack and failure of mortars. Separate mechanisms were proposed for sodium and magnesium sulfate because of the differences in chemistry of the products forming during the attack.

The proposed mechanism for sodium sulfate solution suggests the formation of distinct zones within the mortar. The ultimate failure of the specimen occurs due to a progressive inward movement of the zones. In the case of magnesium sulfate solution, the rate of ingress of the sulfate solution depends on the rate of diffusion of the solution across the surface layer of brucite. Upon subsequent expansion and damage of the surface brucite layer, a direct attack of the C-S-H leads to the ultimate failure of the mortar.

The implications of altering the cementitious content of the mortar, as well as of using air-entraining and retarding admixtures, were identified. The effect of changing the concentration and temperature of the attacking solution was also qualified using the proposed mechanisms.

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References

[1] M. Santhanam, M.D. Cohen, J. Olek, Mechanism of sulfate attack: A fresh look: Part 1. Summary of experimental results, Cem. Concr. Res. 32 (6) (2002) 915–921.

[2] ASTM Standard Designation E 632, Standard Practice for Developing Accelerated Tests to Aid Prediction of the Service Life of Building Components and Materials, American Society of Testing and Materials, Philadelphia, PA, USA 1995.

[3] A. Atkinson, J.A. Hearne, Mechanistic model for the durability of concrete barriers exposed to sulphate-bearing groundwaters, Mater. Res. Soc. Symp. Proc. 176 (1990) 149–156.

[4] C. Ouyang, A damage model for sulfate attack of cement mortars, Cem. Concr. Aggreg. 11 (2) (Winter 1989) 92–99.

[5] K.E. Kurtis, P.J.M. Monteiro, S.M. Madanat, Empirical models to predict concrete expansion caused by sulfate attack, ACI Mater. J. 97 (2) (2000) 156–161.

[6] E.F. Irassar, Sulfate resistance of blended cement: Prediction and relation with flexural strength, Cem. Concr. Res. 20 (1990) 209–218.

[7] C.F. Ferraris, J.R. Clifton, P.E. Stutzman, E.J. Garboczi, Mechanisms of degradation of Portland cement-based systems by sulfate attack, in: K.L. Scrivener, J.F. Young (Eds.), Mechanisms of Chemical Degradation of Cement-Based Systems, E & FN Spon, London, 1997, pp. 185–192.

[8] M. Santhanam, Studies on Sulfate Attack: Mechanisms, Test Methods, and Modeling, PhD Thesis, Purdue University, August 2001.

[9] P.W. Brown, An evaluation of sulfate resistance of cements in a controlled environment, Cem. Concr. Res. (11) (1981) 719–727.