

Sulphate Resistance of Concrete and Effect of Sulphate Attack

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Abstract-- Sulphate attack is one of the most common aggressive actions leading to the deterioration of concrete. It occurs when concrete comes in contact with water containing sulfates (SO₄). Sulphates can be found in some soils especially when dry conditions exist, in seawater, and in wastewater treatment plants. Concrete can be affected by a chemical reaction involving sulphate that when present in contaminated hardcore along with a source of moisture, reacts with cement present in the concrete causing it to expand and crack. Waterborne sulphates react with hydration products of the tri-calcium aluminates (C₃A) phase of Portland cement, and with calcium hydroxide (Ca (OH) ₂) to form an expansive crystalline product called ettringite. Expansion due to ettringite formation causes tensile stresses to develop in the concrete. When these stresses become greater than the concrete's tensile capacity, the concrete begins to crack. These cracks allow easy ingress for more sulfates into the concrete and the deterioration accelerates. In some cases the cement hydration products are broken down resulting in a loss of cementitious properties. Protecting against sulphate attack requires using the appropriate cementitious materials and reducing the ingress of sulphates into the concrete. This paper provides a concrete deterioration due to sulphate attack, the origin of sulphates in concrete, the importance of appropriate concrete processing, forms and physical-chemical mechanisms of concrete deterioration due to sulphates and how to resist sulphate attack from concrete. The mechanisms of sulphate attack are fairly well understood, but in some instances it has proved difficult to establish the origin of the sulphate. Possible sulphate sources include soils and ground water, sea water, atmospheric pollution, contaminated ground-fill and highway de-icing salts.

Index Terms-- Chemical reaction, Concrete, Ettringite, Portland Cement, Sulphate attack, Soil, Tri-Calcium aluminates.

I. INTRODUCTION

Sulphates occur naturally and are used in industry. They can enter concrete in solution from the external environment, or they may be mixed into concrete. They react with cement compounds to form expansive products. Large amounts of sulphate may have deleterious effect on concrete.

An early attempt to increase concrete resistance to sulphate attack was based on the finding that calcium aluminates in cement were the major constituents reacting with sulphate to cause excessive expansion.

Although sulphate attack on concrete has been studied worldwide for more than 60 years. However the mechanisms of attack are still not entirely understood, and deterioration of concrete from sulphate still occurs

There exist many consequences of sulfate attack on

concrete; past research investigations have identified expansion, cracking, disintegration, and strength loss as harmful effects attributed to sulphate exposure. Sulphate attack is a chemical breakdown mechanism where sulphate ions attack components of the cement paste. Sulphate attack can be 'external' or 'internal': One of the most common ways of protecting against sulphate attack is to reduce the alumina content by limiting the C₃A in Portland cement. Historically, Type II Portland cement (with C₃A between 5 and 8 percent) and Type V Portland cement (with C₃A less than 5 percent) have been specified for moderate and severe sulphate environments, respectively. The use of slag cement is also an extremely effective way of reducing the potential for sulphate attack¹. Some sulphate salts also react with the cement hydration products to form gypsum, which also results in a volume expansion. In some cases the cement hydration products are broken down resulting in a loss of cementitious properties. Protecting against sulfate attack requires using the appropriate cementitious materials and reducing the ingress of sulfates into the concrete. Sulphate attack on concrete has the potential to cause serious damage or structural failures. Structures in potentially aggressive environments must be designed to recognize the risk of sulphate attack, and precautions taken in the design process to manage that risk.

The use of fly ash is well documented as a sound and economical method of achieving sulphate attack resistance.

II. WHAT HAPPENS WHEN SULPHATES GET INTO CONCRETE

It combines with the C-S-H, or concrete paste, and begins destroying the paste that holds the concrete together. As sulfate dries, new compounds are formed, often called ettringite. These new crystals occupy empty space, and as they continue to form, they cause the paste to crack, further damaging the concrete. Cured concrete in the presence of moisture can be susceptible to attack by sulphates. Those sulphates may be present in ground water, sea water or from other sources. Attack occurs when the sulphates are able to react with the free lime released during hydration of the Portland cement and with calcium aluminates present in the cement.

This reaction results in the formation of a range of sulphate compounds including sulphaaluminates. Because these compounds occupy a greater volume than the original concrete components they cause expansion and eventual failure of the concrete.

III. TYPES OF SULPHATE STANDARDS

1) *Cementitious Materials Standards Tests*

Excess internal sulphate and Chemical resistance to external sulfate attack.

2) *Concrete codes*

Concrete Standards (ACI, CSA), for external sulphate resistance, Based on degree of exposure, Control concrete quality (w/c) as well as materials, TSA: not mentioned, DEF: Mentioned indirectly through controls on maximum early temperature (CSA A23.4, and possibly coming to ACI C308).

3) *ACI Building Code 318*

Negligible attack: When the sulphate content is under 0.1% in soil, or under 150 ppm (mg/liter) in water, there shall be no restriction on the cement type and water/cement ratio.

Moderate attack: When the sulphate content is 0.1 to 0.2% in soil, or 150 to 1500 ppm in water, ASTM Type II portland cement or portland pozzolan or portland slag cement shall be used, with less than an 0.5 water/cement ratio for normal-weight concrete.

Severe attack: When the sulphate content is 0.2 to 2% in soil, or 1500 to 10,000 ppm in water, ASTM Type V Portland cement, with less than a 0.45 water/cement ratio, shall be used.

Very severe attack: When the sulphate content is over 2% in soil, or over 10,000 ppm in water, ASTM Type V cement plus a pozzolanic admixture shall be used, with less than a 0.45 water/cement ratio.

IV. SULPHATE SOURCES

1) *Internal Sources*

This is more rare but, originates from such concrete-making materials as hydraulic cements, fly ash, aggregate, and admixtures. Portland cement might be over-sulfated. presence of natural gypsum in the aggregate. Admixtures also can contain small amounts of sulfates. Ground (soil) water, sewage water, sea water, or swamp water.

2) *External Sources*

External sources of sulfate are more common and usually are a result of high-sulfate soils and ground waters, or can be the result of atmospheric or industrial water pollution. Soil may contain excessive amounts of gypsum or other sulfate. Ground water is transported to the concrete foundations, retaining walls, and other underground structures. Industrial waste waters. Higher concentrations of sulfate in groundwaters are generally due to the presence of magnesium and alkali sulfates. Ammonium sulfate is frequently present in agricultural soil and water. Local high concentrations of sulfates may be associated with industrial wastes. Effluents from furnaces that use high-sulfur fuels and from the chemical industry may contain sulfuric acid. Decay of organic matter in marshes, shallow lakes, mining pits, and sewer pipes often leads to the formation of H₂S, which can be transformed into sulfuric acid by bacterial action. In masonry, sulfates present in bricks and can be gradually released over a long period of time, causing sulfate attack of mortar, especially where

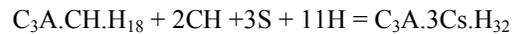
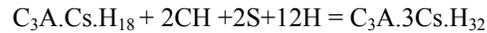
sulfates are concentrated due to moisture movement.

V. NATURE OF REACTION

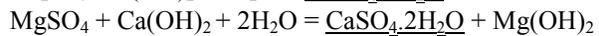
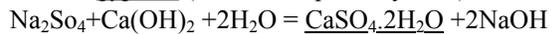
Sulphate attack processes decrease the durability of concrete by changing the chemical nature of the cement paste, and of the mechanical properties of the concrete.

1) *Chemical process*

The sulphate ion + hydrated calcium aluminate and/or the calcium hydroxide components of hardened cement paste + water = ettringite (calcium sulphoaluminate hydrate)



The sulphate ion + hydrated calcium aluminate and/or the calcium hydroxide components of hardened cement paste + water = gypsum (calcium sulphate hydrate)



Two forms of Chemical reaction depending on Concentration and source of sulfate ions .Diagnosis Composition of cement paste in concrete.

2) *Physical process*

The complex physico-chemical processes of "sulfate attack" are interdependent as is the resulting damage. physical sulfate attack, often evidenced by bloom (the presence of sodium sulfates Na₂SO₄ and/or Na₂SO₄.10H₂O) at exposed concrete surfaces. It is not only a cosmetic problem, but it is the visible displaying of possible chemical and microstructural problems within the concrete matrix.

VI. FACTORS AFFECTING SULPHATE ATTACK

The most important mineralogical phases of cement that affect the intensity of sulfate attack are: C₃A, C₃S/C₂S ratio and C₄AF. The level of the water table and its seasonal variation. The flow of groundwater and soil porosity The form of construction The quality of concrete. The addition of a pozzolanic admixture such as fly ash reduces the C₃A content of cement. The sulfate attack tends to increase with an increase in the concentration of the sulfate solution up to a certain level.

VII. SULPHATE ATTACK

Sulphate attack can be external or internal.

External due to penetration of sulfates in solution, in groundwater for example, into the concrete from outside.

Internal due to a soluble source being incorporated into the concrete at the time of mixing, gypsum in the aggregate, for example.

1) *External sulphate attack*

This is the more common type and typically occurs where water containing dissolved sulfate penetrates the concrete. A fairly well-defined reaction front can often be seen in polished sections; ahead of the front the concrete is normal, or near normal. Behind the reaction front, the composition and microstructure of the concrete will have changed. These changes may vary in type or severity but commonly include:

Extensive cracking, Expansion, Loss of bond between the cement paste and aggregate and alteration of paste composition, with monosulfate phase converting to ettringite and, in later stages, gypsum formation. The necessary additional calcium is provided by the calcium hydroxide and calcium silicate hydrate in the cement paste

The above effects are typical of attack by solutions of sodium sulfate or potassium sulfate. Solutions containing magnesium sulfate are generally more aggressive, for the same concentration. This is because magnesium also takes part in the reactions, replacing calcium in the solid phases with the formation of brucite (magnesium hydroxide) and magnesium silicate hydrates. The displaced calcium precipitates mainly as gypsum. Other sources of sulfate which can cause sulfate attack include: Seawater, Oxidation of sulfide minerals in clay adjacent to the concrete - this can produce sulfuric acid which reacts with the concrete, Bacterial action in sewers - anaerobic bacterial produce sulfur dioxide which dissolves in water and then oxidizes to form sulfuric acid In masonry, sulfates present in bricks and can be gradually released over a long period of time, causing sulfate attack of mortar, especially where sulfates are concentrated due to moisture movement

2) *Internal sulphate attack*

Occurs where a source of sulfate is incorporated into the concrete when mixed. Examples include the use of sulfate-rich aggregate, excess of added gypsum in the cement or contamination. Proper screening and testing procedures should generally avoid internal sulfate attack.

VIII. DELAYED ETTRINGITE FORMATION (DEF)

Delayed ettringite formation (DEF) is a special case of internal sulfate attack. Delayed ettringite formation has been a significant problem in many countries. It occurs in concrete which has been cured at elevated temperatures, for example, where steam curing has been used. It was originally identified in steam-cured concrete railway sleepers (railroad ties). It can also occur in large concrete pours where the heat of hydration has resulted in high temperatures within the concrete. DEF causes expansion of the concrete due to ettringite formation within the paste and can cause serious damage to concrete structures. DEF is not usually due to excess sulfate in the cement, or from sources other than the cement in the concrete. Although excess sulfate in the cement would be likely to increase expansion due to DEF, it can occur at normal levels of cement sulfate. A key point in understanding DEF is that ettringite is destroyed by heating above about 70 C. In normal concrete, the total amount of ettringite which forms is evidently limited by the sulfate contributed by the cement initially. It follows that the quantity of ettringite which forms is relatively small. Ettringite crystals form widely-dispersed throughout the paste. If expansion causes cracking, ettringite may

subsequently form in the cracks but this does not mean the ettringite in the cracks caused the cracks initially.

DEF causes a characteristic form of damage to the concrete. While the paste expands, the aggregate does not. Cracks form around these non-expanding 'islands' within the paste - the bigger the aggregate, the bigger the gap. DEF usually occurs in concrete which has either been steam cured, or which reached a high temperature during curing as a result of the exothermic reaction of cement hydration. As the curing temperature of concrete increases, ettringite normally persists up to about 70 C. Above this temperature it decomposes. In mature concrete, monosulfate is usually the main sulfate-containing hydrate phase and this persists up to about 100 C. DEF could occur in concrete which was heated externally, e.g.: from fire. An ettringite molecule contains 32 molecules of water; ettringite formation therefore requires wet conditions.

DEF and ASR appear to be closely linked; in one study (Diamond and Ong, 1994) a mortar made using limestone aggregate was cured at 95 C. Subsequent ettringite formation within the paste was scarce and expansion was minimal. However, if aggregate susceptible to ASR was used instead of limestone, ettringite formation and expansion were both much greater. This, and other studies, suggests that ASR is, or can be, a precursor for DEF expansion. The effect of cement composition on DEF is not well understood. Some factors correlate strongly but the causes are not clear. In laboratory tests, DEF expansion was shown to correlate positively with cement-related factors, including: high sulfate, high alkali, high MgO, cement fineness, high C₃A, high C₃S

IX. THAUMASITE FORM OF SULFATE ATTACK (TSA)

The thaumasite form of sulfate attack (often abbreviated to TSA) requires a source of sulfate and also of carbonate. Thaumasite can occur rarely as a natural mineral as an alteration product of limestones. Thaumasite can form in concrete and in mortar. The cement hydration products normally present, mainly calcium silicate hydrate and calcium hydroxide, are decomposed as a result of both sulfate attack and of carbonation. Since it is the calcium silicate hydrate in concrete that provides most of the strength, thaumasite formation results in severe weakening. Thaumasite has the chemical formula: $\text{Ca}_3\text{Si}(\text{OH})_6 \cdot 12\text{H}_2\text{O}] (\text{SO}_4)(\text{CO}_3)$ or $\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$ It tends to form at low temperatures, typically about 4 C - 10 C. As it forms, the concrete or mortar converts to a friable material often described as a 'mush.' Concrete severely affected by thaumasite formation can easily be broken with the fingers and the coarse aggregate lifted out. A source of additional water is also required for thaumasite formation. Damp cementitious render over brickwork, especially where the render is cracked, and concrete and

masonry in cool, damp cellars are typical examples of where thaumasite may occur. Normal sulfate attack usually results in the formation of ettringite. This uses aluminium provided by the cement and clearly this is limited in quantity in normal concrete. However, thaumasite formation does not involve aluminium; given an adequate supply of sulfate and carbonate, thaumasite can continue to form until the calcium silicate hydrate is completely decomposed. Consequently, while the use of sulphate-resisting Portland cement provides some defence against normal sulfate attack, it does not give any particular protection against thaumasite formation. Sulfate can be supplied from a range of sources; groundwater or bricks are common examples. Carbonate can be supplied from atmospheric CO₂ or from limestone present in the concrete or mortar. Serious damage to concrete or masonry due to thaumasite formation is not a common occurrence, even in cool, damp climates. Thaumasite (CaCO₃·CaSO₄·CaSiO₃·15H₂O) is formed during sulfate attack in the presence of carbonates at low temperatures. Unlike Ettringite the quantity of thaumasite that can form is not limited by the Al₂O₃ content, but only by CaO and SiO₂ can cause severe damage, but is not believed to be the principal cause of concrete deterioration by sulfate attack.

X. PREVENTION OF SULPHATE ATTACK

The quality of concrete, specifically a low permeability, is the best protection against sulfate attack. Adequate concrete thickness, High cements content, Low w/c ratio, Proper compaction and curing.

The key to prevention of sulphate attack is to tie up the free lime and calcium aluminates to eliminate the possibility of ongoing reactions. As far as 1908, Jewett reported the use of natural pozzolans (fly ash is a manufactured pozzolan) to combat sulphate attack in concrete. Dikeou, 1970, prepared the US bureau of reclamation research report no. 23 "fly ash increases resistance of concrete to sulphate attack." In that report Dikeou found that all of the bituminous coal fly ashes greatly improved the resistance of concrete to sulphate attack regardless of the type of cement used.

Increased sulphate resistance of concrete containing fly ash may be explained by the reaction of silica, alumina and ferric oxide found in fly ash with calcium hydroxide liberated during the hydration of Portland cement to form relatively stable cementitious compounds. Greater impermeability of fly ash concrete reduces penetration of sulphate solutions and result in improved resistance to sulphate attack.

The British building research establishment digest 363 (July 1991) entitled "Sulphate and Acid resistance of concrete in the ground". Is strongly recommended for further reading on the impact of sulphates and precautions which can be taken. Recommended options for most levels of exposure include blends of various types of Portland cement with fly ash. In this technique it is claimed to be effective particularly

when the proportion of fly ash is between 25 to 40 percent of the total cementitious material.

The American concrete institute guide to durable concrete also recommends the use of fly ash as an aid to the prevention of disruptive expansion of concrete exposed to sulphates.

XI. HELPFUL UNITS

A. Figures



Fig. 1 Bridge Column in Sulphate Soils Due to External Sulphate attack.



Fig.2 Concrete Box Beam due to sulphate attack

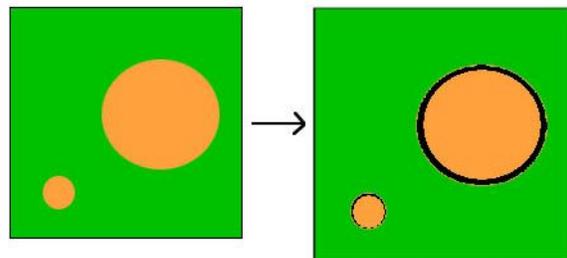


Fig.3. Diagram showing how paste expansion produces a small gap around small aggregate particles and a bigger gap around larger particles.

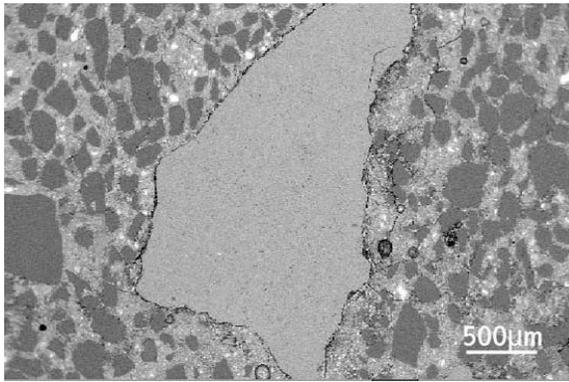


Fig.4. Scanning electron microscope image of limestone aggregate particle. The cement paste has expanded and a gap has formed between the aggregate and the cement paste. This is characteristic of damage to concrete due to DEF. The aggregate is no longer contributing to concrete strength, since it is effectively detached from the cement paste. Often, these gaps become filled with ettringite.



Fig.5. Spalling due to Sulphate attack

XII. CONCLUSION

Some of the important factors influencing the rate concrete deterioration are the flow of groundwater and soil porosity the form of construction and the quality of concrete. By adding a pozzolanic admixture such as fly ash reduces the C3A content of cement. The sulfate attack tends to increase with an increase in the concentration of the sulfate solution up to a certain level.

Any other of fly ash in the concrete is likely to be better than none. A binder containing 40% by mass of fly ash is commonly favoured. Given that enough cement must be present to ensure adequate early strength and long term durability of total binder content will vary depending on application.

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