Sulfate Attack on cement based materials: An overview

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Abstract

This paper overviews the present understanding of sulfate attack on concrete and or cementitious materials (CBM), with importance on the sources, behavior, and deterioration mechanism. This paper considers the physical and chemical perspective degradation of CBM. Thus attempts to provide general guidance to diagnose the sulfate attack and its progress in the attack and consequences. The main factors for sulfate attack like the presence of carbonates, sulfates, moisture, and low temperatures ($<15^{o}C$) are discussed. The sulfate attack depends on the surrounding environment, atmospheric conditions, processing conditions of the CBM, and proportions and quality of the mixed ingredients. In conclusion, to understand the deterioration process by sulfate attack, the surrounding environment/site conditions and material composition of the CBM are to be considered for enhancing the service life of concrete/cement-based structures.

Keywords: Cement-based materials, concrete, cement mortar, durability, sulfate attack.

Introduction

Cement is the most common binder material that is extensively used in all construction environments. It is well known that cement undergoes degradation when comes into contact with sulfate-rich environments. The actuality is that cement is almost unstable and reacts chemically in all service environments. A sulfate attack is associated with physical and chemical interactions that happen between sulfates and hardened cement matrix. However, the behavior of sulfate attack is still not established and the experimental test procedures followed for measuring the sulfate attack and specifications/standards are not universally accepted, and are controversial. Furthermore, we are still deficient in trustworthy mitigation procedures. Although small portions of sulfates are present in cement, generally as gypsum for preventing the fast hardening.

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Frequently, sulfate attack causes volume expansion and leads to cracks and spalling of cementitious materials and or concrete (further referred to as cement-based materials: CBM). In some cases, the products formed by the sulfate attack are good and friendly and do not affect the dimensional stability and mechanical properties (Alexander et al.2013; Whittaker et al. 2015).

External sulfate attack occurs by the increase in sulfate quantity in the surrounding location. The sulfate might present in the surrounding environment as an outcome of disturbance, by oxidation of sulfides in the aggregate, in soil, and or normally. To understand the behavior of sulfate attacks, it is vital to know the considerations such as the effects and nature of the chemical interaction between hydrated products and sulfates, the distribution of sulfate in the CBM, and the concentration of sulfates present in the surrounding environment (Marchand et. al. 2002, Neville, 2004, and Lee et. al. 2008). Furthermore, to better understand the behavior of sulfate attack, researchers primarily made three types of approaches (i) modeling of the durability of CBM (ii) design tests, and customarily tests to be conducted in control conditions in the laboratory for predicting the behavior of CBM. (iii) collection of CBM samples affected by sulfate attack and compare their properties with the samples collected from other sources and service conditions (Alexander et al.2013).

The damage to the CBM caused by the sulfate attack depends on the following factors.

(i)   Characteristics of CBM, and their constituents.
(ii)   Performance of bulk material such as stresses and cracks.
(iii)   development of expansive products in the interior of CBM.
(iv)   Chemical reactions between the sulfate compounds and hydrated cement matrix.
(v)   Transportation of ions into the CBM through their voids and pores.

The key aspects of the degradation of CBM by sulfate attack are the dissemination of the sulfate ions, by either diffusion or absorption, or both, and on the saturation level. Furthermore, the major outcome is also the interaction of sulfate ions with the hydrated cement matrix to form ettringite and gypsum or modify the calcium silicate hydrate (CSH). The role of cations cannot be neglected. The degree of deterioration and kinetics depend on (Brown 1981; and Marchand et al. 2002):

(i)   pH of the sulfate solution that interacts with the CBM.
(ii)   The availability of sulfate ions in resources like soil, flowing water, seawater, and or stagnant water.
(iii)   Whether the CBM is subjected to constant immersion or contact and wet-dry cycles.
(iv)   The quantity of sulfate available in water or soil that is in contact.

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The key aspects in analyzing the sulfate attack are to estimate and know about (Ferraris et al. 2006):

    (i)   Sorptivity coefficient of CBM for sulfate.
    (ii)   Influence of cations related to sulfate.
    (iii)   Chemical reactive nature between sulfate ions and cement matrix.
    (iv)   Diffusion coefficient of the constituents.

Process of Sulfate attack

Deterioration of CBM by sulfate attack is a usual phenomenon. The process happens when water-encompassing sulfates (SO_4) comes into interaction. Sulfates are generally found in seawater, in some soils, and in wastewater. Sulfates present in wastewater interact with the hydrated compounds of tri-calcium aluminate (C_3A) and also react with calcium hydroxide ($Ca(OH)_2$), tetra-calcium ferrite aluminate to form expansive crystalline compounds (ettringite (Aft), mono-sulfate (AFm), or gypsum). Expansion caused by the ettringite generally forms internal tensile stresses and when these stresses are increased, the tensile capacity of the CBM forms cracks. These cracks permit more sulfates and accelerate the deterioration process (Tian, et. al. 2000, Caijun et. al. 2012, Santhanam et al. 2003).

The key aspects that govern the severity and rate of sulfate attack are (Alexander et al.2013, and Caijun et. al. 2012):

    (i) $Ca(OH)_2$ content.
    (ii) C_3A content in cement
    (iii)   Exposure temperatures
    (iv)   Concentration and presence of other dissolved salts like carbonate and chloride.
    (v)   pH value of sulfate solution
    (vi)   Motility of sulfate content present in the sources
    (vii) Concentration of sulfate in aquatic solutions
  (viii)   Permeability nature of CBM.
    (ix)   Impermeability property of the hardened cement that helps as an obstruction for sulfate ions to penetrate.
    (x)   Behaviour of reaction compounds formed by the attack of sulfate solution.
    (xi)   Behaviour of existing cations like Ca^{2+}, Mg^{2+}, or Na^+, etc.
   (xii)   Extent of stresses produced by the result of sulfate attack.

The sulfate attack environment comprises (i) acid attack by sulfuric acid (ii) internal and external sulfate attack (iii) crystallization of sulfate salts. The Spanish code on structural concrete (EHE-08) classifies the potential damage to the concrete and or cementitious materials as a function of the sulfate quantity in soils and water. The presence of sulfate in surface or groundwater or wastewater, soils, and materials treated with sulfates. The soils and groundwater can be

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characterized by their ability of aggressiveness toward CBM or cementitious materials, depending on the sulfate quantity. The sulfates quality present in groundwater is influenced by the characteristics of layers of soil through which water flows. In turn, the characteristics of soils mainly depend upon the type of land use, acid rain, industrial effluents, and activities. The major ingredients of water and aggressive soils are potassium, magnesium, calcium, and sodium (electro-neutral sulfate) (Alexander et al.2013, and Caijun et. al. 2012). Hydrated aluminates in supplementary cementitious materials or cement clinker can react with sulfate ions that are present in hydrous solutions to form ettringite. The formation of ettringite in hardened concrete causes volume change or expansion that generates cracks and voids.

Ettringite can also be formed by the reaction caused between the external sulfates and the sources of aluminum like unreacted ferrite or C_3A, idyllically C_4AF. Cement with low C_3A content is said to have good chemical resistance against sulfate. Sulfate attack on CBM results in the loss of cohesion, macro-cracking, de-lamination, and also spalling. These consequences of degradation are caused by the chemical processes such as recrystallization, crystalline phases, dissolution-precipitation of colloidal, and also by adsorption-desorption phenomena (Caijun et. al. 2012, Skalny 2002, and Metha and Monteiro 1993).

Leaching by sulfate attack

The sulfate attack on the pore solution/cement matrix leads to the removal or decomposition of calcium hydroxide as leaching, releasing calcium (Ca^{2+}) and hydroxyl ions (OH^-) (Adenot et. al. 1992; Planel et al., 2006; and Kamali et al., 2003, 2008). The discharge of $Ca(OH)_2$ reduces the pH of the concrete pore solution causing the decalcification of CSH. This can be noticeable by a progressive reduction in the silicon/calcium of the hardened cement matrix. The pH< 10.7 causes the decomposition of ettringite to gypsum. This leaching phenomenon leads to the loss of strength and softening of the hardened cement matrix. The quantity of leaching depends upon the nature and the use of supplementary cementitious materials, the temperature of the solution, the pH, and the sulfate source (Adenot et al., 1992; Gabrisova et al., 1991).

Transport process

The progress of a sulfate attack requires penetration and absorption of sulfate ions into the hardened cement matrix. This occurs when the voids or pores of CBM when coming into contact with a sulfate-rich source. This interaction between the pore solution and the external sulfate source turns the aqueous media's equilibrium conditions that lead to mass flow. The behavior of the mass flow is expressed by the saturation level of the pore structure. Under no pressure gradients and in saturated conditions, penetration of sulfate and other ionic flows is mostly guided by electrochemical potential gradients. The electrical potential gradient is produced in the pore solution (alkaline solution) by the difference in the rate of flow of the charged solutions. The chemical potential modification refers to the diffusion and transfer of charged solutions from high to low-concentration areas.

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In saturated conditions and the electrochemical potential gradient, the other transport mechanisms may also affect the flow of ionic species (Hall et al., 2009). Furthermore, thermal diffusion or the Soret effect may also occur in non-isothermal systems, where the temperature gradients boost the ionic flow. In conclusion, the flow of ionic species may change by the chemical activities that are related to the ion solvent interactions at the higher levels of ionic strength of the pore solution (Rahman et al., 2014; Samson et al., 1999). In unsaturated situations, ionic flow happens indirectly by the flow of solutions from the surfaces of CBM into the pores and void systems. The high-concentration sulfate solutions are absorbed into the CBM by capillary action that occurs between the liquid phase and pores of materials (Hall et al., 2009; Siegesmund et al., 2014)

Chemical reactions

The reactive structure of concrete consists of the hydrated and unhydrated solid phases of the cement matrix and the liquid pore solution, vapor, and moisture phase in the pores and voids (aggregates are commonly assumed as inert). The mass flow induced by the interaction between the reactive system and the external aqueous source during the sulfate attack modifies the equilibrium state and encourages a sequence of chemical reactions for re-establishing the minimal energy in the system, which is by the second law of thermodynamics. The degree of chemical reactions produced by the sulfate attack depends mainly on the sulfate quantity present in the surrounding environment. The impact of sulfate attack on the chemical reactions and consequent deterioration is interpreted by the solvability and interaction between sulfate and the other reactive constituents of concrete.

The key sulfate salts related to the sulfate attack are magnesium sulfate ($MgSO_4$), sodium sulfate (Na_2SO_4), and calcium sulfate ($CaSO_4$) (Alexander et al., 2013). Table 1 presents the sulfate concentration in a saturated state and solvability in water at $20^{o}C$. The damage caused by $MgSO_4$ and Na_2SO_4 solutions is highly considered by their crystallization pressures produced during the sulfate attack and high sulfate concentrations. The solvability of $CaSO_4$ is around a hundred times smaller than the solvability of $MgSO_4$ or Na_2SO_4. The sulfate attack that occurs by the $MgSO_4$ is greatly influenced by the magnesium ions present in the solution. This forms magnesium hydroxide ($Mg(OH)_2$) that reduces the pH of the pore solution and supports the alteration of the C-S-H gel to form a magnesium silicate hydrate (M-S-H) gel. This alteration creates softening and deterioration of the cement matrix and results in the development of brucite and gypsum (Dean, 1985; Baghabra et al., 2002). The sulfate attack that occurs by the Na_2SO_4 is a different mechanism characterized by the development quantity of gypsum and ettringite that supports chemical and physical damage. Sulfate penetration into the hardened concrete causes chemical damage associated with the deterioration of the mechanical properties of the cement matrix.

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Table-1 Sulfate concentration and solubility in water (Dean, 1985)

Sulfate salt	$[SO_4^{2-}]_{aq}$ (g/l)	Solubility (g/l)
$MgSO_4$	268.9	337.0
$CaSO_4 \cdot 2H_2O$	1.5	2.6
Na_2SO_4	131.9	195.0

The predominant chemical reactions are shown in Table 2 (Tixier et al., 2003; and Sarkar et al., 2010). Equations (1) to (3) show the reactions between Na_2SO_4 ions with C_3A, CH, and C_4ASH_{12} to $C_6AS_3H_{32}$, CSH_2 and NaOH. However, gypsum is formed in particular sulfate pH conditions and concentrations of the solution. Lower sulfate concentrations form very little or no gypsum precipitation, while high sulfate concentrations lead to gypsum precipitation (Lothenbach et al., 2010; and Maltais et al., 2004).

Equations (4) and (7) show the development of ettringite when gypsum is precipitated and reacts with the hydrated aluminate phases like the hydro garnet (C_3AH_6), mono-sulfate, tetra calcium aluminate hydrate (C_4AH_{13}) and tricalcium aluminate. In general, it is known that the sodium from the sources of sulfate salt may not considerably change the development of the sulfate attack. However, some researchers propose the influence of sodium ions in modifying the solvability of the silicate phases and changing the structure of the CSH gel (Mota et al., 2015; and Kumar et al., 1994).

As seen in equations (1) to (7), ettringite and gypsum formation require calcium that is generally available by the disintegration of $Ca(OH)_2$. However, calcium may be acquired from C-S-H gel under a deficit of portlandite or at late phases of sulfate attack. The C-S-H gel present in the cement matrix is the key to the stiffness and strength of the CBM and when it disintegrates leads to form micro-cracks and loss of mechanical strength. The molar volumes of the reactive compounds are given in table 3. The sulfate sources and their impact is given in table 4.

Thaumasite sulfate attack

This type of sulfate attack varies by involving the external sulfate sources with C-S-H gel. Thaumasite without binding properties looks like a white soft incohesive mush. In a thaumasite sulfate attack (TSA), the silica and the calcium react collectively with carbonates and sulfates. This phase commonly precipitates at temperatures <15°C (Crammond et al., 1995; and Report of the Thaumasite Expert Group, 1999.). Even though some researchers mentioned the formation at higher temperatures. Limestone-based types of cement are less resistant to TSA. Cement with rich aluminium oxide and tricalcium aluminate showed high quantities of thaumasite. Furthermore, types of cement with low amounts of tricalcium aluminate are also sensitive to

TSA. From the structural point of view, thaumasite resembles ettringite, where alumina is substituted by six-fold interconnected silicate ions. The existence of ettringite is also expressed as a precursor for the formation of thaumasite. Thaumasite is effortlessly stabilized at higher levels of aluminum oxide/sulfur trioxide ratios. However, ettringite suppresses the rate of development of thaumasite.

Two distant methods propose the formation mechanism of thaumasite. Primarily, a direct way, where carbonates react with the silicates, sulfates, and calcium, in the presence of water. Secondly, a woodfordite way, where carbonates, ettringite, and silicates react combinedly. Thaumasite can also be formed topochemical from ettringite, replacing $[SO_4^{-2} + H_2O]$ and $[Si]$ for $[CO_3 + SO_4^{-2}]$ and $[Al]$, respectively, or by solution (Bensted, 2003; and Crammond, 2003).

Table 2 Key chemical reactions associated with external sulfate attack caused by Na_2SO_4 salts and their expansive factors (Ikumi et al., 2019).

Equation No.	Chemical reaction	Primary reactive	Expansion factor
1.	$CH + Na_2SO_4 + 2H \rightarrow CSH_2 + 2NaOH$	CH	1.27
2.	$C_3A + 3Na_2SO_4 + 3CH + 32H \rightarrow 6NaOH + C_6AS_3H_{32}$	C_3A	2.76
3.	$3C_4ASH_{12} + 3Na_2SO_4 \rightarrow 6NaOH + 2Al(OH)_3 + 21H + 2C_6AS_3H_{32}$	C_4ASH_{12}	0.52
4.	$C_3A + 3CSH_2 + 26H \rightarrow C_6AS_3H_{32}$	C_3A	1.25
5.	$C_4AH_{13} + 3CSH_2 + 14H \rightarrow C_6AS_3H_{32} + CH$	C_4AH_{13}	0.48
6.	$C_4ASH_{12} + 2CSH_2 + 16H \rightarrow C_6AS_3H_{32}$	C_4ASH_{12}	0.54
7.	$C_3AH_6 + 3CSH_2 + 2OH \rightarrow C_6AS_3H_{32}$	C_3AH_6	0.89

Table 3: Molar volumes of the reactive compounds (Ikumi et al. 2019).

Name	Primary reactive	Molar volume (cm³/mol)
Tricalcium aluminate	C_3A	89
Gypsum	C_3AH_6	75
Portlandite	CH	33
Tetracalcium aluminate hydrate	C_4AH_{13}	274
Monosulfate	C_4ASH_{12}	309
Hydrogarnet	C_3AH_6	150
Ettringite	$C_3AS_3H_{32}$	707

Table 4: Sulfate sources and their impact (Whittaker et al. 2015).

Sulfate source	Impact
Calcium sulfate	Leads to minimum damage
Alkali sulfate (sodium and potassium sulfates)	Rapid expansion; formation of ettringite and syngenite.
Magnesium sulfate	Reacts with $Ca(OH)_2$ and forms gypsum and $Mg(OH)_2$ (brucite); may form magnesium silicate hydrate; accelerate degradation mechanism.

Damage by sulfate attack

The physical damage caused by the sulfate attack is generally observed by the production of expansive forces in the cement matrix at the pore level. This is by the chemical reactions that occur between the pore solution and the cement matrix thus forming spalling, cracking, and expansion of the hardened CBM. The volume increase approach and crystallization pressure theory are the two mechanisms that help in understanding the dissolution/precipitation process creating expansion of CBM (Marchand et. al. 2002; and Kunther, 2013) .

The chemical changes caused by the sulfate attack in CBM include (Skalny et al. 2002):

1. Formation and crystallization of sulfate salts.
2. Penetration of sulfate ions into the CBM
3. Formation of magnesium silicate hydrate by recrystallization of magnesium hydroxide
4. Formation of thaumasite, gypsum, and ettringite
5. Dissolution of primary hydration products
6. Decomposition of clinker minerals
7. Formation of silica gel/ hydrated silica
8. Changes in the pore solution
9. Decomposition of calcium hydroxide and or CSH by the removal of Ca^{2+}

The physical changes caused by the sulfate attack on CBM include (Skalny et al. 2002):

1. Decreased modulus of elasticity
2. Loss of strength
3. Deposition of sulfate salts on the formed cracks and surface.
4. Decreasing hardness and softening of the cement matrix
5. Failure of the interaction transition zone of aggregates and cement matrix
6. Microcracking formed by the volumetric expansion
7. Increased permeability and porosity

8. Complete changes in the solid micro and pore structure

Crystallization pressure theory and Volume increase approach

This mechanism assumes that the additional expansive products precipitated during the sulfate attack will cause volume change. The products which are precipitated by the sulfate attack occupy and occupy more space and are said to be expansive products or expansive phases. The molar values of $Al(OH)_3$, $NaOH$, and Na_2SO_4 are not considered as they are assumed to dissolve in the aqueous phase. At present, no experimental evidence is available in suggesting the expansion of CBM by the additional volume formed by the gypsum or ettringite formation. Even though there seems a relation between the coexistence of gypsum and ettringite in the expansion phases (Clifton et al., 1994; Tixier et al. 2003). Crystallization pressure theory states that the formation of ettringite helps in the development of crystallization pressure and is applied to the surface layers of CBM leading to the expansion phases. This theory also states that the high activities of the reactive compounds are the driving force in the deterioration of CBM during sulfate attack. Two essential circumstances exist for the expansion phases to occur (Flatt et al. 2008; Scherer, 1999, 2004).

Conclusion

Sulfate attack on CBM is a widely studied deterioration mechanism. External sulfate attack has a sequence of relations that occur in the cement matrix and concrete and can be established by physical and chemical examinations. In chemical sulfate attacks, macroscopic studies are extensively needed to understand the spalling, expansion, and cracking behavior of CBM. Concrete and or cement mortar expansion is the general form of degradation by sulfate attack. The loss in dynamic modulus, strength, and mass creates damage. De-cohesion and softening of CBM can also occur. The small pores and the resulting damage is produced by the reaction caused between sulfates and aluminate hydrates that results in internal tension. The gypsum role in the damage of CBM is still debated and some observations have noticed that high quantities of gypsum in the weaker portions of sulfate affected CBM. However, the use of a low water-to-binder ratio and alternative/supplementary cementitious materials lowers the sulfate attack by improving the performance of CBM. In conclusion, to understand the deterioration process by sulfate attack, the surrounding environment/site conditions, and material compositions are to be considered for improving the service life of structures constructed by CBM/cement-based materials.

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