

Understanding the Effects of Pyrrhotite in Concrete

By Kevin E Miller

The Oxidation of Pyrrhotite

To understand the deterioration of concrete structures we must first study the quarry process as aggregate containing the mineral pyrrhotite is extracted from the earth for use in the production of concrete. It is the blasting and rock crushing that starts the exposure to moisture and oxygen leading to the oxidation of the iron sulphides. As the aggregates are incorporated into concrete there is a drastic acceleration of the natural oxidation and deterioration of the pyrrhotite because of the high PH level of the cement paste.

Multiple Reactions Taking Place

Pyrrhotite is known to be unstable in the presence of water. What takes place next is a series of physical and chemical changes. The first change being the oxidation of the iron oxides. The iron oxides being very similar rusting steel, start to occupy more space leading to internal pressure in the hardened concrete. The next stage is the formation of iron hydroxide and sulfuric acid. Portland Cement used in the production of concrete contains 90% limestone which is susceptible to weakening when exposed to sulfuric acid attack. The sulfuric acid reacts with the calcite in the limestone and changes the hydration process of the cement with the formation of additional expansive products (ettringite) causing large cracks and irreversible damage to the concrete.

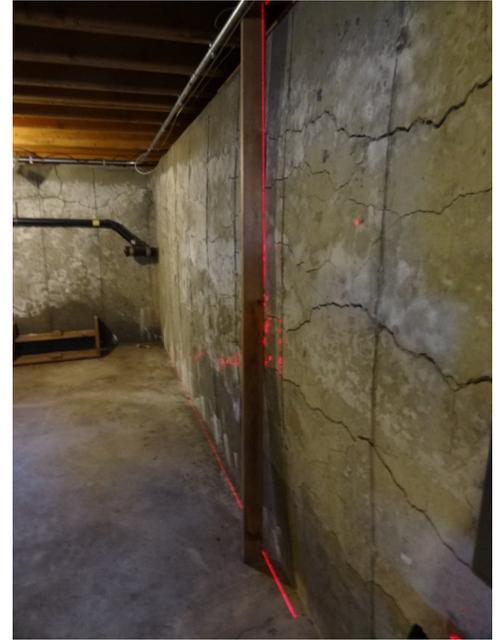


Expanding Concrete

While signs of Pyrrhotite include staining, map cracking, and efflorescence the most damaging aspect is the expansion of a mineral formation known as ettringite contained within the cement resulting in large cracks and inward bulging walls. In many cases the expansion is more severe when plenty of oxygen is available such as above grade and inside the basement spaces.

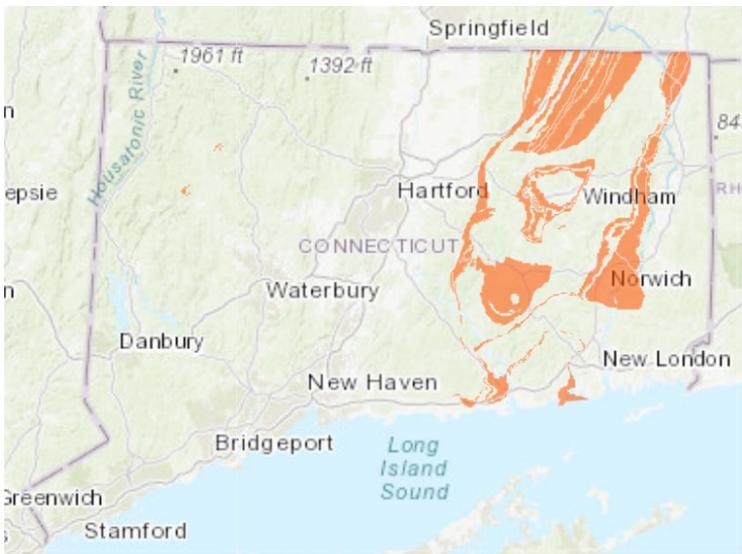
The rate of expansion remains unpredictable due to all the variables such as condition of the concrete when constructed, applied waterproofing, presence of groundwater and existing cracks which could be a conduit for moisture and oxygen. Recommended repair methods are limited to entire concrete foundation replacement.

The photo to the right shows the use of a laser to determine the bowing of the wall. Noticeable inward movement of a concrete wall should be viewed by a structural engineer to determine the integrity of the structure.

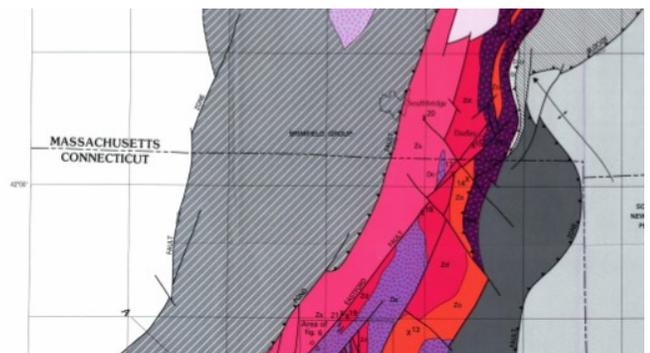


“Internal Sulfate Attack is Caused by Aggregates Containing Sulfates and Sulfides”

Pyrrhotite in Connecticut & Massachusetts



Where is the source of Pyrrhotite? A quarry in West Willington was the source on many of the Connecticut homes. The host aggregate was identified as Brimfield Schist, comprised of interlayered schist and gneiss, and a host of other minerals including garnet, sillimanite, graphite, and pyrrhotite. The map to the left highlights areas in Connecticut containing sulfidic aggregates. The photo below shows the continuance of the path into Massachusetts.





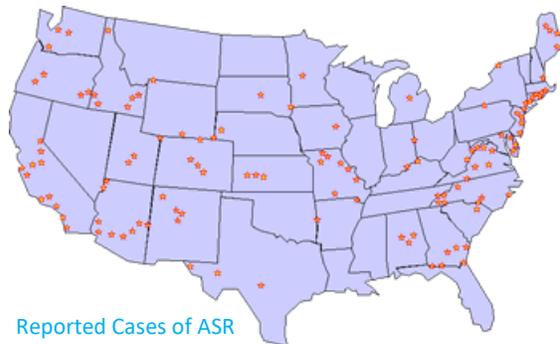
ASR, Alkali-silica Reaction

ASR versus Pyrrhotite

ASR, Alkali-silica Reaction like pyrrhotite will result in the expansion and cracking of the concrete structure leading to a reduction of the service life. Cases of ASR are widespread throughout North America and the rest of the world.

The map cracking as shown in the photo above is caused by a reaction between the cement paste and reactive silica minerals. The alkali hydroxides in the portland cement react with the silica and alkali-silica gel is formed around the aggregate. The gel under certain circumstances when exposed to water will expand and cracking of the concrete will occur. The major differences are, ASR ceases below a relative humidity of 80% and does not exhibit the weakening of the cement paste, as is characteristic of pyrrhotite damaged concrete.

It would be unlikely to witness ASR damage on the inside walls of a cast-in-place foundation, more commonly ASR damage would found on exposed exterior surfaces and exposure to multiple freeze/thaw conditions would propagate and widen the cracks. In comparison, aggregate that contains an unstable form of pyrrhotite in a large enough concentration to cause deterioration of concrete is far less common than cases of ASR.



Testing Concrete for Pyrrhotite

Currently, standards have not been established universally to determine the amount of pyrrhotite in concrete aggregate that may be present without affecting the service life of the concrete.

Trinity Test is a combination of sulfur content and thermomagnetic measurement. The two tests can estimate the presence of pyrrhotite as low as 0.5% from pulverized concrete obtained from a sample.

XRF X-Ray Fluorescence identifies the elements in a sample. While pyrrhotite is a mineral XRF will determine the ratio of sulfur to iron and results can be used to estimate the concentration of pyrrhotite.

XRD X-Ray Diffraction will identify the mineral composition of a concrete sample. The detection limit requires concentrations greater than 1% which exceeds potentially harmful limits that according to experts could be as low as 0.3%.

Microscopy Optical/Electron are the most common petrography methods and requires the trained eye to identify pyrrhotite. Sample preparation and quantitative evaluation is time consuming and subject to error.

Glossary

Ettringite is an important part of the hydration of portland cement for control of set times and strength gains at early ages. When exposed to the sulfates from the pyrrhotite, expansive secondary ettringite is formed causing cracking and expansion of the concrete structure.

Hydration is defined as combining an item with water. In this publication we are referring to the reaction created when water is added to cement. The reaction of cement hydration is exothermic, which means that the reaction will generate heat. The resulting compounds that are formed are called “hydration products”, ettringite is a product of hydration.

Internal Sulfate Attack is harmful to concrete when aggregates containing sulfates and sulfides cause changes to the cement hydration process.

Oxidation is a chemical substance change with the addition of oxygen. The oxidation of pyrrhotite produces iron hydroxides and sulfates.

Secondary Ettringite Expansion takes place as the oxidation of the pyrrhotite is accelerated by the high pH solution within the cement and the pore connectivity of the concrete allowing access for the moisture and oxygen. These secondary products can occupy 3-8 times the space of the original products.

Facts About Pyrrhotite

Pyrrhotite is named after the Greek word pyrrhos which means flame-colored. Pyrrhotite is an iron sulfide mineral closely related to iron pyrite commonly known as Fool’s Gold. Pyrrhotite is weakly magnetic and has a lower sulfur content than pyrite.

The damaging effects of pyrrhotite in concrete will begin to appear in as little as 5 years, while some cases are not discovered until around 10 years. The concentration level of pyrrhotite in the concrete, quality of the concrete and many other factors determine the service life of the concrete structure.

Pyrrhotite is the second most common iron sulfide in nature. In addition

to the Connecticut and Quebec homes in North America, pyrrhotite and pyrite has been the source of damage to concrete structures in Norway, Spain, Ireland, Great Britain, Russia, Australia and many other countries. One of the earliest discoveries of iron sulfide damage in concrete was reported in Oslo, Norway in 1959.



A Note from CFSIC

Background and Qualifications of Kevin E Miller

Kevin Miller has been employed in the concrete industry for the past 30 years. Kevin, well-versed and educated in concrete technology, troubleshooting concrete defects, and designing concrete mixtures for commercial and residential applications, is an industry veteran. Additionally, during his seven-year term as President of the Connecticut Ready Mix Concrete Association, he witnessed and was instrumental in supporting legislative changes and the incorporation of stricter quarry inspections to assure the long-term durability of concrete used in roads, bridges, and highways as well as in other commercial and residential uses. Kevin continues to remain active in the industry as a consultant on Government projects and as a troubleshooter on residential and commercial concrete issues. CFSIC has engaged with Kevin to create the only comprehensive concrete failure training course available in the state of Connecticut. He continues to serve as consultant and advisor to CFSIC.

Michael Maglaras
Superintendent, CFSIC