ResearchReport

Testing Structural Concrete Aggregate for Pyrrhotite

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Issue

Are there reliable methods of checking pyrrhotite levels in structural concrete aggregate, before it is mixed into concrete?

Summary

While there are accurate methods of determining whether an aggregate sample contains pyrrhotite, it appears that there are no widely accepted test standards (i.e., guidelines for sampling and sample preparation). Additionally, there are no widely accepted standards for the amount of pyrrhotite in concrete aggregate that may be present without impacting the concrete's integrity. According to information prepared by the Army Corps of Engineers and UConn (see "Attachments") in the context of "crumbling foundations" (i.e., foundations that have deteriorated due to the presence of pyrrhotite), more research must be done to identify (1) appropriate and cost-effective testing methods and (2) a threshold

Petrography

Petrography is the description and classification of rock by any means, from visual observations to highly technical chemical and instrumental analyses (e.g., electron microscopy and x-ray fluorescence analysis). It is generally conducted by microscopic study.

Sulfur

The element sulfur is present in several chemical forms (also called "chemical species") in nature. Two species are relevant in the aggregate context: (1) sulfate, the oxidized form, and (2) sulfide, the reduced form. Sulfide can combine with elements such as iron or copper to make different crystal structures, called minerals.

Pyrrhotite

Pyrrhotite is composed of the elements iron and sulfur; it is an iron sulfide mineral. Pyrrhotite's chemical formula varies, as it presents in several crystal structures.

Pyrrhotite expands when exposed to water and oxygen, which can cause concrete containing it to crack and swell, and eventually crumble.

above which pyrrhotite levels in aggregate impact concrete's integrity.

Below, we briefly outline the testing methods used to test for pyrrhotite in aggregate. Notably, as Table 1 shows, there is no simple method of determining an aggregate sample's pyrrhotite *concentration* (detecting the *presence* of pyrrhotite is much easier). There is no technology capable of quantifying mineral concentration (pyrrhotite or otherwise) in a complex mixture (e.g., aggregate) using an automated process, if one requires a detection limit lower than 1% by weight.

Many of the test methods analyze aggregate for sulfur content generally ("total S"). If aggregate has a high total S concentration, it is not suitable for structural concrete, regardless of the minerals making up the sulfur content (e.g., pyrrhotite or pyrite). Measuring aggregate's sulfur concentration enables one to develop a conservative estimate of the maximum pyrrhotite concentration (many minerals other than pyrrhotite contain sulfur). Tests that yield total sulfide content, or information on the relative occurrence of sulfide in a sample, provide a more nuanced estimate (pyrrhotite is a sulfide mineral (see sidebar)).

Testing Methods

According to a recent UConn presentation (see Attachment 1), there are three umbrella approaches for detecting pyrrhotite in aggregate: microscopy, chemical, and microstructural. Within the microscopy category, there are two methods: optical and electron. Within the chemical category, there are two methods: chromatography and x-ray fluorescence. Within the microstructural category, there are three methods: x-ray diffraction, x-ray photoelectron spectroscopy, and thermomagnetic (see slide 7 in Attachment 1). As shown in Table 1, only the microscopy and microstructural approaches specifically look for pyrrhotite; the chemical approaches rely on total S (see above).

According to researchers at Trinity College and UConn, it is hard to quantify the amount of pyrrhotite in a sample based on the total S concentration because (1) pyrrhotite is one of many minerals containing sulfur and (2) pyrrhotite can be made up of different ratios of iron to sulfur. However, certain methods of analysis may yield quantitative results, especially if calibrated to the regional pyrrhotite composition (i.e., the specific formula for pyrrhotite in a geographic region). Notably, certain methods of analysis, while generally able to quantify the amount of pyrrhotite in a sample, are not sensitive enough to be practical in the context of aggregate analysis. It appears that the amount of pyrrhotite in a sample that could be deleterious to concrete's structural integrity generally requires very sensitive testing (i.e., a test that can quantify pyrrhotite in very low concentrations, below 1% by weight).

Table 1: Methods of Detecting Pyrrhotite in Aggregate Samples

Umbrella Category and Method	*Specifically Checks for Pyrrhotite*	*Method Yields Quantitative Data on Pyrrhotite Concentration*	*Brief Explanation of Method*
Microscopy: Optical	✔	Depends	Uses a light microscope to magnify thin section (polished slice) of a sample; one of the most common petrography methods; requires trained eye to identify pyrrhotite crystals; quantitative measurement is time consuming and prone to human error
Microscopy: Electron	✔	Depends	Uses an electron microscope, which has a much higher magnification and resolving power than a light microscope; can be quantitative, but with the same limitations that apply to light microscopy, amplified by the higher degree of magnification
Chemical: Chromatography	No	No (but yields total S)	Separates a mixture of chemical substances into its individual components; yields total S, which can be used to estimate the maximum concentration of pyrrhotite, if the sample's mineralogy is known, among other factors
Chemical: X-Ray Fluorescence (XRF)	No	No (but yields total S and total sulfide)	Identifies the *elemental* composition of sample; while pyrrhotite is not an element, using XRF one can determine the ratio of sulfur to iron and, if pyrrhotite is the only sulfur mineral in the sample, estimate pyrrhotite concentration Wavelength dispersive XRF can distinguish between total sulfide and total sulfate, thus giving a more nuanced estimate of the maximum concentration of pyrrhotite
Microstructural: X-Ray Diffraction (XRD)	✔	✔	Identifies the *mineral* composition of sample; in the aggregate context, can measure pyrrhotite concentration only if sample has concentration exceeding at least 1%; XRD's detection limit is generally too high to be helpful in the aggregate testing context, where potentially harmful pyrrhotite concentrations may be less than 1% (detection limit is between 1% and 5%)

Umbrella Category and Method	*Specifically Checks for Pyrrhotite*	*Method Yields Quantitative Data on Pyrrhotite Concentration*	*Brief Explanation of Method*
Microstructural: X-Ray Photoelectron Spectroscopy (XPS)	✔	No (but yields estimate of sulfide versus sulfate content)	Identifies the *chemical species* on a sample's surface; provides a chemical analysis; can distinguish between sulfur species and yields an estimate of the relative percentage of sulfide versus sulfate minerals in a sample; if total S is known, can estimate maximum pyrrhotite concentration
Microstructural: Thermomagnetic	✔	No (but yields total S and total sulfide)	Measures magnetic susceptibility of sample as temperature increases (a sample with pyrrhotite will change magnetic susceptibility at a particular temperature); can detect low concentrations of pyrrhotite (cf. XRD); when combined with total S analysis by chromatography, can estimate the maximum possible concentration of pyrrhotite (more accurate estimates possible if testing calibrated to identify local pyrrhotite composition)

Table populated with assistance from Dr. Maria Chrysochoou (UConn) and Dr. Christoph Geiss (Trinity College)

Attachments

Attachment 1: UConn's June 19, 2019, Presentation

Attachment 2: Army Corps of Engineers' October 19, 2018, Presentation

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