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Corrosion Detection in Steel-Reinforced Concrete Using a Spectroscopic Technique

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Abstract. Detecting the early corrosion of steel that is embedded in in reinforced concrete (rebar) is a goal that would greatly facilitate the inspection and measurement of corrosion in the US physical infrastructure. Since 2010, the National Institute of Standards and Technology (NIST) has been working on a large project to develop an electromagnetic (EM) probe that detects the specific corrosion products via spectroscopic means. Several principal iron corrosion products, such as hematite and goethite, are antiferromagnetic at field temperatures. At a given applied EM frequency, which depends on temperature, these compounds undergo a unique absorption resonance that identifies the presence of these particular iron corrosion products. The frequency of the resonances tends to be on the order of 100 GHz or higher, so transmitting EM waves through the cover concrete and back out again at a detectable level has been challenging. NIST has successfully detected these two iron corrosion products, and is developing equipment and methodologies that will be capable of penetrating the typical 50 mm of cover concrete in the field. The novel part of this project is the detection of specific compounds, rather than only geometrical changes in rebar cross-section. This method has the potential of providing an early-corrosion probe for steel in reinforced concrete, and for other applications where steel is covered by various layers and coatings.

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INTRODUCTION

The US physical infrastructure relies on steel, which is almost always protected from corrosion in some way. This dual arrangement could be in the form of reinforced concrete, which protects the reinforcing steel from corrosion. Other examples include wire tendons in post-tensioned concrete, protected by cementitious grout or polymeric grease, bridge cables protected by grease and sheaths of various materials, water pipes in power plants, protected by polymeric wrappings and/or insulation, and steel bridge girders and tanks, protected by polymeric coatings. Furthermore, the technique may be well-suited as an NDE method in other growing areas of concern, e.g. bio-corrosion.

According to a 2002 National Association of Corrosion Engineers and Federal Highway Administration (NACE/FHWA) report [1], the annual costs of steel corrosion in the US infrastructure and in industry exceed $200 billion per year. A National Research Council (NRC) Corrosion Committee report [2] lists corrosion detection as one of 11 Grand Challenges for U.S. corrosion science. Obviously, this refers to detecting corrosion through the protective layer, whatever that may be. Early corrosion detection is desirable, before corrosion impacts the protective layer via mechanical expansion and damage (cracking).

Technical challenges that make this kind of corrosion detection difficult include the small amounts of corrosion present before exterior effects are noticed (when structural health monitoring can still make a difference), the wide variety of time-dependent corrosion products that are generated depending on the corrosion environment (humidity and salt conditions), the random topology and geometry of corrosion products, the simultaneous presence of multiple products, and the complex geometry of the surfaces on which they form, such as a rebar in concrete.

NEW TECHNICAL IDEAS

A five-year NIST project that started in October, 2010 is developing a new method of sensing iron corrosion products. Instead of just detecting a geometric change or an image of existing corrosion, the goal of the project is to use spectroscopy to uniquely identify the presence of certain in-situ iron corrosion products that are anti-ferromagnetic (AFM). Some common AFM iron corrosion products include hematite, goethite, akaganeite, lepidocrocite, and wustite [3]. In AFM materials, the iron electron spins are ordered but have subsets that are anti-parallel, so there is no macroscopic magnetic moment. Nevertheless, AFM materials can display absorption resonances that approach the terahertz (THz) range. EM waves can couple to a magnon, which is a collective motion (wave) among the oriented spins. The frequency of the wave depends on the interaction strength between the two spin sets, analogous to how the wave speed of sound in a rope depends on the tension in the rope. Estimates of these strengths can give estimates of frequencies at which to search. The new idea is then to detect the presence of early corrosion by detecting these AFM resonances (AFMR), which then implies the presence of these specific corrosion products. This idea was conceived by Dr. William Egelhoff of NIST, who started this project but sadly passed away after the first year.

The project objectives include the following tasks. First, identify what corrosion products are present in which applications, which means that corrosion products need to be characterized. There must be AFM corrosion products present or the detection process will not work. Second, detect AFM resonances (AFMR) in the laboratory and determine their sensitivities to variables like concrete temperature and saturation (moisture content). Third, to enable corrosion detection in reinforced concrete, the AFMR signals need to be detected through a realistic thickness of concrete, such as actually covers the reinforcing steel in bridge decks. As part of this task, the electromagnetic response of concrete needs to be determined, since the electromagnetic signals must go and return through concrete. Fourth, detect AFMR in a mixture of real, composite corrosion products. Finally, a proof-of-concept prototype should be assembled in order to hand-off the technology to commercial vendors, since part of the mission of NIST is to develop technology to benefit to industry, either through standards or tools (as in this case).

RESULTS TO DATE

Full characterization of a suite of samples, including chemically pure powders, mm-scale crystals, and field samples, has been carried out using X-ray diffraction, optical microscopy, and scanning electron microscopy (SEM). Hematite and goethite have definitely been found in field samples, as well as akaganeite in accelerated corrosion samples of steel reinforcing bars covered with a mortar and subject to an impressed voltage. Akaganeite is similar to goethite but with chlorine atoms incorporated into the molecular structure.

Electromagnetic characterization of relevant concrete samples and components, as well as iron corrosion minerals, has been carried out, using standard techniques [4], measuring attenuation, dielectric permittivity, and magnetic susceptibility as a function of frequency, composition, and temperature [5,6]. Dr. James Baker-Jarvis of NIST led this part of the project until his sudden death from an accident in 2011. The approximate attenuation at ≈100 GHz is exponential, about 1.1 dB/mm – details are given elsewhere [5]. The attenuation, at least as measured at lower frequencies, increases with frequency. For 50 mm of concrete, the signal power is estimated therefore to be attenuated by approximately a factor of 110 dB (50 mm in and 50 mm return). Electromagnetic scattering from rebars with a non-uniform surface has been modeled [7] to help with signal deconvolution from AFMR detection in real geometries.

Using an existing terahertz apparatus [8] and a patented signal generation and detection system [9,10], the AFMRs in hematite [11] and goethite [12] have been measured, in fine powders (1 μm to 3 μm particle size) and in real corrosion products. Figure 1 shows the hematite measurements, along with a theoretical fit based on one-magnon scattering [11]. The uncertainty bars are contained within the data point symbols. One can notice the strong dependence of the AFMR frequency ($1\ cm^{-1} = 30$ GHz) on the temperature. The measurements go up to about 350 K. For higher temperatures, as the Neel temperature of about 950 K is reached at which the AFM order vanishes, the AFMR frequency is expected to go to zero (not shown in Figure 1). This value of the Neel temperature [12] has been confirmed by SQUID (superconducting quantum interference device) measurements made at NIST. However, the AFMR frequency dip below this temperature, at around 250 K, is due to the Morin transition [3], where the net AFM spin orientation changes alignment within the crystal without destroying the AFM order. In goethite, the AFMR transition is at substantially higher frequency, on order $17\ cm^{-1} \approx 500$ GHz at room temperature. Therefore, goethite is not a good candidate for corrosion detection through concrete. However, for steel corrosion under a polymeric protective layer of some kind, like a coating or a wrap, goethite should be readily detected by the NIST terahertz apparatus, since there is little attenuation expected in polymers. In this area, one infrastructure application could be a painted steel bridge.

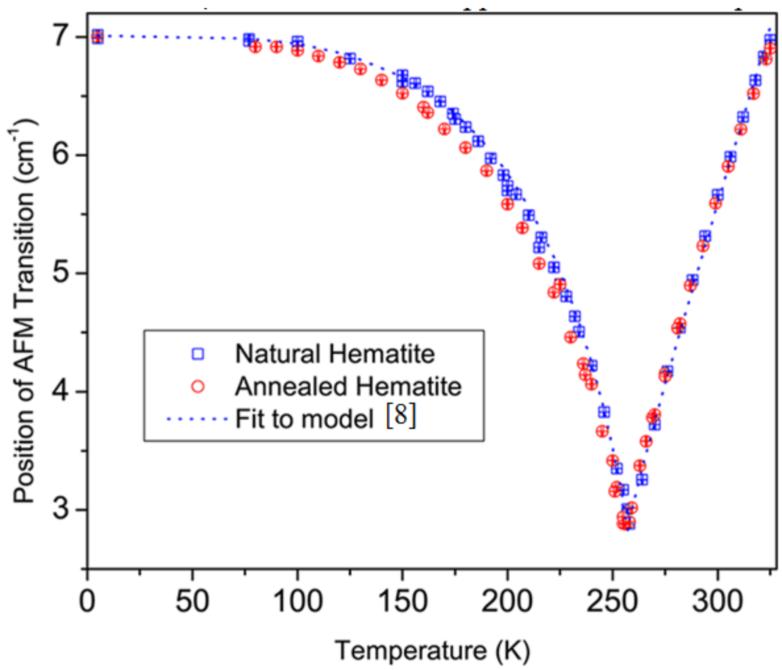

FIGURE 1. The AFMR frequency for hematite as a function of temperature. Note that 1 $cm^{-1} \approx$ 30 GHz.

An accelerated corrosion testing apparatus with galvanic control of the acceleration has also been developed. A rebar specimen, either bare or coated with a mortar, is wired to a bundle of graphite rods and all are immersed in simulated concrete pore solution. The mortar is made at a high water:cement mass ratio for good flowability into the narrow forms around the rebar. Increasing the number of graphite rods also increases the corrosion current roughly linearly in the surface area of the graphite rod bundle. The oxygen content is controlled by either bubbling lab air constantly through the solution or bubbling nitrogen to reduce the oxygen content of the pore solution. This set-up will be used to study the abundance of various corrosion products as a function of oxygen content in the surrounding solution. A micro-Raman instrument is being used to study the topology and geometry of corrosion products on a real rebar. Samples from the accelerated corrosion experiments will be used for this purpose.

FUTURE WORK DURING THE LAST YEAR OF THE PROJECT

The five-year project will end in September, 2014. During this last year, the project will be focused on improving the understanding of the topology, geometry, and mineralogy of corrosion products formed in realistic environments and how this might affect the AFMR response of the material. These tests will be accomplished by using the project's accelerated corrosion apparatus to produce samples under varying environmental conditions, characterize them with micro-Raman, and then detect AFMRs using the NIST terahertz apparatus. The plan is to demonstrate that AFMR for hematite in real corrosion products can be detected through up to 50 mm-thick layers of concrete and other materials. The power and sensitivity of the detection apparatus is being improved to make this possible. A successful prototype has been developed and talks are being planned with commercial vendors about further improvement of this technology. The electromagnetic modeling of waves passing through a random medium, reflecting from a non-smooth iron surface, and then passing back through the random medium, will be further developed. Magnetite is also a common iron corrosion product but it is ferromagnetic, not AFM. Based on the project's spectroscopic measurements of the frequency dependence of various parameters in magnetite, a low-frequency (i.e. below 10 GHz) induction method to detect its presence is being developed.

CONCLUSIONS

Progress has been made in developing an iron corrosion detection process using resonances in anti-ferromagnetic iron corrosion products. This method has been successful – the primary question that remains is how it can be made into a reliable and practical method for detecting early corrosion in protected steel in the US physical infrastructure. This method being developed by NIST could contribute to meeting this national need.

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