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AGGREGATE EXPANSIVITY DUE TO SULFIDE OXIDATION - II. PHYSICO-CHEMICAL MODELING OF SULFATE ATTACK

I. Casanova, A. Aguado, and L. Agulló
Departament d'Enginyeria de la Construcció, Edifici C1 Universitat Politècnica
de Catalunya, E-08034 Barcelona, Spain

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ABSTRACT

Weathering of sulfide-bearing aggregates in concrete causes the release of sulfate ions that can react with cement components to yield expansive products. The extent of the sulfate attack of the paste is controlled by the composition and size of the aggregate, the kinetics of sulfide oxidation, the composition of cement and mix proportioning of concrete. The extent of sulfate attack has been successfully simulated using a combined kinetic-thermodynamic approach. © *1997 Elsevier Science Ltd*

Introduction

Sulfate attack is one of the most widespread types of concrete deterioration during the service life of the material. It is actually a complex process, generally involving a sequence of different chemical reactions, whose character and mechanisms depend on a variety of parameters, including cement composition, nature of the aggregates and additives, and environmental factors. Damage of concrete materials undergoing sulfate attack often appears as cracks resulting from the formation of expansive products. It is generally accepted that these arise from the reaction of sulfate ions with portlandite producing gypsum which, in turn, will react with tricalcium aluminate from the cement yielding to monosulfoaluminate and/or ettringite. The two most common sources of sulfate ions are natural waters and gypsum used for the concrete mix. Sulfate attack associated with these kinds of sources generally becomes evident at early ages, depending on cement composition and mix proportioning. Another potential source of sulfate ions may result from the degradation of sulfur-bearing aggregates. The mechanism and evolution of these types of reactions depend strongly on the mineralogy and size of the aggregate, as well as the kinetics of the degradation process itself.

In this work, a model for the estimation of the extent of sulfate attack due to sulfide oxidation is presented. Calculated dimensions for sulfate attack aureoles around sulfide-bearing aggregates are in very good agreement with microstructures observed in aggregate-paste interfaces in mass concrete, strengthening the usefulness of chemical kinetics as a tool for assessing the potential deleterious effects of sulfur-bearing aggregates in concrete.

Thermodynamics and Kinetics of Sulfide Oxidation

Sulfides (especially pyrite, FeS_2, and pyrrhotite, $Fe_{1-x}S$) are common minor constituents in most rocks and, hence, the study of their degradation under the physico-chemical conditions in concrete is of special relevance for the assessment of the durability of cement-based materials. Previous work of sulfide oxidation has focussed on the oxidation of pyrite (perhaps the most abundant sulfide on the Earth's surface) applied to the assessment of mine waste acidic drainage (1,2,3). Some recent studies (4,5) have addressed the influence of sulfide oxidation in the durability of concrete with pyrite and/or pyrrhotite-bearing aggregates. From these works, it becomes clear that there are three major factors affecting the mechanisms of sulfide oxidation: concentration of molecular oxygen, alkalinity (pH), and particle size and shape. Prior to studying the evolution in time of sulfide oxidation and its effects on sulfate attack and subsequent expansion phenomena in concrete, it is necessary to evaluate the equilibrium conditions under which such reactions take place. For this, different possible sulfide oxidation reactions have been considered (6), yielding goethite (FeOOH), hematite (Fe_2O_3) and ferrihydrite ($Fe(OH)_3$) as dominant sulfide degradation products. Another potential reaction product is melanterite ($FeSO_4 \cdot 7H_2O$), but it has little relevance in this study due to its extreme instability and rapid evolution, by dehydration, to szomolnokite ($FeSO_4 \cdot H_2O$). As mentioned above, pH conditions control the predominance of one or another reaction. This, in turn, affects the relative amounts of sulfate released into the system and the subsequent reactivity with the cement paste. Therefore, we have carried out a thermodynamic study to determine the predominant reaction in order to identify the most stable oxidation product. For this, a conventional pH-pε equilibrium diagram has been constructed (Figure 1).

Two major conclusions relevant to the study of sulfide oxidation under the physico-chemical conditions typical of concrete may be derived from the results of this thermodynamic approach. First, the predominant phase at alkaline pH values (>7) is ferrihydrite, with only minor amounts of siderite, an iron carbonate, at pH between ~7 and 10. Second, no sulfide will be stable at pH values above 10. The sulfide oxidation rate at or around neutral pH values (between 7.5 and 8.5) is mostly independent of the alkalinity, and seems to be mainly controlled by oxygen availability and grain size (7). However, there is experimental evidence that the speed of oxidation is greatly enhanced under strongly alkaline conditions ($12.5 < pH < 13.7$), the rate increasing a factor of 50 over a 1.2 pH units interval (5).

Modeling Sulfate Attack

Oxidation of sulfides induces only minor volume changes as compared to other, more expansive reactions. Specifically, concrete expansivity due to sulfate attack is mostly controlled by the formation of high molar volume ettringite ($C_6A\bar{S}_3H_{32}$) and/or monosulfoaluminate ($C_4A\bar{S}H_{12}$). Ettringite becomes a stable hydration product only when there is an ample supply of sulfate available, following the reaction:

$$C_3A + C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32} \qquad (1)$$

If all the sulfate is consumed before the tricalcium aluminate is completely hydrated, then ettringite transforms to monosulfoaluminate (which contains less sulfate):

$$2C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow C_4A\bar{S}H_{12} \qquad (2)$$

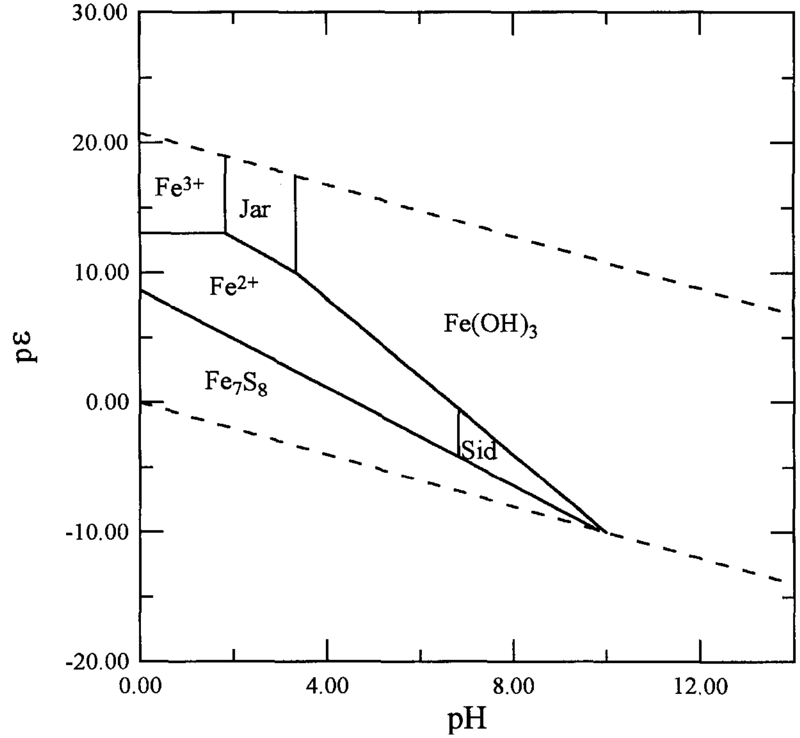

FIG. 1.

Equilibrium pH-pε diagram showing the stability fields of different ionic and mineral species involved in pyrrhotite (Fe_7S_8) oxidation. Jar = Jarosite, $KFe_3(SO_4)_2$; Sid = siderite, $FeCO_3$. Boundaries calculated for arbitrary values of $P(CO_2) = 10^{-2}$ atm., $a(Fe^{2+}) = 10^{-4}$, and $a(SO_4^{=}) = 10^{-2}$. Dashed boundaries limit the stability of water under atmospheric conditions.

The formation of ettringite or monosulfoaluminate according to reactions (1) and (2), respectively, is controlled by the gypsum/tricalcium aluminate ($C\bar{S}H_2/C_3A$) molar ratio in a given system (Table 1).

We have adopted a geometric model (Figure 2) to calculate the dimensions of the sulfate attack aureole induced by reaction of sulfate ions, released by sulfide oxidation, with tricalcium aluminate from the cement, using a kinetic model (9) and procedures described in (6).

Calculation from the chemical composition of the Portland cement used in the case studied (see Table 3 in ref. 10) yields a value of $C\bar{S}H_2/C_3A = 0.66$ suggesting, according to the criteria listed in Table 1, that monosulfoaluminate should be the only stable expansion product. However, petrographic observations and X-ray diffraction analyses have revealed the presence of non-negligible amounts of ettringite, while no monosulfoaluminate has been detected (11). Consequently, an additional source of sulfate, most likely from the, is necessary to account for the formation of the observed ettringite. This observation validates the hypothesis of sulfate attack induced by oxidation of sulfides.

The simulation has been carried out to reaction completion (i.e., all sulfide in the aggregate becomes oxidized) in order to estimate worst-case conditions; therefore, the results overes-

TABLE 1
Formation of hydration products from C_3A (Ref. 8).

$C\bar{S}H_2/C_3A$ molar ratio	Hydration Products Formed
3.0	Ettringite
3.0–1.0	Ettringite + monosulfoaluminate
1.0	Monosulfoaluminate
<1.0	Monosulfoaluminate solid solution(1)
0	Hydrogarnet

(1) When small amounts of gypsum are present, some unreacted C_3A may remain upon conversion of ettringite to monosulfoaluminate. Then, a solid solution between two isostructural hydrates ($C_4A\bar{S}H_{12}$ and C_4AH_{13}) may be formed.

timate the actual effects of sulfate attack but provide useful information for safety assessments of concrete pathologies due to sulfide-bearing aggregate reactivity. The model has been successfully applied to a real case of aggregates containing pyrrhotite in mass concrete of two gravity dams (10). Calculations of the sulfate attack aureole around aggregate grains of 5–25 mm in radius (R_1 in Figure 2) yield R_2 values ranging between 0.1 and 0.6 mm, in excellent agreement (within a factor of 2) with the dimensions observed in hand specimens of concrete after 30 years of service.

Expansivity due to volume changes from the conversion of sulfide into ferrihydrite is only

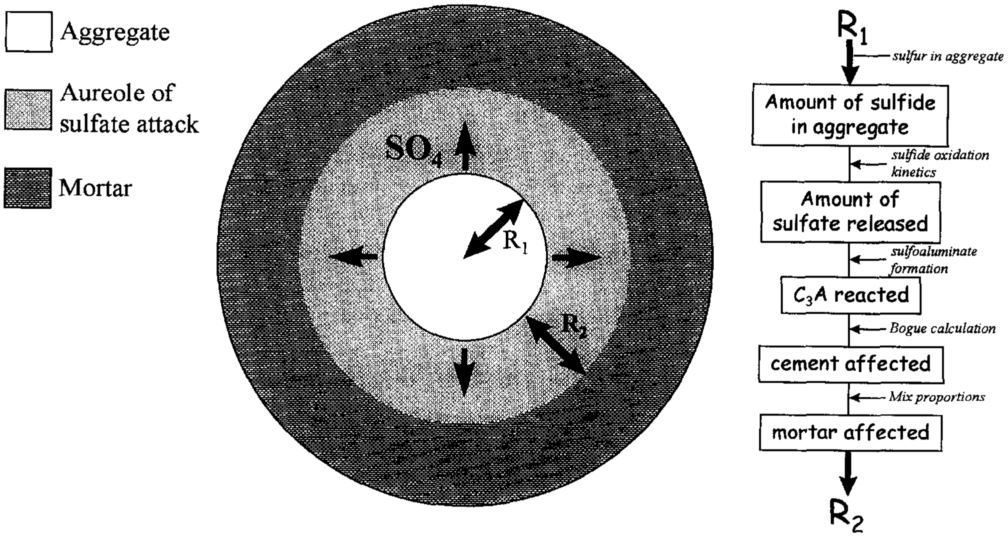

FIG. 2.

Sketch showing the theoretical geometric model and flow diagram used for the calculation of the extent of the sulfate attack aureole (R_2) generated by leaching of sulfate ions from oxidation of sulfides in an aggregate of known dimensions (R_1) and sulfur content.

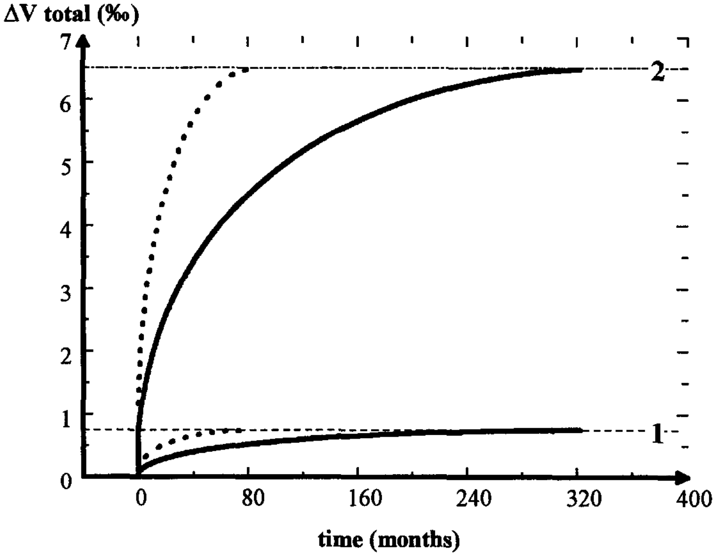

FIG. 3.

Time evolution of aggregate expansion induced by sulfide grains of 100 (dotted) and 200 (solid) microns in radius. The dashed horizontal lines labeled “1” and “2” represent, respectively, the maximum concrete ΔV values achieved by primary expansion (oxidation of all the sulfide mass) and sulfate attack (ettringite formation). Pore volume in mass concrete is considered negligible, and rigid behavior is assumed.

about 13% of that induced by sulfate attack on the paste and subsequent formation of ettringite, as it becomes evident in Figure 3. The absolute value of concrete expansion (6.5‰) is about 15–20 times larger than the unit strain due to shrinkage in mass concrete. This must be considered, however, an upper limit for the maximum expansion that a given block in the dam may undergo, since no geometric or pressure confinement effects are considered in this model.

Summary and Conclusions

Oxidation of sulfide-bearing aggregates induces a sulfate attack reaction on the surrounding mortar through the release of sulfate ions and reaction with tricalcium aluminate from the cement. The rate of oxidation is slow, and depends strongly on the alkalinity of the pore solutions, the availability of molecular oxygen and the grain size of the aggregate. However, the sulfate attack reaction are much faster and can be modeled using equilibrium thermodynamics. The extent of sulfate attack (dimensions of the reaction aureoles) have been successfully simulated using a spherical geometry model, aggregate and cement compositions, and mix proportions for each case studied. The good agreement between calculated values and aureoles observed in concrete specimens strengthens the validity of physicochemical modeling as a tool for the prediction of pathologies due to sulfate attack.

Acknowledgments

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