Cement and Concrete Research 115 (2019) 1–7

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

A thermomagnetic technique to quantify the risk of internal sulfur attack due to pyrrhotite

Christoph E. Geiss*, Jonathan R. Gourley

Environmental Science Program, Trinity College, 300 Summit Street, Hartford, CT, USA

ARTICLE INFO

Keywords:
Sulfate attack
Magnetic properties
Pyrrhotite

ABSTRACT

The use of pyrrhotite-containing aggregate in concrete has led to the premature deterioration of building foundations in Connecticut (U.S.A.). Pyrrhotite is a highly reactive iron-sulfide mineral that can initiate internal sulfate attack in concrete structures, because it serves as a source of sulfate ions for secondary minerals. Associated increases in mineral volume can lead to spalling, cracking and a loss of structural integrity. Since pyrrhotite is a strongly ferrimagnetic mineral with a Curie-temperature of 325 °C and several diagnostic phase transitions, we measured the variation of magnetic susceptibility between room-temperature and 700 °C. Such a thermomagnetic measurement serves as a rapid and sensitive semi-quantitative indicator of pyrrhotite in aggregate or concrete samples. In combination with measurements of total sulfur concentrations, pyrrhotite concentrations as low as 0.1% can be detected. The analysis can aid in the quantification of risk of internal sulfur attack due to the presence of pyrrhotite.

1. Introduction

1.1. Internal sulfate attack (ISA) in concrete

Aggregate containing the mineral pyrrhotite ($Fe_{1-x}S$, $0 \le x \le 0.125$) was unwittingly used in concrete construction for over twenty-five years in a rapidly growing region of eastern Connecticut, USA. Since the early 1980s until 2016, it is likely that thousands of structures were built with the afflicted rock material. Pyrrhotite is an iron-sulfide mineral that has been well-documented to be linked to internal sulfur attack (ISA) of concrete [e.g., [1–3]]. ISA has led to the premature deterioration of concrete throughout the world including Quebec [4], Spain [5,6], South Africa [7], the Arabian Peninsula [8], Switzerland [9], Iowa, USA [10] and most recently in Connecticut, USA [11]. Many homes in eastern Connecticut that were built 20 years ago or later are already showing signs of degradation including significant map cracking, wall budging and structural failure (Fig. 1).

In a pyrrhotite-mediated ISA, pyrrhotite serves as a source of sulfate ions, which react to a variety of secondary minerals, such as ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$). These mineral transformations are associated with an increase in volume and can result in spalling or cracking of the concrete [e.g., [12,13]]. While pyrrhotite is not the only sulfide involved in such attacks it is often the most reactive [e.g., [6,9,14,15]]. Therefore, the presence of pyrrhotite, even is small amounts (< 1% by weight), can have devastating effects on concrete foundations. As such, a quantitative rapid method of testing existing concrete is crucial to determine if pyrrhotite is present or not. Common methods for pyrrhotite analysis include thin and polished section work [3], X-ray diffraction (XRD) [16], X-ray fluorescence (XRF) [5], and scanning electron microscopy (SEM) [3]. These testing methods are often expensive and time consuming. While these methods can certainly detect the presence of pyrrhotite, quantifying the concentration of this mineral is elusive. Staining tests can provide a quick screen of the potential reactivity of sulfide-bearing aggregates, but these tests must be followed up by long-term reactivity tests [15,17].

This paper presents a robust and rapid method to semi-quantitatively identify pyrrhotite in concrete using the thermomagnetic properties of pyrrhotite. In combination with a direct sulfur measurement through elemental purge-and-trap chromatography, and XRD to identify specific post-reaction sulfur minerals, this method can detect the presence of pyrrhotite to levels as low as 0.1%.

1.2. Traditional methods to determine pyrrhotite in concrete

Traditional testing methods for concrete include visual inspections [e.g., [18]] for cracking or spalling, mortar bar tests, which simulate weathering and degradation under accelerated conditions [15], or the petrographic analysis of concrete cores [3]. Visual inspections are

---

* Corresponding author.
E-mail address: christoph.geiss@trincoll.edu (C.E. Geiss).

https://doi.org/10.1016/j.cemconres.2018.09.010
Received 2 February 2018; Received in revised form 13 August 2018; Accepted 21 September 2018

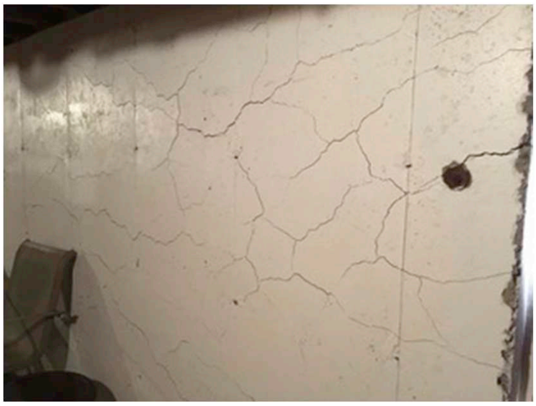

Fig. 1. Basement wall affected by internal sulfate attack.

limited to already affected concrete and are non-quantitative with little predictive value, while mortar bar tests are time consuming with testing extending over several months or sometimes years. Petrographic analysis of core samples can detect the presence of iron-sulfide minerals, such as pyrite, marcasite, chalcopyrite, or pyrrhotite, but the analysis is time consuming and requires significant technical expertise. If the minerals of interest occur at low concentrations, petrographic techniques, such as point counts or lineal traverses require a high number of analyzed grains to ascertain statistical significance. In some instances, however, it may be possible to automate the investigation through computer-aided image analysis [3]. Traditional petrographic work can be complemented with SEM or XRF analyses. SEM and XRF analyses of single crystals or grains, however, are often poorly suited for the routine analysis of large numbers of samples. XRF analyses performed on bulk samples, on the other hand, can easily be applied to large sample sets and provide valuable information about the chemical composition of the sample. XRD investigations can identify iron-sulfide and other potential sources of sulfate, but this technique is unable to identify minor (< 1%) mineral components [19].

Thermomagnetic analyses as described below have been employed for decades to identify the magnetic minerals of geologic specimens [e.g., [20,21–25]]. As shown below, these analyses are well suited to identify even minute amounts of pyrrhotite. When combined with the direct measurement of total sulfur concentrations thermomagnetic analyses can yield at least semi-quantitative estimates of pyrrhotite concentrations.

1.3. Magnetic properties of pyrrhotite

Pyrrhotite is a solid solution of iron sulfide compounds with a range of compositions ($Fe_{(1-x)}S$, where $0 \leq x \leq 0.125$). Naturally occurring pyrrhotite is limited to FeS ($x = 0$, troilite), Fe_7S_8 ($x \approx 0.125$) and several intermediate compositions [26]. Fe and S are arranged following a NiAs structure with alternating layers of Fe and S. Troilite and

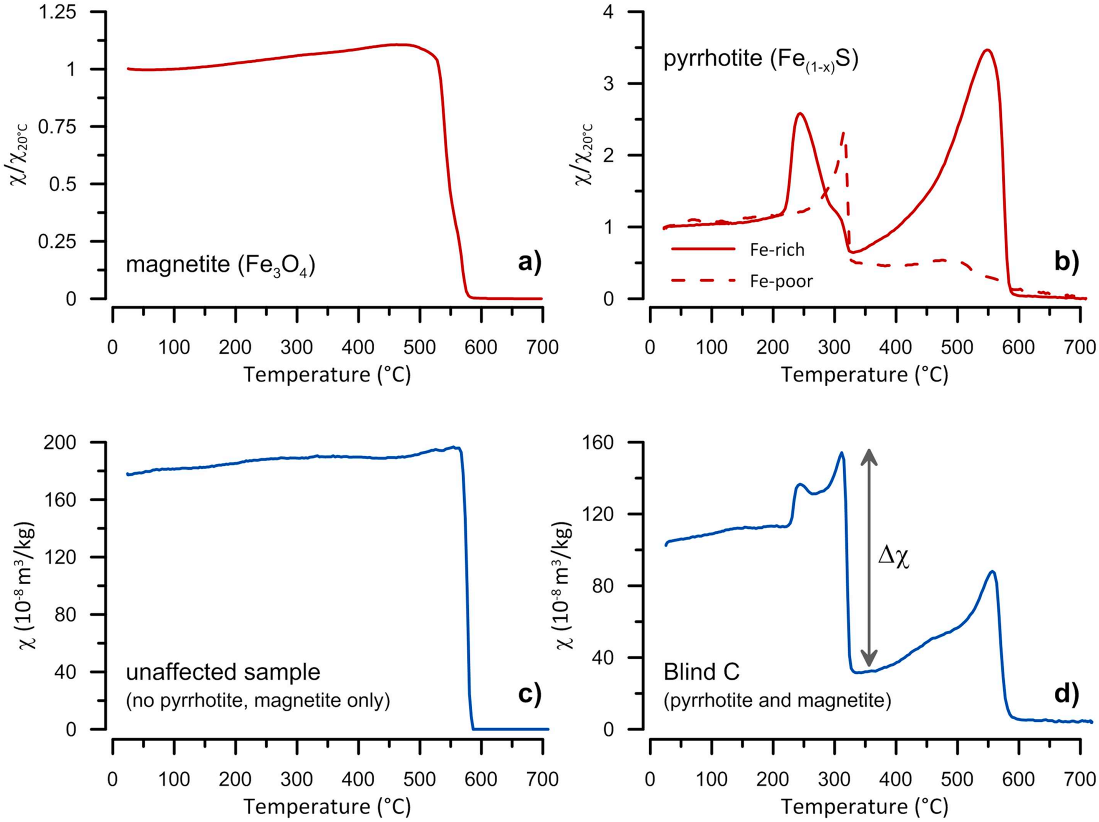

Fig. 2. Thermomagnetic analyses of three known minerals and two concrete samples. The thermomagnetic curves of known minerals (a, b) are normalized to the initial value of χ at room temperature to highlight the changes in magnetic susceptibility. The thermomagnetic curves for concrete samples show mass-normalized magnetic susceptibility. a) For magnetite the magnetic susceptibility χ remains relatively constant until the sample reaches the Curie temperature (T_C) at 580 °C. At T_C χ decreases rapidly and is zero for $T > T_C$. b) Fe-rich pyrrhotite (solid line) undergoes a reorganization of Fe-vacancies, which increase χ above 200 °C. The newly-formed phase undergoes a further phase transition near 265 °C. The final Curie-temperature of pyrrhotite is reached at 325 °C. In Fe-poor pyrrhotite (dashed line) reorganization of Fe-vacancies leads to an increase in χ before χ drops at $T \approx 325$ °C. At higher temperatures pyrrhotite can convert to magnetite. c) Thermomagnetic analysis of a concrete sample containing magnetite as the sole ferrimagnetic mineral. d) Thermomagnetic analysis of a concrete sample affected by ISA. The sample contains a mixture of Fe-rich and Fe-poor pyrrhotite as well as magnetite. The drop in magnetic susceptibility $\Delta\chi$ between 310 °C and 325 °C can be used as a semi-quantitative measure of pyrrhotite abundance.