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	A B S T R A C T
<i>Keywords:</i> Sulfate attack Magnetic properties Pyrrhotite	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 Available online 11 October 2018

0008-8846/ © 2018 Elsevier Ltd. All rights reserved.



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 $0 \le x \le 0.125$). Naturally occurring pyrrhotite is limited to FeS (x = 0, troilite), Fe₇S₈ (x ≈ 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 magnetic. 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.

Fe-rich compositions up to x < 0.1 are hexagonal. The iron vacancies in these hexagonal phases are arranged in several superstructures and incommensurate compositions are frequent. Higher concentrations of Fe-vacancies slightly deform the crystal lattice in Fe-poor pyrrhotite. As a result, Fe₇S₈ and compositions very close to it are monoclinic [e.g., [27]]. Pyrrhotite compositions and crystalline structures are discussed extensively by [28-30]. The magnetic moments lie in the basal plane and are ferromagnetically coupled within each Fe-layer, but neighboring Fe-layers are antiferromagnetically coupled [31]. However, Fevacancies are not randomly distributed but organized into several superstructures. As a result, Fe-rich pyrrhotite (x < 0.1) displays antiferromagnetic properties, while in Fe-poor, monoclinic Fe₇S₈ $(x \approx 0.125)$ the distribution of Fe-vacancies between adjacent Fe-layers is such that the cancelling of magnetic moments is incomplete resulting in a ferrimagnetic mineral phase [26,32]. The arrangement of Fe-vacancies into several possible superstructures, often within the same crystal [32], leads to a large range of observed values for magnetic susceptibility (χ). Magnetic susceptibility can range between 10 and $30,000 \times 10^{-8} \text{ m}^3/\text{kg}$ [33]. The saturation magnetization (M_s) for Fe_7S_8 is approximately 20 Am²/kg.

Monoclinic Fe₇S₈ is ferrimagnetic at room temperature and reaches the Curie-temperature (T_C) at 325 °C [26,32]. At T > T_C pyrrhotite is paramagnetic and χ decreases to near zero. The exact value of T_C is slightly composition-dependent. Ni-substituted pyrrhotite, for example, displays significantly lower Curie-temperatures [34]. Hexagonal pyrrhotite with compositions close to Fe₉S₁₀ will undergo a reordering of its Fe-vacancies when heated above 200 °C, the so-called λ - transition. As a result, it becomes ferrimagnetic between 210 °C and a further phase transition at 265 °C [29]. This mineralogical transition is reversible at low cooling rates [26] but causes irreversible changes at the cooling rates applied in this study.

A thermomagnetic measurement (Fig. 2) monitors changes in χ as the sample is heated above room-temperature. Since the Curie-temperature and the associated changes in χ are mineral-dependent, a measurement of χ as a function of T can be used to identify and quantify magnetic minerals such as pyrrhotite.

2. Methods

Samples were provided to us by the Connecticut Coalition against Crumbling Basements (CCACB), a grass-roots organization of homeowners committed to finding solutions to deteriorating basements. Submitted samples varied in size from large concrete cores (several kg in mass) to small concrete fragments. Using a ceramic mortar and pestle, samples were ground into a fine powder and homogenized for further analysis. For initial testing of the methodology, CCACB provided us with 20 blind samples. CCACB knew the origin of these samples and whether they came from homes affected by ISA, but these details were unknown to us.

2.1. Magnetic susceptibility

Magnetic susceptibility was measured continuously between roomtemperature and 700 °C using a KLY-4S Kappabridge (AGICO s.r.o.) equipped with a CS-3 furnace apparatus. Between 0.15 and 0.35 g of powder were heated in an argon atmosphere (flow rate: 50 ml/min) at a rate of approximately 12.5 °C/minute. For the sample size used in this study, the sensitivity of the instrument is approximately 0.3×10^{-8} m³/kg (2×10^{-8} SI). Data were corrected for the magnetic properties of an empty furnace and reported as mass-normalized susceptibility χ . All corrections and normalizations were performed using the software Cureval 8.02 (AGICO Corp.).

Most samples undergo conversion to magnetite at high temperatures and during cooling χ is often higher between 580 °C and room temperature. These cooling curves are not included when plotting thermomagnetic results to make the diagnostic features in the heating curves more apparent. The full thermomagnetic curves are included in the electronic supplement to this article.

2.2. Sulfur determinations

Total sulfur concentrations were determined using a *vario EL cube CNS* elemental analyzer (Elementar Analysensysteme GmbH), which uses purge and trap chromatography to determine C, N, and S concentrations in powdered samples. Samples consisted of 20 to 30 mg of finely ground concrete powder. As individual sample sizes were quite small, these measurements were repeated at least three times to address possible variability in sulfur concentration. The sensitivity of the instrument for Sulfur is approximately 0.002 wt%.

2.3. X-ray analyses

X-Ray diffraction (XRD) was used to identify both pyrrhotite phases and other non-magnetic sulfur bearing minerals in the concrete samples. We use a PanAlytical X'Pert Pro XRD with a Cu K α tube and an X'Celerator detector (with an optional monochromator) which rapidly scans the sample using Real Time Multiple Strip (RTMS) technology. The step size was 0.02° 2 θ and the equivalent dwell-time per step was 30 s. Powdered samples on a rotating stage were analyzed between 2 θ angles of 8° and 90°. Peak analyses were performed using HighScore Plus (v. 4.7) and the ICDD catalog of mineral phases.

3. Results

3.1. Thermomagnetic analyses

Fig. 2a), b) show thermomagnetic analyses for known minerals. To highlight relative changes in γ the susceptibility data are normalized by the room-temperature susceptibility ($\chi_{20^{\circ}C}$) of the investigated sample. For magnetite (Fig. 2a)) χ is relatively constant between room-temperature and 580 °C, the Curie-temperature (T_C) of magnetite. For $T > T_C \chi$ is near zero. Fig. 2b) shows thermomagnetic analyses for two pyrrhotite samples. Fe-rich pyrrhotite (solid line) displays constant χ until approximately 240 °C, when it undergoes the λ -transition, a reordering of Fe-vacancies. The reordering process leads to an increase in χ until the newly formed phase undergoes further reordering at 265 °C [26,29]. At T \approx 325 °C the sample reaches the Curie-temperature of monoclinic pyrrhotite which results in a further drop in χ [e.g., [26,35]]. At higher temperatures pyrrhotite is chemically unstable and converts to magnetite with $T_C\approx$ 580 °C. Fe-poor pyrrhotite (dashed line) undergoes a non-reversible increase in χ between 260 °C and 310 °C and displays a sharp drop in χ at 325 °C. This particular pyrrhotite sample is more stable at higher temperatures and very little magnetite is formed. Fig. 2c) displays the thermomagnetic analyses of a concrete sample that is free of pyrrhotite (Quikrete high-strength concrete mix, purchased at a local hardware store). The thermomagnetic curve is nearly identical to Fig. 2a), indicating that magnetite is the only magnetic mineral present in the sample [e.g., [36,37,38]].

Fig. 2d) shows a thermomagnetic measurement for a concrete sample that has been affected by ISA. It displays a clear pyrrhotite signal. χ is relatively constant at T < 220 °C, when it increases sharply to reach a peak at T ≈ 240 °C, and an even higher peak at T ≈ 310 °C. χ then decreases sharply between 310 and 325 °C. Upon further heating χ rises gradually to a peak at T ≈ 560 °C and then drops sharply to zero by T ≈ 580 °C. The susceptibility increases at 240 °C and 310 °C are both irreversible at the heating rates employed in the thermomagnetic experiment and likely due to a reordering of iron-vacancies and a corresponding change in ferrimagnetic properties [26]. The pyrrhotite present in this sample is a mixture of Fe-poor and Fe-rich pyrrhotite, and the resulting thermomagnetic curve is a mixture of the two curves displayed in Fig. 2b) [26,39]. Detailed heating experiments (not shown) demonstrate that these reordering processes are not necessarily

completed in the time it takes to heat the sample from 240 to 300 °C. The newly formed pyrrhotite phase remains ferrimagnetic until 265 °C [29] while monoclinic, ferrimagnetic pyrrhotite reaches its Curie-temperature at 325 °C [35]. The gradual increase in χ between 350 °C and 580 °C is due to the formation of magnetite with a Curie-temperature of 580 °C. Once the sample is heated beyond 580 °C γ drops to near zero. A slight susceptibility signal at T > 580 °C is either due to the presence of hematite (not observed in these samples) or due to an imperfect correction for the magnetic properties of the heating apparatus. In contrast, a strong susceptibility signal between 580 °C and 700 °C can be due to contamination from the sampling process. For example, several concrete samples were taken using a carbide drill bit. The analysis of a masonry drill bit (not shown) has revealed that drill bit fragments are still magnetic at temperatures above 700 °C. Even though the pyrrhotite signal is likely unaffected by such contamination, such samples were excluded from further analyses.

Fig. 2 does not include the variation in χ with temperature as the sample is cooled back to room temperature. Complete thermomagnetic analyses (heating and cooling curves) are shown in the electronic supplement.

3.2. Analysis of concrete with known admixtures of pyrrhotite

We consider the drop in magnetic susceptibility ($\Delta \chi$) between 310 °C and 325 °C a semi-quantitative measure of pyrrhotite abundance. Fig. 3 shows values in $\Delta \chi$ for various mixtures of natural pyrrhotite (Ward's Science, bulk sample from Galax, VA) and pyrrhotite-free concrete mix (Quikrete high-strength cement mix). $\Delta \chi$ shows excellent correlation ($r^2 = 0.96$, n = 15) with pyrrhotite abundance, justifying the use of $\Delta \chi$ as a pyrrhotite abundance proxy. Abundance estimates, however, are semi-quantitative at best, since the susceptibility of pyrrhotite depends on several factors including chemical purity, crystal size and shape, and the ordering of iron-vacancies across basal layers as discussed earlier. Therefore, the magnetic susceptibility of pyrrhotite from different localities can vary widely. Since the pyrrhotite containing aggregate in this study comes from one location in Connecticut, it is reasonable to assume that many of these factors are similar and higher values of $\Delta \chi$ correspond to higher abundances of pyrrhotite.



Fig. 3. Drop in magnetic susceptibility $\Delta \chi$ between 310 °C and 325 °C for a series of cement-pyrrhotite mixtures. $\Delta \chi$ can be considered a semi-quantitative measure of Pyrrhotite content if the investigated pyrrhotites have similar chemical compositions and crystallographic superstructures.

3.3. Comparison with non-magnetic analyses

The identification of pyrrhotite through thermomagnetic means is consistent with X-ray diffraction analyses. Fig. 4 shows an example of a pyrrhotite-containing sample. Both Pyrrhotite (po) and ettringite (ett), a secondary sulfate mineral are clearly identified through the presence of several characteristic peaks. Since both minerals occur only as minor components in the sample, our XRD analyses are merely qualitative, and a quantification of pyrrhotite or ettringite was not attempted.

The loss in magnetic susceptibility due to pyrrhotite ($\Delta \chi_{310^\circ \text{C}=325^\circ \text{C}}$) is positively correlated ($r^2 = 0.754$, n = 44) with total sulfur content (Fig. 5), although the data display considerable scatter because pyrrhotite is only one of several sulfur-containing minerals present in the samples. The color coding used in Fig. 5 indicates the observed condition of the sample and its pyrrhotite content. Fig. 5 also identifies samples from location STF 20, where several walls from the same foundation were sampled. These samples were analyzed multiple times to quantify variability of pyrrhotite abundance among samples from the same structure as well as pyrrhotite variability within a single core sample. All samples come from deteriorated walls, and samples show clear evidence of the presence of pyrrhotite. Overall pyrrhotite concentrations, however, vary significantly between walls, possibly reflecting various batches of concrete and variability of pyrrhotite abundance in the aggregate. The large error bars in both sulfur abundance and pyrrhotite content for sample STF 20-north suggest that sulfur-bearing minerals are localized, even in the powdered, homogenized sample. Despite these variations between individual walls and between subsamples from the same core, pyrrhotite was clearly identified in every thermomagnetic curve. Given the variability of sulfur and pyrrhotite concentrations within a foundation it is recommended that more than one core is analyzed per structure.

The histograms in Fig. 6 summarize the results of a detailed analysis of two core samples from different walls of the same basement (samples SF 20-E and STF 20-N, indicated by arrows in Fig. 5). Nine repeated thermomagnetic measurements for each sample from site STF 20 demonstrate that the error bars shown in Fig. 5 are due to true sample variability rather than limitations in instrument sensitivity and precision. The variability observed in Fig. 5 may be reduced by grinding the sample into a finer powder and assuring a better homogenized sample.

4. Discussion

Our study applies thermomagnetic analyses to concrete samples. The combination of magnetic and non-magnetic analyses shows that the thermomagnetic investigation of concrete samples can be a rapid, sensitive, and reliable means to detect and quantify the presence of pyrrhotite in concrete or aggregate samples.

Thermomagnetic analyses have been used for decades in the rockmagnetic investigation of geological specimens, including the detection of pyrrhotite. The technique is widely used in paleomagnetic or environmental studies where the identification of ferrimagnetic minerals is of vital interest [e.g. [22–24,26,40–46]]. Thermomagnetic analyses have two additional benefits: sample preparation is minimal, and measurement times can be as low as 45 min per sample. Samples simply need to be ground into a fine powder and homogenized. A full thermomagnetic analysis, which includes heating a sample from roomtemperature to 700 °C and cooling it back to room-temperature takes approximately 2.5 h. That time can be reduced to approximately 1 h if susceptibility is only monitored between room-temperature and 400 °C, which is still 75 °C above the Curie-temperature of pyrrhotite.

4.1. Sensitivity of the thermomagnetic analysis

Several authors have noted that very low concentrations of pyrrhotite in aggregate can lead to internal sulfate attack and cause concrete deterioration. Oberholster and Krüger [7], for example, found that



Fig. 4. X-ray diffraction pattern for a concrete sample containing pyrrhotite (po) and ettringite (ett). The diagnostic peaks for both minerals are indicated.



Fig. 5. Sulfur concentrations and semi-quantitative pyrrhotite estimates for approximately 50 concrete and natural samples. Green squares denote samples that show neither signs of concrete deterioration or evidence for pyrrhotite. Red circles denote samples that show distinct signs of concrete deterioration and do contain pyrrhotite. Orange diamonds denote samples that do contain pyrrhotite as deduced from thermomagnetic data but do, at this point, not show any signs of concrete deterioration. Gray crosses denote samples for which no information on concrete deterioration is available. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

pyrrhotite concentrations as low as 0.5% lead to expansion and cracking of concrete structures, and European standards (BS EN 12620, DIN EN 12620) recommend that sulfur concentrations due to unstable pyrrhotite should be < 0.1% [3].

The sensitivity of the thermomagnetic analyses presented here is limited by the nominal sensitivity of the susceptibility meter and the magnetic susceptibility of the pyrrhotite phase present in the aggregate (which may vary widely as discussed earlier). The susceptibility meter employed in this study (Kappabridge KLY-4s) uses a sample mass of 0.2–0.3 g. As a result, the nominal sensitivity of the instrument used in this study is $0.3 \times 10^{-8} \text{ m}^3/\text{kg}$. If one conservatively requires a ten-fold drop in susceptibility ($\Delta \chi$) at the Curie-temperature of pyrrhotite to discriminate between the loss of susceptibility due to pyrrhotite and background noise, the instrument can detect pyrrhotite as long as

 $\Delta\chi \geq 3 \times 10^{-8}\,m^3/kg.$

For pyrrhotite-containing aggregate from Connecticut the sensitivity of the analysis can be estimated from Fig. 5. A linear fit through all data yields:

 $S = 8.18 \times 10^{5} \text{kg/m}^{3} \Delta \chi + 0.205$

where S is the sulfur concentration in percent and $\Delta \chi$ is the loss in susceptibility across the Curie-temperature of pyrrhotite. If we assume that the offset reflects non-magnetic sulfur-bearing minerals and that the increase in sulfur above this background value is solely due to the presence of monoclinic pyrrhotite (Fe $_7S_8$), which contains 40% sulfur by weight, then a slope of $8.19\times 10^5\,\text{kg/m}^3$ corresponds to a magnetic susceptibility $\chi_{po} = 40/8.19 \times 10^5 \, \text{kg/m}^3 = 4884 \times 10^{-8} \, \text{m}^3/\text{kg} \approx 5000 \times 10^{-8} \, \text{m}^3/\text{kg}$ kg for the pure pyrrhotite phase. Such a susceptibility estimate is well within the range of susceptibility values $(10-30,000 \times 10^{-8} \text{ m}^3/\text{kg})$ compiled by Hunt et al. [33]. Assuming a susceptibility value of $5000 \times 10^{-8} \text{ m}^3/\text{kg}$ results in a nominal sensitivity of 3/5000 = 0.0006or 0.06% of pyrrhotite by weight. An analysis of a small (m = 0.0372 g)fragment of aggregate from site STF 20-E yielded a clear susceptibility signal at the Curie-temperature of pyrrhotite of $\Delta \chi = 17 \times 10^{-8} \, \text{m}^3/\text{kg}$, indicating a pyrrhotite concentration of approximately 20/4500 = 0.0044 = 0.4% pyrrhotite by weight. Considering that the masses of most analyzed concrete samples are at least 5-times larger than the analyzed aggregate fragment, detecting pyrrhotite concentrations as low as 0.1% by weight and Sulfur concentrations as low as 0.05% by weight seems certainly feasible for the set of samples analyzed in this study.

The sensitivity estimate discussed above assumes that all sulfur above a certain background value is due to the presence of pyrrhotite. This may be an unlikely assumption. If pyrrhotite covaries with another sulfur mineral (e.g., pyrite or secondary sulfate minerals) the actual value for the magnetic susceptibility of pure pyrrhotite would be higher than our estimate. As the sensitivity of the thermomagnetic analysis depends on the magnetic susceptibility of the investigated pyrrhotite phase, the sensitivity estimate of 0.1% pyrrhotite by weight for thermomagnetic analyses may therefore be an underestimation.

4.2. Presence of other non-magnetic sulfur minerals

The thermomagnetic method described here is only diagnostic for ferrimagnetic pyrrhotite. Iron-sulfide phases such as pyrite (cubic FeS₂), marcasite (orthorhombic FeS₂), chalcopyrite (CuFeS₂) or other sulfur minerals, such as gypsum are not ferrimagnetic and will not be detected. Iron-rich, hexagonal pyrrhotite is antiferromagnetic at room temperature and will only be detected after the reordering of iron-vacancies at temperatures between 210 °C and 325 °C and the associated



Fig. 6. Detailed thermomagnetic analyses for two samples from site STF 20. STF 20-E, from the east wall of the basement, contains less pyrrhotite (lower $\Delta \chi$) but pyrrhotite concentrations are less variable than in sample STF 20-N, from the west wall of the basement. Pyrrhotite concentrations in sample STF 20-N are higher (larger $\Delta \chi$) and more variable.

formation of ferrimagnetic phases. A careful analysis of thermomagnetic curves can distinguish and quantify these phases [26].

Nevertheless, the thermomagnetic technique is a valuable screening tool. It is extremely useful in areas where pyrrhotite has been identified as a major driver of ISA as in the case of Connecticut. Most other ironsulfide phases are also far less reactive than pyrrhotite [3,7,15], and thermomagnetic analyses reliably identify the most detrimental ironsulfide compound. In this case, magnetic analysis can be used as a screening tool to detect the presence of even minor amounts of pyrrhotite and determine the variability of pyrrhotite concentrations within an aggregate or concrete structure. If pyrrhotite is detected through magnetic means the aggregate can either be rejected, or be subjected to more detailed but time consuming analyses, such as petrographic investigations.

4.3. Combination of magnetic and non-magnetic analyses

Thermomagnetic analyses are most valuable when combined with non-magnetic determinations of total sulfur content and possibly XRD analyses. XRD analyses allow for the identification of all sulfur minerals, provided they occur in high-enough concentrations. Once established for a particular region, a comparison of magnetic susceptibility and total sulfur concentrations (Fig. 5) illustrates the possible role of pyrrhotite in ISA and allows for a straightforward comparison between samples. The color coding employed in Fig. 5 links sulfur and pyrrhotite content to the structural condition of the analyzed foundations. With their analysis results plotted in Fig. 5 or a similar plot, homeowners or other stakeholders can easily learn how their home compares to other homes in the region and whether ISA is likely to occur or not.

Fig. 5 can be combined with other data to increase its usefulness even further. If linked to other factors relevant in ISA, such as age of the structure, observed damage, drainage conditions or concrete porosity it may be possible to develop a statistical score that informs homeowners or policy makers about the risk of ISA for a given structure.

5. Conclusions

Thermomagnetic analyses of concrete are capable of detecting pyrrhotite, a highly reactive iron-sulfide mineral that can cause internal sulfate attack (ISA) in concrete structures. In a blind test of twenty concrete samples the technique identified all specimens that were collected from houses known to be affected by ISA.

The sensitivity of the method depends on the magnetic susceptibility of the investigated pyrrhotite, which can vary widely. For the pyrrhotite investigated in this study the method is likely to detect pyrrhotite in concentrations as low as 0.1% by weight.

Our magnetic analyses are supported by X-ray diffraction analyses which detected pyrrhotite and ettringite in all afflicted concrete samples.

The detection of pyrrhotite through magnetic means in combination with the determination of total sulfur concentrations through elemental analysis can be used as a rapid tool to estimate the likelihood of future ISA in existing structures.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cemconres.2018.09.010.

Acknowledgements

The authors would like to thank Tim Heim and the Connecticut Coalition against Crumbling Basements for their continued support. We appreciate Joe Ruggiero's tireless assistance with sample preparation and measurements. Comments by Dr. Mark Dekkers significantly improved the manuscript.

Financial support was provided by the Ingraham Fund for Special Opportunities in Environmental Science. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Conflict of interest statement

The authors may potentially benefit financially if Trinity College is successful in providing products or services that are related to the research described in this manuscript. The terms of this financial arrangement have been reviewed and approved by Trinity College in accordance with its applicable policies.

References

- A. Lugg, D. Probert, 'Mundic'-type problems: a building material catastrophe, Constr. Build. Mater. 10 (1996) 467–474.
- [2] N. Belzile, Y.-W. Chen, M.-F. Cai, Y. Li, A review on pyrrhotite oxidation, J. Geochem. Explor. 84 (2004) 65–76.
- [3] A.B. Poole, I. Sims, Concrete Petrography, 2nd ed., CRC Press, Boca Raton, FL, 2016.
- [4] A. Rodrigues, J. Duchesne, B. Fournier, B. Durand, P. Rivard, M. Shehata, Mineralogical and chemical assessment of concrete damaged by the oxidation of sulfide-bearing aggregates: importance of thaumasite formation on reaction mechanisms, Cem. Concr. Res. 42 (2012) 1336–1347.
- [5] J.S. Chinchón, A. López-Soler, X. Querol, R. Vaquer, Determination of pyrrhotite (Fe_{1-x}S) occurring in aggregates by X-ray flourescence, Cem. Concr. Res. 20 (1990) 394–397.
- [6] C. Ayora, S. Chinchón, A. Aguado, F. Guirado, Weathering of iron sulfides and concrete alteration: thermodynamic model and observation in dams from Central Pyrenees, Spain, Cem. Concr. Res. 28 (1998) 591–603.

- [7] R.E. Oberholster, J.E. Krüger, Investigation of alkali-reactive, sulphide-bearing and by-product aggregates, Bull. Int. Assoc. Eng. Geol. 22 (1984) 273–277.
- [8] P.G. Fookes, L. Collis, Problems in the Middle East, Concrete 9 (1975) 12–17.
 [9] T. Schmidt, A. Leemann, E. Gallucci, K. Scrivener, Physical and microstructural aspects of iron sulfide degradation in concrete, Cem. Concr. Res. 41 (2011) 263–269.
- [10] H. Lee, R.D. Cody, A.M. Cody, P.G. Spry, The formation and role of ettringite in Iowa highway concrete deterioration, Cem. Concr. Res. 35 (2005) 332–343.
- [11] K. Wille, R. Zhong, Investigating the deterioration of basement walls made of concrete in CT, Report Produced to the Attorney General of the State of Connecticut, University of Connecticut, Department of Civil and Environmental Engineering, 2016, p. 93.
- [12] H.F.W. Taylor, C. Famy, K.L. Scrivener, Delayed ettringite formation, Cem. Concr. Res. 31 (2001) 683–693.
- [13] H. Bouzabata, S. Multon, A. Sellier, H. Houari, Effects of restraint on expansion due to delayed ettringite formation, Cem. Concr. Res. 42 (2012) 1024–1031.
- [14] M.J. Gomides, Investigação de agregados contendo sulfetos e seus efeitos sobre a durabilidade do concreto, Programa de Pós-Graduação em Engenharia Civil., Universidade Federal do Rio Grande do Sul. Escola de Engenharia, 2009.
- [15] A. Rodrigues, J. Duchesne, B. Fournier, A new accelerated mortar bar test to assess the potential deleterious effect of sulfide-bearing aggregate in concrete, Cem. Concr. Res. 73 (2015) 96–110.
- [16] Y.L. Mikhlin, A.V. Kuklinskiy, N.I. Pavlenko, V.A. Varnek, I.P. Asanov, A.V. Okotrub, G.E. Selyutin, L.A. Solovyev, Spectroscopy and XRD studies of the air degradation of acid-reacted pyrrhotites, Geochim. Cosmochim. Acta 66 (2002) 4057–4067.
- [17] V. Ramos, A. Rodrigues, B. Fournier, J. Duchesne, Development of a quick screening staining test for detecting the oxidation potential of iron sulfide-bearing aggregates for use in concrete, Cem. Concr. Res. 81 (2016) 49–58.
- [18] Royal Institution of Chartered Surveyors (RICS), The Mundic Problem, 3rd ed., RICS guidance note, RICS, London, 2015.
- [19] H. Toraya, S. Tsusaka, Quantitative phase analysis using the whole-powder-pattern decomposition method. I. Solution from knowledge of chemical compositions, J. Appl. Crystallogr. 28 (1995) 392–399.
- [20] M.J. Dekkers, Magnetic properties of natural pyrrhotite. II. High- and low-temperature behaviour of J_{rs} and TRM as a function of grain size, Phys. Earth Planet. In. 57 (1989) 266–283.
- [21] A. Roberts, G.M. Turner, Diagenetic formation of ferrimagnetic iron sulphide minerals in rapidly deposited marine sediments, South Island, New Zealand, Earth Planet. Sci. Lett. 115 (1993) 257–273.
- [22] A. Kontny, G. Friedrich, H.J. Behr, H. De Wall, E.E. Horn, P. Moller, G. Zulauf, Formation of ore minerals in metamorphic rocks of the German continental deep drilling site KTB, J. Geophys. Res. 102 (B8) (1997) 18323–18336.
- [23] C.-S. Horng, M. Torii, K.-S. Shea, S.-J. Kao, Inconsistent magnetic polarities between greigite- and pyrrhotite/magnetite-bearing marine sediments from the Tsailiao-chi section, southwestern Taiwan, Earth Planet. Sci. Lett. 164 (1998) 467–481.
- [24] R. Weaver, A.P. Roberts, A.J. Barker, A late diagenetic (syn-folding) magnetization carried by pyrrhotite: implications for paleomagnetic studies from magnetic iron sulphide-bearing sediments, Earth Planet. Sci. Lett. 200 (2002) 371–386.
- [25] A.P. Roberts, Q. Liu, C.J. Rowan, L. Chang, C. Carvallo, J. Torrent, C.-S. Horng, Characterization of hematite (-Fe2O3), goethite (-FeOOH), greigite (Fe3S4), and pyrrhotite (Fe7S8) using first-order reversal curve diagrams, J. Geophys. Res. B:

Solid Earth 111 (2006).

- [26] E.J. Schwarz, Magnetic Properties of Pyrrhotite and Their Use in Applied Geology and Geophysics, Geological Survey of Canada, Ottawa, ON, Canada, 1975.
- [27] J.C. Ward, The structure and properties of some iron sulphides, Rev. Pure Appl. Chem. 20 (1970) 175–206.
- [28] N. Morimoto, A. Gyobu, H. Mukaiyama, E. Izawa, Crystallography and stability of pyrrhotites, Econ. Geol. Bull. Soc. Econ. Geol. 70 (1975) 824–833.
- [29] S.A. Kissin, S.D. Scott, Phase relations involving pyrrhotite below 350 °C, Econ. Geol. 77 (1982) 1739–1754.
- [30] H. Wang, I. Salveson, A review on the mineral chemistry of the non-stoichiometric iron sulphide, Fe1 x S ($0 \le x \le 0.125$): polymorphs, phase relations and transitions, electronic and magnetic structures, Phase Transit. 78 (2005) 547–567.
- [31] A. Menyeh, W. O'Reilly, The magnetization process in monoclinic pyrrhotite (Fe₇S₈) particles containing few domains, Geophys. J. Int. 104 (1991) 387–399.
- [32] M.J. Dekkers, Magnetic properties of natural pyrrhotite part I: behaviour of initial susceptibility and saturation-magnetization-related rock-magnetic parameters in a grain-size dependent framework, Phys. Earth Planet. In. 52 (1988) 376–393.
- [33] C.P. Hunt, B.M. Moskowitz, S.K. Banerjee, Magnetic properties of rocks and minerals, Rock Physics and Phase Relations. A Handbook of Physical Constants, AGU Reference Shelf, 1995, pp. 189–204.
- [34] D.J. Vaughan, E.J. Schwarz, D.R. Owens, Pyrrhotites from the Strathcona Mine, Sudbury, Canada: a thermomagnetic and mineralogical study, Econ. Geol. 66 (1971) 1131–1144.
- [35] M.J. Dekkers, Magnetic properties of natural pyrrhotite. II. High- and low-temperature behaviour of Jrs and TRM as function of grain size, Phys. Earth Planet. In. 57 (1989) 266–283.
- [36] S. Akimoto, Magnetic properties of FeO-Fe₂O₃-TiO₂ system as a basis of rock magnetism, J. Phys. Soc. Jpn. 17 (1962) 706-710.
- [37] W. O'Reilly, P.W. Readman, The preparation and unmixing of cation deficient titanomagnetites, Z. Geophys. 37 (1971) (321–311).
- [38] K. Fabian, V.P. Shcherbakov, S.A. McEnroe, Measuring the Curie temperature, Geochem. Geophys. Geosyst. 14 (2013) 947–961.
- [39] F. Hrouda, K. Zapletal, Thermomagnetic curves of selected minerals and monomineralogic fractions, AGICO Print No. 24, 1–16.
- [40] M.J. Dekkers, Magnetic monitoring of pyrrhotite alteration during thermal demagnetization, Geophys. Res. Lett. 17 (1990) 779–782.
- [41] M.J. Dekkers, Magnetic properties of natural goethite III. Magnetic behaviour and properties of minerals orginating from goethite dehydration during thermal demagnetization, Geophys. J. Int. 103 (1990) 233–250.
- [42] D.J. Dunlop, O. Ozdemir, D.A. Clark, P.W. Schmidt, Time-temperature relations for the remagnetization of pyrrhotite (Fe7S8) and their use in estimating paleotemperatures, Earth Planet. Sci. Lett. 176 (2000) 107–116.
- [43] P. Rochette, G. Fillion, R. Ballou, F. Brunet, B. Ouladdiaf, L. Hood, High pressure magnetic transition in pyrrhotite and impact demagnetization on Mars, Geophys. Res. Lett. 30 (2003).
- [44] C.-S. Horng, A.P. Roberts, Authigenic or detrital origin of pyrrhotite in sediments?: resolving a paleomagnetic conundrum, Earth Planet. Sci. Lett. 241 (2006) 750–762.
- [45] J.C. Larrasoana, A.P. Roberts, R.J. Musgrave, E. Gracia, E. Pinero, M. Vega, F. Martinez-Ruiz, Diagenetic formation of greigite and pyrrhotite in gas hydrate marine sedimentary systems, Earth Planet. Sci. Lett. 261 (2007) 350–366.
- [46] E. Szabo, H.C. Halls, Deformation of the Sudbury structure: paleomagnetic evidence from the Sudbury breccia, Precambrian Res. 150 (2006) 27–48.