

Well Cements Exposed to Sulfate-Bearing Formation Water: Barrier Integrity Damage and How to Mitigate It

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Summary

Destructive effects of reactions between hardened Portland cement and formation water containing dissolved sulfate ions, termed “sulfate attack”, is well documented. However, mechanisms of sulfate attack and resulting damage to cement seal integrity caused from decades of exposure are not well understood. This document presents a brief summary of current knowledge regarding sulfate attack mechanisms along with well cement design practices demonstrated to minimize sulfate attack’s damage to well barriers.

Introduction

One of the primary functions of Portland cement as a well sealant is as a barrier to flow of unwanted fluids. This function usually places at least a portion of the well cement in contact with formation water. Many formation waters contain sulfate ions which can react with hydrated cement products to degrade the physical integrity of the barrier seal. Exposure of hydrated Portland cement to water containing calcium, sodium, or magnesium sulfate produces swelling and cracking of the cement sufficient to destroy its integrity as a flow barrier. This destruction occurs more rapidly at lower temperatures, and, under the right conditions, it can result in uncontrolled flow of well fluids up the annulus to the surface. Deterioration of a cement well barrier by sulfate attack also exposes casing to the corrosive effects of the formation water.

Damaging effects of sulfate anions on Portland cement had been recognized in the 19th century by the construction industry (Eglinton, 1998). Deterioration to concrete structures, usually extending below ground such as building foundations or dams, was recognized as sulfate attack. Adjusted Portland cement chemistry to reduce the amount of tricalcium aluminate (C3A) had proven to reduce or prevent the damage.

The potential for sulfate attack to Portland cement well barriers was recognized early on. Rordam and Willson (1938) reported studies of Portland cement degradation from corrosive waters containing sodium sulfate, magnesium sulfate, and magnesium chloride. Swelling, spalling, and disintegration were noted in relatively short times well cements exposed to these fluids at 70°F with little effect occurring at 200°F.

Lowering tricalcium aluminate (C3A) content of the cement had reduced degradation of construction cement by corrosive sulfate waters, and this fix proved to be effective for oilwell cements, too. The authors recommended limiting C3A content of oilwell cement to less than 3% to prevent degradation of cement integrity by sulfate attack.

Sulfate Attack Mechanisms

Sulfate attack mechanisms were originally believed to be relatively simple and straight forward. Chemical reactions of C3A and SO_4^- form the crystalline phase, ettringite (calcium sulfo-trialuminate). These crystalline products were greater in volume than the reactants, and induced internal stresses resulting in failure of the crystalline matrix and cracking. This is the same mechanism that explains expansion of high-C3A cement formulated with small amounts of gypsum. So, limiting C3A concentration did produce well cements resistant to sulfate attack by secondary sulfate sources. Hence, the API specifications for sulfate resistant cement classes (API Spec 10A, 2019).

However, it turns out that sulfate attack mechanisms are not nearly as straightforward as first believed. Literature review summarized below reveals the complexity of sulfate attack.

Santhanam et al (2001) reviewed level of knowledge concerning mechanisms of sulfate attack compared to construction industry practices used to preclude damage. Effects of ettringite on cement expansion were best understood, but four different ettringite structures with different reaction rates and expansion characteristics discouraged simple, unified description of damage resulting from ettringite formation. The possibility of carbonation of ettringite to produce thaumansite, a non-cementitious carbonate-substituted form of ettringite widely thought to form only at temperatures close to freezing point of water, was also raised due to recent identification of the mineral associated with sulfate attack in warm climates. Gypsum formation effects were not as well quantified, but several studies linked gypsum formation due to sulfate attack with significant expansions of high C3S cements. Magnesium anions were noted as a detriment to CSH phases in cement. Magnesium can displace calcium to form M-S-H phase which is non-cementitious. Thus, water containing MgSO_4 can result in strength deterioration of cements with no C3A. The physical damage caused by solubility gradients in pore structure of cement was briefly mentioned as well. The paper concluded that sulfate attack mechanism is sufficiently understood to generally combat sulfate attack, but the understanding was not always applied appropriately in the construction industry.

Thermodynamic and kinetic effects of crystallization with respect to sulfate attack occurring in porous cement or concrete is discussed by Scherer (2004). The study describes physical and mechanical gradients that can result from chemical reactions of sulfate attack occurring in material porosity. Small confined space in which reaction occurs can result in chemical non-equilibrium within porosity generating stresses well above the cement's crystalline matrix tensile strength.

Abba et al (2017) further documented chemical and physical sulfate attack mechanisms in concrete. Ettringite formation from reaction of C3A and sulfate and gypsum formation from reaction of portlandite (Ca(OH)_2) and sulfate were chemical reactions contributing to expansion and disintegration. Physical stresses in cement porosity resulting from sulfate attack chemical reactions and non-equilibrium were also summarized.

Morales et al (2003) performed an extensive study of sulfate attack mechanism and methods to alleviate damage to Class A oilwell cement. This study pulled sulfate attack chemistry into the realm of well cementing. This relatively short term study confirmed ettringite and gypsum formation as drivers for sulfate attack. A two-stage mechanism of ettringite formation was proposed. Stage one, incubation, involved ettringite deposition into pore spaces without accompanying expansion or damage. Stage two, propagation, occurred when porosity was full and resulted in expansion and degradation. No damage to test specimens was noted over this 240-day test period at temperature above 150oF. However, the secondary sulfate attack mechanisms not associated with stable ettringite formation discussed above might still manifest at higher temperature and longer timeframe. This potential is mentioned since Morales states that typical well cement permeability is two orders of magnitude less than that of typical concrete. Diffusion control of the sulfate attack reactions might extend the timing of evident damage for well cement. Morales noted that three cement additive classes reduced extent of sulfate attack in the study: latex, sodium silicate, and microsilica. All three additives are believed to lower cement porosity and permeability.

Minimizing Damage to Cement Well Barriers due to Sulfate Attack

In spite of the various complicated and poorly-understood mechanisms by which sulfate ions react with hydrated Portland cement to degrade cement seal integrity, cement chemistry specification and admixture design practices identified early on appear to successfully mitigate sulfate attack.

While no magic bullet can negate this long-term degradation process for cement with higher concentrations of C3A, cements low in C3A curb formation of ettringite and produce well cement barriers that remain durable in presence of secondary sulfate ions. Further, addition of pozzolan or slag reduces ettringite formation and increases availability of portlandite to react with sulfate. Finally, reduction of the hardened cement's porosity and permeability by reduction of water ratio or addition of ultrafine or nano particles further mitigates progression of and damage due to sulfate attack.

The keys to designing durable cement barriers resistant to sulfate attack include:

- Low-C3A Portland cement (< 3% C3A)
- Addition of reactive diluents such as pozzolan or slag
- Minimize porosity and permeability with fine particulates or reduced water

Unfortunately, these formulation adjustments to remedy sulfate attack are not always logistically practical or applicable to well conditions governing placement of the cement barrier. A magic bullet to render high C3A cement resistant to sulfate attack would allow use of locally-available, high-C3A cements in regions without easy access to sulfate-resistant cement supplies. Also, treated high-C3A cements could be designed with low-density additives that tie up excess water to dilute and lower density of the cement with accompanying increased in porosity and permeability.

At first glance, addition of stoichiometric amounts of Na₂SO₄ to react with C3A forming ettringite as the cement hardens would negate effects of secondary sulfate attack. The bullet is a blank rather than magic since the secondary reactions of ettringite and portlandite with sulfate ions produce cement disintegration and resulting barrier seal degradation.

Thus, for well environments with water containing dissolved sulfate ions, the only sure design approach to formulate cement barriers resistant to sulfate attack is by starting with low-C3A cement.

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