The Sulfate Attack in Concrete by Degradation of Iron Sulfides and the Effect of the Host Rock

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ABSTRACT

In this study we deal with the problems of durability of concrete made with reactive aggregates, and more particularly those containing oxidizable iron sulfides. These sulfides are oxidized in the presence of water, to generate sulfates. Those sulfates react with the cement aluminates to form ettringite and/or thaumasite, which are highly expansive nature.

We present an experience that demonstrates the differences in the amount of expansive compounds that are generated based on the type of iron sulfides (pyrite and pyrrhotite). The paper also makes clarifications on the role of host rock. In the case of limestone, the buffering effect of calcite minimizes the effects of degradation of sulfides in contrast to the shale type lithology.

KEY WORDS

Reactive aggregates, Iron sulfides, Ettringite, Thaumasite, Host rock.

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1 REACTIVE AGGREGATES

The durability problems in portland cement concrete due to reaction between cement alkalis with certain types of aggregates are well known. The most popular reactions are the alkali-aggregate AAR among which are the alkali-carbonate and alkali-silica. There is less documentation of the expansions produced in concrete as a result of the degradation of iron sulfides contained in aggregates, a phenomenon known as "internal sulfate attack".

The alkali-carbonate reaction occurs in some concretes with dolomitic rocks as aggregates. In an alkaline medium, portlandite reacts with dolomite (calcium-magnesium carbonate) to form brucite (magnesium hydroxide) and calcium carbonate in a reaction called dedolomitization. When brucite absorbs water, it increases in volume and causes expansions [Min and Mingshu 1993].

The alkali-silica reaction (ASR) is the most studied alkali-aggregate reaction, and it commonly occurs when the alkali present in the concrete pore solutions react with low crystallinity siliceous aggregates. After this reaction it is formed a gel that when imbibes water, increases in volume and expands [Hobbs 1988; Garcia-Diaz, et al 2006] (Fig. 1).

Fig. 2 shows the appearance of white gel, a symptom of alkali-silica reaction. The right part of the sample was stained with a selective staining to visually enhance and recognize these signs and the reaction products.

![Figure 1. Characteristic features of the AAR. We can see the typical rims and the expansive gel. Photo of the authors.](image-url)
Figure 2. Photograph that shows in the left side the typical (unstained) halos of AAR. In the right side, it has been applied a solution for staining the potassium. Photo of the authors.

The Internal sulfate reaction (ISR) is a phenomenon that occurs in some concrete made with aggregates with oxidizable iron sulfides. This type of reaction has been less studied and is less documented than the AAR but our Research Group has worked for years in the expansions of concrete dams with aggregates containing pyrite or pyrrhotite [Araújo et al 2008; Chinchón et al. 1990, 1993]. The identification of the type of iron sulfide is simple by SEM, by seeing its morphology and the S / Fe obtained from a precise EDX analysis by backscattered electrons, because the sample is conductive (Figs. 3 and 4).

![Morphology and EDX analysis of pyrite.](image)

**Figure 3.** Morphology and EDX analysis of pyrite.
When these sulfides are in an aqueous medium with dissolved oxygen they are oxidized to produce sulfates (equations 1 and 2) which can then form gypsum, secondary ettringite and in some cases thaumasite.

\[
\text{FeS}_2 + \frac{7}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \tag{1}
\]

\[
\text{Fe}_{1-x}\text{S} + (2-(1/2)x)\text{O}_2 + x\text{H}_2\text{O} \rightarrow (1-x)\text{Fe}^{2+} + \text{SO}_4^{2-} + 2x\text{H}^+ \tag{2}
\]

In the literature there are references about the influence of the degradation of iron sulfides contained in aggregates on concrete durability, although nearly all the authors refer to the ettringite as the only neoformed expansive product [Ayora et al 1998; Tagnit-Hamou et al 2005], however under certain conditions thaumasite can be formed (Figs. 5 and 6).

The ettringite can form thaumasite if low temperatures and calcium carbonate are available. To form thaumasite there must be small ettringite crystals so that from them, epitaxially, the thaumasite crystals grow [Taylor 1997; Barnett et al 2003]. The thaumasite formation by sulfate attack is harmful to the durability of concrete because its formation causes expansion and because it consumes the CSH cement phase [Sahu et al 2002; Mehta 1993]. Although both ettringite and thaumasite have very similar acicular appearance when viewed by SEM, the presence of Si and the Al absence in thaumasite, and the presence of Al and no Si in the ettringite EDX analysis are decisive for its identification.

![Figure 4. Morphology and EDX analysis of pyrrhotite.](image)

![Figure 5. The SEM photograph shows an overall growth of ettringite crystals on the surface of concrete. Ettringite is filling the pores. A superficial crack in the cement paste can be appreciated.](image)
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The SEM photograph shows an abundant acicular growth. EDX analysis confirmed that this is thaumasite crystals.

The Regulations governing the presence of iron sulfides in aggregates for concrete do not distinguish between pyrite and pyrrhotite, they neither refers to the importance of the host rock [EHE-08 2008; ASTM C294-05 2005]. These two aspects have been discussed in a recent paper that we sent, and is being evaluated, to the Engineering Geology magazine [Chinchón-Payá et al 2010].

2 DIFFERENCES BETWEEN DIFFERENT IRON SULFIDES

In the cited study [Chinchón-Payá et al 2010] we evaluated the oxidative degradation in aqueous of two iron sulfides, a sample of pyrite and another of pyrrhotite, in the same experimental conditions to differentiate the behavior they exhibit (Table 1).

Table 1. Analytical results of the dissolution of pyrite and pyrrhotite. It includes iron and sulfate concentrations solutions and the pH value when considered constant for both.

<table>
<thead>
<tr>
<th></th>
<th>Pyrite</th>
<th>Pyrrhotite</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe] (ppm)</td>
<td>270</td>
<td>455</td>
</tr>
<tr>
<td>[SO$_4^{2-}$] (ppm)</td>
<td>1238,7</td>
<td>1517,8</td>
</tr>
<tr>
<td>pH</td>
<td>3.1</td>
<td>4.3</td>
</tr>
</tbody>
</table>

According to these results pyrrhotite provides over 20% more of sulfates to the water of dissolution. If these waters come into contact with a concrete could lead an aggressive attack to the concrete.

A fast decrease in pH is observed at the moment of putting them in contact with water, and a slight gradual decrease, until they reach constant values 50 days after beginning the experiment. According to the results, it seems clear that the pyrite dissolution leads to an environment with more protons than the pyrrhotite dissolution. This can be explained considering that the reactions that take place in the medium depend on the steechiometry of the sulfides (FeS$_2$ for pyrite and Fe$_{1-x}$S to pyrrhotite). (See also equations 1 and 2).
3 THE ROLE OF THE HOST ROCK

Later to the aforementioned work [Chinchón-Payá et al 2010], an experience of dissolution of sulfides was designed similar to above but this time adding two different types of aggregates. The aggregate type A is a mixture of calcite, quartz and feldspar in proportions of 22%, 58% and 20% respectively, the aggregate type B is a silica sand used in Spain as a standard quartz that comes from the Institute of cement and construction Eduardo Torroja and having a SiO$_2$ content over 95%.

It were also evaluated, among other parameters, the change in pH and concentration of major ions Fe and SO$_4^{2-}$ (see Table 2).

Table 2. Analytical results of the concentrations of sulfate and iron (ppm) and pH value of solutions when considered constant. Py and Po represent pyrite and pyrrhotite, respectively, while A is the aggregate with 22% calcite and B the silica aggregate.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Sample Py +A</th>
<th>Sample Po +A</th>
<th>Sample Py + B</th>
<th>Sample Po + B</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4^{2-}$</td>
<td>89,0</td>
<td>130,9</td>
<td>419,9</td>
<td>182,9</td>
</tr>
<tr>
<td>Fe</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>53,8</td>
</tr>
<tr>
<td>pH</td>
<td>8.1</td>
<td>8.2</td>
<td>6.1</td>
<td>5.3</td>
</tr>
</tbody>
</table>

When in the dissolution medium there are aggregates with carbonates, these will dissolve and mitigate the effect of the pure, and without influence, dissolution of iron sulfides.

In the dissolution of the iron sulfides with siliceous aggregates, this behaved as an inert component, since the solution from the very beginning presented pH values similar to those of the solution prepared with iron sulphurs but without any additions. That experience was considered complete after 10 days.

In the second one, the jointly dissolving of iron sulfides and carbonates, what we can see is the initial increase of pH due to the fast solution capacity of calcium carbonates:

CaCO$_3$ + H$_2$O $\rightarrow$ Ca$^{2+}$ + HCO$_3^-$ + OH$^-$

As the system tends to equilibrium, pH will gradually fit the values typical of the carbonate buffer system.

As for the content of SO$_4^{2-}$ in solution, approximately one third is generated in the solution containing the limestone coarse aggregate than in the solution which does not contain it (See Table 2), which should be understood as a shock-absorbing effect of carbonates.

4 DISCUSSION

There are certain types of aggregates that after its reaction with some components of the concrete will form expansive compounds that affect the concrete durability. The most studied process is known as alkali-aggregate reaction and affects dolomitic aggregates or those containing low crystallinity silica.

The internal sulfate reaction is a less documented expansion process that happens when oxidizable iron sulfides are as aggregates in the manufacture of concrete. The iron sulfides are oxidized in the presence of water to produce sulfate and then form gypsum, ettringite or thaumasite.

The Regulations governing the presence of iron sulfides in aggregates for concrete in some cases make no distinction between pyrite and pyrrhotite and others only the pyrrhotite is responsible. In this communication we refer to a study showing that both are bad but pyrrhotite is worse than pyrite.
Finally we show the results of an experiment in which we have evaluated the role of the host rock. The limestone rocks buffer the damaging effects of the dissolution of the sulfides (both pH and concentration of sulfate available for subsequent sulfate attack) while siliceous aggregates are more harmful.

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**REFERENCES**


