

# Deterioration of Some Concrete Structures of a Sulfuric Acid Plant

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The paper describes an investigation of deteriorated concrete structures of a sulfuric acid plant, including some isolated concrete structures, the foundation of an acid silo, and a harbor quay for storage of pyrites. Thin-section examinations of samples of the concrete showed that the cement paste had been transformed into a microcrystalline porous substance resembling gypsum. Chemical analyses of the groundwater, of the water in the harbor, and of the water in a ditch of the quay revealed a high content of sulfate ions and, in the water in the ditch, a high content of iron (+2) ions. The atmosphere smelled of sulfur dioxide. It is concluded that the concrete is probably deteriorated by the attack caused by (a) sulfur trioxide in the atmosphere combining with water, (b) sulfuric acid waste, and (c) the lowering of pH in the disintegration of pyrites. Low- $C_3A$  cement was recommended for the future construction of concrete structures at the plant.

•THIS PAPER deals with the problem of deterioration of concrete structures near a sulfuric acid plant as a result of the aggressive environment. The investigation involved isolated concrete structures, the foundation of an acid silo, and a quay for storage of pyrites.

An investigation of the isolated structures revealed disintegration to such an extent that the aggregates became visible. The reinforcement bars in the structures were corroded. The concrete of the existing quay was not attacked, but the inspection was difficult because the foundation was coated with a layer of white mud.

## ENVIRONMENT AND EXAMINATION OF THIN SECTIONS

The atmosphere smelled of sulfur dioxide. Sulfur dioxide and probably sulfur trioxide existed in the atmosphere and reacted with water, giving acid. Samples of the water in the harbor, of the groundwater, and of the water in a ditch of the quay were taken. Chemical analyses of these water samples showed a high content of sulfate ions and, in the water in the ditch of the quay, a high content of iron (+2) ions.

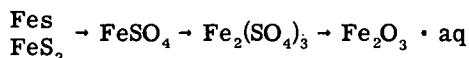
Specimens were taken of concrete from the isolated structures, from the foundation of the acid silo, and from the quay, and thin sections of the specimens were made. Examinations of the thin sections (thickness  $20\ \mu$ ) showed that most of the cement paste was replaced by a microcrystalline substance. The substance had a gray color in crossed nicols and was colorless in parallel nicols. Some of the small crystals had a distinct cleavage. Some cracks were filled by a substance that had a banded structure in crossed nicols; this substance resembled gypsum.

## DISCUSSION OF RESULTS

The indications from the observations were of an acid attack on the concrete structures and on the foundation of the acid silo, and an attack on the quay caused by weathering of pyrites. Sulfur trioxide combines with water to yield sulfuric acid. The acid attacks the concrete by dissolving calcium hydroxide and thereafter the cement gel, precipitating gypsum. As sulfuric acid is formed on the surface, the deterioration

mechanism will not be serious until the concrete has been exposed to acid attack for a period of time. The attack on the structures was most likely due to acid made from sulfuric dioxide and sulfur trioxide. The foundation from the acid silo seemed to have been exposed to acid attack, probably because some sulfuric acid had been spilled.

The disintegration of the pyrites was as follows:



A small amount of oxygen leads to oxidation of pyrites to iron (+2) sulfate and sulfuric acid. Iron (+2) sulfate is dissolved in the solution ( $\text{pH} < 10$ ) and comes into the cement paste. Hydroxide ions in the cement paste precipitate iron (+2) ions as iron (+2) hydroxide, which is oxidized by the oxygen dissolved in the water to iron (+3) hydroxide or iron (+3) oxide. The solution in contact with the solid iron (+3) oxide has  $\text{pH} < 3$  (1). The attack inside the pores of the concrete is caused by the low pH solution.

Oxidation of pyrites to iron (+3) sulfate gives iron (+3) oxide on the surface and sulfuric acid; iron (+3) sulfate is only dissolved in solutions with a  $\text{pH} < 6$ . The attack is consequently concentrated at the surfaces of the concrete and is therefore not as dangerous as the attack of iron (+2) sulfate.

The high concentration of sulfate ions offers a risk of sulfate reaction leading to precipitation of gypsum and expansion of the cement paste.

#### CONCLUSION

The deterioration of the concrete was found mainly to be due to an attack of acid and an attack caused by lowering of the pH in the disintegration of pyrites. The following procedures were recommended:

1. Use limestone as subgrade under the concrete pavement of the quay. Maintain a high pH in the concrete.
2. Use cement with a small content of  $\text{C}_3\text{A}$ . The high concentration of sulfate ions offers a risk of sulfate reactions.
3. Specify the manufacture of a high-quality, impermeable concrete.
4. Inspect the concrete structures periodically and check the chemical composition of the groundwater.

#### REFERENCE

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