Spectroscopic identification of protective and non-protective corrosion coatings on steel structures in marine environments

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Abstract

Corrosion research, and the need to fully understand the effects that environmental conditions have on the performance of structural steels, is one area in which Mössbauer spectroscopy has become a required analytical technique. This is in part due to the need to identify and quantify the nanophase iron oxides that form on and protect certain structural steels, and that are nearly transparent to most other spectroscopic techniques. In conjunction with X-ray diffraction and micro-Raman analyses, the iron oxides that form the rusts on steels corroded in different marine and other environments can be completely identified and mapped within the rust coating. The spectroscopic analyses can be used to determine the nature of the environment in which structural steels have been, and these act as a monitor of the corrosion itself. Mössbauer spectroscopy is playing an important role in a new corrosion program in the United States and Japan in which steel bridges, old and new, are being evaluated for corrosion problems that may reduce their serviceable lifetimes. Mössbauer spectroscopy has been used to characterize the corrosion products that form the protective patina on weathering steel, as well those that form in adverse environments in which the oxide coating is not adherent or protective to the steel. Mössbauer spectroscopy has also become an important analytical technique for investigating the corrosion products that have formed on archeological artifacts,

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and it is providing guidance to aid in the removal of the oxides necessary for their conservation.

1. Introduction

Corrosion, deterioration, and weathering of materials are age-long problems that have faced mankind for millennia. From the world's ancient man-made and natural monoliths to today's most modern buildings, bridges and transportation facilities, the longevity of structures are closely controlled by the environments in which they are located. Having little control over these local environments, we must carefully select the materials that are best suited to the conditions to which they are exposed. Often this requires a protective coating to be applied to the material of choice. History shows however that our predecessors have often lacked the ability to predict the interaction of structures with their surroundings, and today we see deterioration of historic icons and the loss of cultural relics that mark the development and achievements of humanity. Even after 100 years of industrial revolution, and the development of technologically advanced testing and monitoring procedures, we must wonder if our knowledge of today's structural materials and their interactions with the environment, is sufficient to produce long lasting structures that will benefit present society and future generations over the next few centuries.

One feature that is common to each of the above scenarios is mankind's inability to accurately predict the performance of a particular material in a given environment. Although significant effort is generally made to determine the mechanical integrity of our structures, very little time is spent on determining their corrosion and weathering properties. Such prediction would typically require the exposure of selected materials to different environments, an evaluation of their performance, and the development of a predictive model. The slow nature of most corrosion and weathering processes requires monitored exposure testing over perhaps as many as 20 years. This is often viewed as an unrealistic and expensive undertaking that can delay product marketability, or retard the development of a portion of society's infrastructure. Quite often however, a material's corrosion behavior is investigated after the structure has been built. As such, potentially serious corrosion problems are not identified until well after the structure has been placed in service. Predictive corrosion behavior through computer modeling would greatly reduce the time for corrosion evaluation. However, to date this technology has not reached maturity due to the lack of knowledge of the separate and combined contributions each environmental parameter has to the corrosion of a particular material.

Nowadays, the most commonly used structural materials are steel and concrete. Whereas corrosion is mostly identified with steel products, concrete also suffers

serious weathering through exposure to the environment, and deterioration by chemical interaction. Additionally, concrete structures commonly contain reinforcing steel bars that are located internally and often in corrosive environments where they can deteriorate un-noticed until the stage of catastrophic failure of the complete structure. The corrosion and weathering of the world's buildings and bridges require constant monitoring by local authorities, typically a time consuming and expensive undertaking. Investment in high quality corrosion research that would provide sufficient data, knowledge, and models to allow corrosion prediction and prevention, appears to be one advantageous and economic course of action. In addition, such information would be invaluable to other areas of science that require detailed knowledge of the corrosion products that form on materials, and methods by which they can be removed or transformed. One broad area of importance here is archeology and the restoration and conservation of historic artifacts that have been subjected to environments that exasperate the corrosion processes, either before or after recovery.

The total cost of corrosion and corrosion related issues in the United States is significant, amounting to about 6% GDP or $500 billion per year [1]. This figure is divided evenly between direct costs (materials and structures), and indirect costs (loss of productivity). About 90% of the corrosion is associated with iron-based materials. Highway bridges are an integral part of the US infrastructure and transportation system, and allow a high level of mobility and freight activities. The total number of bridges in the United States is approximately 586,000, of which half were built between 1950 and 1994. Most are constructed of steel or reinforced concrete [1]. About 15% of the bridges are structurally deficient, primarily due to corrosion of the steel and steel reinforcement. The annual direct cost of corrosion for highway bridges is estimated to be $8.3 billion, of which $3.8 billion is for bridge replacement, $4 billion is for maintenance of concrete bridges and $0.5 billion is for maintenance of steel bridges. It is estimated that indirect costs to the user due to traffic delays and lost productivity are about $38 billion annually [1]. The recent introduction of high performance steel, a new high-strength weathering steel that does not require painting, has dramatically increased the number of steel bridges being built throughout the US. Weathering steel bridges, when atmospherically exposed to regular wet–dry cycling, form a very adherent rust layer which, after about 8 years of service, protects the steel from the environment and reduces the corrosion by about 75% relative to unpainted carbon steel [2,3]. The cost savings for these maintenance-free bridges is significant relative to painted carbon steel, and concrete bridges. Additionally, weathering steel bridges now have an expected lifetime of 100 years compared to 15–30 years expected from concrete bridges.

The monitoring and evaluation of the corrosion performance of bridges and other steel structures have been extremely limited over the past 40 years. It may be considered that the serious corrosion and deterioration problems that are presently being experienced in steel and concrete bridges that are less than 25-year-old, have resulted from the lack of knowledge of the performance of coated and uncoated structural steels and rebar in the adverse environments in which they are often located. Under the guidelines of the American Society for Testing and Materials, ASTM, and the

International Organization for Standardization, ISO, it is common to evaluate the corrosion properties of steel, by exposing steel coupons at environmentally monitored test sites worldwide, for periods typically up to 30 years [4]. The test sites are classified as rural, industrial or marine according to their levels of the common airborne pollutants containing chlorides and sulfides [5]. The classification of corrosivity of a test site is calculated by measuring the daily chloride and sulfide depositions as well as the time-of-wetness, which is defined as the time for which the relative humidity exceeds 80% [6]. At regular intervals, often starting at 1 year, some of the steel coupons are retrieved, the corrosion products removed, and the steel mass-loss measured [7]. Plots of mass-loss with exposure time permit the corrosion rates of the steels to be determined for their particular exposure site and its corrosivity classification [6].

Mass-loss measurements provide valuable information on the corrosion in certain environments and to some extent permit selection of specific steels for specific environmental conditions. Mass-loss data permit structural integrity to be predicted after a given number of years of service. Structural engineers typically use the mass-loss data to overbuild a structure, allowing for a given mass-loss over the predicted lifetime, without structural failure. However it is now being realized that structures such as bridges are often being built in regions whose environmental conditions are much more severe than those of standard test sites. As a result the corrosion rates of the steel and rebar are significantly greater than originally predicted, and their serviceable lifetimes may be reduced to 20% of that originally predicted. Therefore there is a need to improve the mass-loss data by exposing coupons in more extreme environments, a program that has been underway in Japan for many years, but is a very recent innovation in the United States.

2. Identification of corrosion products

The longevity of steel in a particular environment is calculated by measuring its corrosion rate or mass-loss after different exposure times. While the corrosion rates are commonly measured as a function of environmental conditions and steel chemistry, the data provide no information concerning the oxides or the chemistry of the corrosion layers that form on the steel. However identification of the oxides, as well as the fraction of each in the corrosion products, is important if a better understanding of the corrosion processes is to be obtained, and improved steels with lower corrosion rates are to be developed. For example, the corrosion coating on weathering steel is itself the final protection against further corrosion. Therefore understanding the make-up of these corrosion products, and whether specific oxides form or transform under certain environmental conditions, is important for the corrosion protection of uncoated steel. The iron oxides commonly identified as corrosion products on steel, are listed in Table 1. The oxy-hydroxides, FeOOH, are commonly observed in atmospheric corrosion, whereas the others tend to form more in very specific exposure conditions such as high temperature, high friction or aqueous environments, which are generally less oxidizing than normal atmospheric exposure.

Table 1
List of iron oxides identified in different rusts formed on structural steels

Oxide name	Formula	Oxide name	Formula
Ferrihydrite	$5Fe_2O_3 \cdot 9H_2O$	Wustite	FeO
Geothite	α-FeOOH	Hematite	α-Fe$_2$O$_3$
Akaganeite	β-FeOOH	Maghemite	γ-Fe$_2$O$_3$
Lepidocrocite	γ-FeOOH	Magnetite	Fe_3O_4
Feroxyhite	δ-FeOOH		

To understand how the various atmospheric conditions control the formation of corrosion products, and the role of some of these oxides in protecting the steel through increased corrosion resistance, a full analysis of the chemical and phase composition of the coatings, as well as a mapping of their location within a coating, is required. The analytical capabilities of Mössbauer spectroscopy, micro-Raman spectrometry, X-ray diffraction and Infrared spectrometry are important for complete oxide identification including measurement of the fraction of each phase present. Corrosion coating impurity content and morphology require the use of electron probe micro-analysis (EPMA), energy and wavelength dispersive X-ray analysis (EDS), and scanning electron microscopy (SEM). X-ray diffraction (XRD) has been the most popular method for identifying the oxides in rust. Only with careful calibration can XRD be used to determine the amount of each oxide comprising the corrosion products. Over the past decade, the extensive application of Mössbauer spectroscopy to the study of the atmospheric corrosion of structural steels has shown that XRD frequently provides very incorrect identification of the composition of the rust formed on weathering and carbon steels. One common example of this is the separate identification of magnetite, Fe_3O_4, and maghemite, γ-Fe$_2$O$_3$. Both oxides have cubic structure and nearly identical lattice parameters at room temperature, making them nearly indistinguishable by XRD [8]. However their magnetic and electric properties are quite different, thereby allowing Mössbauer spectroscopy to uniquely identify each. For corrosion investigations, these two oxides are known to form under different exposure conditions, and then often with lattice defects or substituted impurities which do not noticeably change the lattice parameters. Mössbauer spectroscopy has proven invaluable in identifying magnetite and maghemite and providing information concerning impurity concentration, and the exposure conditions in which they formed.

The ability of Mössbauer spectroscopy to accurately measure the temperature dependent magnetic and electric properties of the oxides has resulted in very precise characterization of the corrosion products and a better understanding of the environmental and chemical factors controlling their formation. Mössbauer spectroscopy has now become a required analytical technique in corrosion research, and when used with some of the above-mentioned techniques, can provide a very accurate correlation between the corrosion process and the local environment. The following sections summarize some of the most recent advances in the understanding of oxide formation and corrosion of steel, as provided by Mössbauer spectroscopy.

3. Millscale and corrosion magnetite

Millscale is a thin, adherent oxide coating that forms on steel during heat treatment, hot rolling and forging processes. Oxidation of the steel occurs during exposure to air and while cooling from the rolling temperature, generally around 560 °C. The thickness of the millscale is about 10–20 μm and depends on the type of steel, its thickness, and its thermal, chemical, and mechanical processing history. Identification of the oxides comprising the millscale has been made using Mössbauer scattering geometry with the 6.3 keV resonantly emitted X-rays, XMS [9,10]. Such spectra can be recorded in situ, with the millscale still attached to the steel, thereby preserving the integrity of the coating. Fig. 1 shows the room temperature XMS spectrum of the millscale coating formed on the surface of a sheet of Type A-36 grade carbon steel rolled to a thickness of 0.375″ at 560 °C. Spectral analysis showed that the millscale consists of three iron oxides, wustite, FeO (53%) magnetite, Fe_3O_4 (33%), and hematite, α-Fe_2O_3 (14%). Optical and micro-Raman spectrometry on metallographic cross-sections of the millscale coating show that the oxides are layered with wustite forming next to the steel substrate and hematite forming at the outer millscale surface. It was concluded that during the millscale formation, the potentially stable oxide phases form in sequence. The most oxygen-rich compound was formed at the millscale–oxygen (air) interface and the most metal-rich compound was formed at the metal–millscale interface.
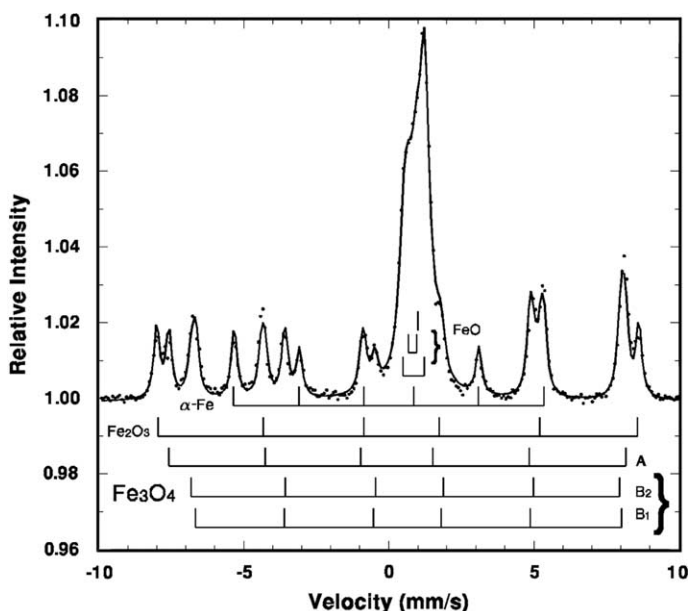

Fig. 1. Scattering Mössbauer spectrum (XMS) recorded at 300 K, of millscale formed on carbon steel rolled at 560 °C. The composition is wustite, 53%, hematite, 14% and magnetite, 33%. The component labeled α-Fe is from the steel substrate.

Wustite is only stable at high temperatures and at room temperature may decompose to iron and magnetite. Therefore millscale offers very little long-term protection to atmospherically exposed steel. For many structural steel applications, for example bridges and power poles, the millscale is removed prior to use by acid pickling. In the case of carbon steel this allows easy painting of the completed structure. For high-strength low-alloy weathering steels that do not require painting, the bare steel needs to be exposed to the local environment to permit formation and growth of an adherent rust layer which then protects the steel from further corrosion. Following years of service, there have been occasions when the complete removal of millscale has been questioned. Debate and litigation have resulted in controversy as to whether the magnetite and/or hematite identified on corroded steel, was formed in the millscale, or as a result of subsequent atmospheric corrosion while the structure was in service or waiting to be built. X-ray diffraction can identify both oxides but is unable to identify the conditions of their formation. In this case Mössbauer spectroscopy is a valuable analytical procedure, being able to identify the different magnetic environments that characterize the high temperature magnetite in the millscale and corrosion magnetite that forms due to atmospheric exposure.

Formation of magnetite on steel by high temperature oxidation, as in millscale, usually results in a stoichiometrically pure compound whose two octahedral B_1 and B_2 sites containing Fe(III) and Fe(II), and one tetrahedral A site containing Fe(III), have unique and stable magnetic environments. The Mössbauer spectrum of pure magnetite, which is typically synthesized at high temperature, has been well characterized by Mössbauer spectroscopy, and shows a single valued magnetic field for each of the three iron sites [11–14]. The Mössbauer area ratio at 300 K is A(oct)/A(tet) = 1.88, which gives an expected iron concentration ratio of 2.00 when the recoilless fraction of each site, $f(B)/f(A) = 0.94$, is taken into account. However for the case of magnetite formed by aqueous corrosion at ambient temperatures, the magnetic structure of the octahedral site is not defined by a unique hyperfine magnetic field but rather a distribution of magnetic fields. The Mössbauer spectrum of corrosion magnetite is therefore different to that of the high temperature magnetite. Examples of the room temperature Mössbauer spectra of high temperature and corrosion magnetite formed on steel surfaces are shown in Fig. 2. The Mössbauer scattering spectrum of Fig. 2(a) is the magnetite component of the millscale shown in Fig. 1. The iron substrate, wustite and hematite components have been computer subtracted. The Mössbauer fit parameters agree with those of pure (99.999%) synthetic magnetite, [11], and the published data of Murad for pure magnetite [12]. A detailed description of the millscale analysis can be found elsewhere [9,15]. The iron concentration ratio for the two sites was measured to be 2.00 showing the millscale magnetite to be stoichiometrically correct and containing no substitutional impurities or defects. As comparison, Fig. 2(b) shows the corrosion products formed on finely chopped steel filings which were placed in a closed vial of distilled water for 2 years. The rust was entirely magnetite whose transmission Mössbauer spectrum (TMS) is similar to, but not the same as, the millscale magnetite. It can be seen that the octahedral sextet of the corrosion magnetite is broadened and reduced
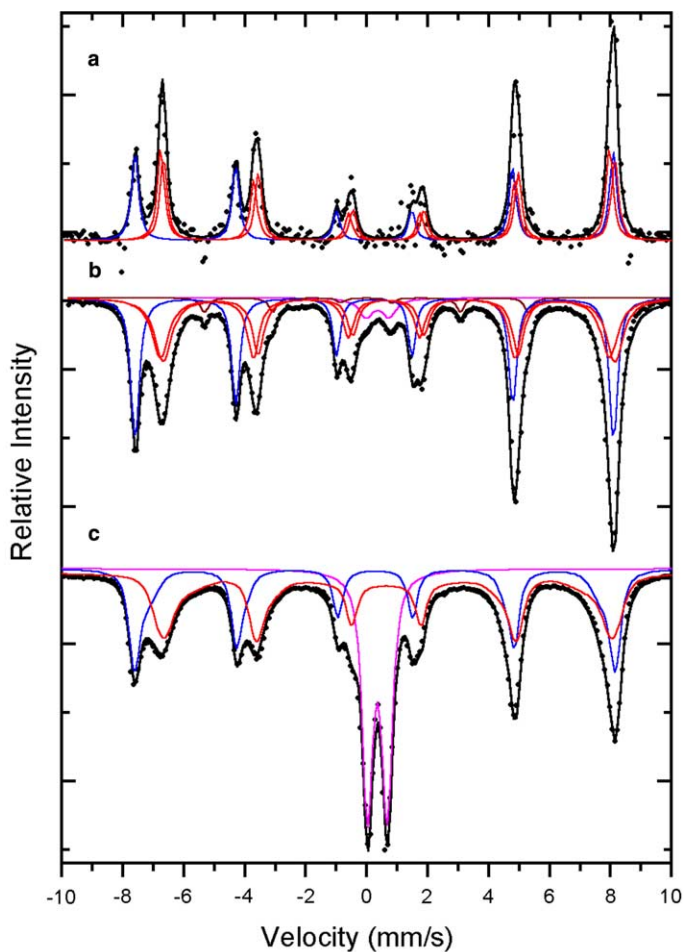
Fig. 2. Mössbauer spectra of high temperature and corrosion magnetite and showing (a) the high temperature magnetite component of the millscale shown in Fig. 1, (b) corrosion magnetite formed on steel filings submerged in pure water for 2 years, and (c) corrosion magnetite formed on an American Civil War ironclad artifact submerged for 160 years.

in intensity. The spectrum was fitted to three iron components having broadened Lorentzian lineshapes. The fit parameters again agreed with those of pure synthetic magnetite [11]. The best, and most meaningful, fit to the corrosion magnetite was obtained using a magnetic field distribution for each of the octahedral B_1 and B_2 sites. Both fitting methods gave the site area ratio of $A(oct)/A(tet) = 1.94$, resulting in an iron concentration ratio of 2.06, which indicates that the octahedral site is nearly defect and impurity free. We have also observed magnetite formed by seawater corrosion of iron on several historically important artifacts recently recovered off the east coast of the United States. Mössbauer spectroscopy of the corrosion

products removed from the Civil War ironclad, *USS Monitor*, [16], and the *CSS Hunley*, [17], the first US submarine, has shown that corrosion magnetite formed on the wrought iron due to extended underwater exposure. Fig. 2(c) shows a typical room temperature spectrum that contains the doublets of akaganeite and lepidocrocite, as well as the magnetic component of corrosion magnetite, whose fit parameters are very similar to those of Fig. 2(b). The subspectral area ratio for the corrosion magnetite was found to be $A(\text{oct})/A(\text{tet}) = 1.76$, giving an iron concentration ratio of 1.88.

4. Atmospheric corrosion: Protective corrosion coatings

Structural steels can be separated into two main categories, carbon steel and alloyed steel. Carbon steel must be used in situations where it is very well protected from exposure to both water and oxygen, and this is usually achieved by painting the clean, bare surface. With time the coating will fail due to direct environmental exposure, or become porous and allow the steel beneath to corrode. For bridges, roadside guide-rails, and other large structures, this results in significant and regular repair, replacement and maintenance costs, as well as environmental problems with coating removal. If left uncoated in a normal atmospheric environment, carbon steel will corrode and the rust layer will peel from the substrate, exposing more steel to the atmosphere. The rust layer therefore offers very little protection to the carbon steel that continually loses mechanical strength and will eventually fail.

High-strength low-alloy steels are also very popular structural materials that are used mainly for bridges and power poles. Known as weathering steel, it has high corrosion resistance and is generally used for structures requiring extended longevity under low-maintenance conditions. Protection from environmental corrosion is offered through the formation of an adherent, fully covered, protective rust layer. Two commonly used types of weathering steels classified by the ASTM are types A242 and A588 [18,19]. They differ predominantly by the amounts of silicon, nickel, copper and chromium present as alloying elements, with type A588 containing larger fractions of each. The complete formation of the corrosion coating depends on the environmental conditions to which the steel has been exposed, as well as the type and fraction of alloying elements. In comparison to carbon steels, which have little or no alloying elements, weathering steels may have corrosion rates, which are over an order of magnitude less, depending on the environmental conditions [2,3]. In marine environments, it has been shown that unpainted carbon steel plates can corrode 10 times faster than weathering steel plates [3]. In industrial and rural environments the factor drops to about four. Weathering steels corrode about twice as fast in a marine environment compared with a rural environment.

Mass-loss measurements for carbon and weathering steels exposed at rural, industrial, and marine test sites for up to 16 years have been reported [2,3]. The data showed that, independent of test-site location, the uncoated carbon steel coupons continued to corrode over the full exposure time and often to failure prior to 16 years. However, it was determined that over the first 8 years of exposure at each

of the three test sites, the weathering steel coupons developed a protective rust layer that reduced their corrosion rates to levels acceptable for most structures exposed to the same atmospheric conditions. The measurement of mass-loss and the determination of the corrosion rates of steel coupons at test sites, provide no information on the causes and control of corrosion and the effects of the environmental parameters on the longevity of the structure. On the other hand, a detailed analysis of the corrosion products that form on the steel can provide valuable information concerning the basic corrosion mechanism as well as the suitability of the steel to the particular location. For example, it is well known from mass-loss measurements, that steel bridges located in marine environments have higher corrosion rates than those located in rural environments. The reasons for this can be determined by correlating the rust composition with the local environmental parameters, or micro-climate, in the vicinity of the structure. Such analysis in fact can provide valuable information concerning the serviceable lifetime of the structure well before the mass-loss measurements can.

To investigate the corrosion properties of the two categories of steel, the corrosion products on the coupons used in the above-mentioned mass-loss measurements were studied by Mössbauer spectroscopy, XRD, micro-Raman spectrometry and EPMA. A full description of the findings is presented in a series of recent publications [20–23]. It was determined that the composition and morphology of the protective corrosion coating formed on weathering steel were very different to the non-protective coating formed on carbon steel. The Mössbauer analysis showed the presence of a large percentage of nanophase goethite, of particle size <15 nm, in the protective coating on weathering steel, but not on the carbon steel. Mössbauer spectra of an adherent, protective corrosion coating that formed on weathering steel exposed for 15 years at the Bethlehem, PA test site are shown in Fig. 3. The XMS spectrum, Fig. 3(a), of the intact 40 μm thick coating, and the TMS spectrum, Fig. 3(b), of the removed coating, both recorded at 300 K, show the presence of a small fraction of magnetic goethite, α-FeOOH(m) corresponding to particle size >15 nm. Most of the spectral area is located in the central doublet which was identified by low temperature analysis to be lepidocrocite, γ-FeOOH, and superparamagnetic goethite α-FeOOH(s) having particle size <15 nm. The steel substrate signal is also present in each spectrum. The TMS spectrum recorded at 77 K, Fig. 3(c), now shows a much larger component of magnetic goethite resulting from the reduced magnetic relaxation rate at the lower temperature. This component is labeled α-FeOOH(m + s1), and is comprised of the magnetic component and part of the superparamagnetic component seen in the doublet at 300 K. The doublet remaining at 77 K is comprised of mainly lepidocrocite plus a small fraction of superparamagnetic goethite, α-FeOOH(s2), estimated to have a particle size <8 nm [20]. Table 2 summarizes the fraction of each iron oxide component in the corrosion products of the weathering steel and carbon steel coupons.

It has subsequently been shown that the nanophase goethite formed, and remained nanocrystalline, <15 nm, due to substitution of chromium from the weathering steel, into the diaspore structure [24,25]. The nanophase chromium substituted goethite was mapped by micro-Raman spectrometry and EPMA, and
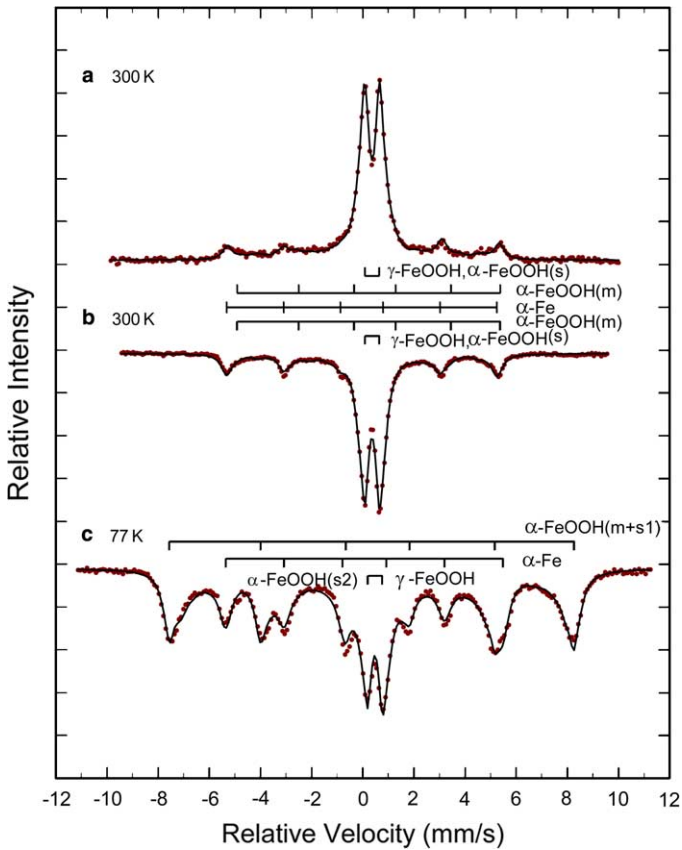
Fig. 3. Mössbauer spectra recorded at (a) XMS, 300 K, (b) TMS, 300 K, and (c) TMS, 77 K, of the iron oxides in the adherent and protective corrosion coating formed on weathering steel following atmospheric exposure at Bethlehem, PA for 15 years. The coating is comprised of 75% goethite of which 75% is nanophase of particle size <15 nm, and has $(\alpha/\gamma) = 4.9$ and $(\alpha_m/\gamma) = 1.0$.

was located in an inner oxide layer adjacent to the steel substrate to which it is adherent [23]. The Mössbauer analysis of the carbon steel rust coatings showed that much less nanophase goethite, and more large particle, >15 nm, goethite formed. This was attributed to the lack of alloying elements that are known to terminate crystal growth through substitution for iron [26]. The carbon steel rust coatings also contained a high fraction of large particle maghemite, which has also been observed in other non-adherent steel rusts, [20,27], and which will be discussed below.

Analysis of the weathering steel and carbon steel rust coatings by X-ray diffraction showed that this method significantly underestimates the goethite fraction in the corrosion products, especially for weathering steel. This is due to the presence of the nanophase oxides whose diffraction lineshapes are very much broadened and are usually overlooked since they overlap with the sharper peaks due to the larger

Table 2
Composition of the protective and non-protective corrosion coatings on structural steels exposed to different atmospheric environments

Steel type and exposure conditions	Goethite[a] α-FeOOH (m) (>15 nm)	Goethite[b] α-FeOOH (s1) (<15 nm)	Goethite[c] α-FeOOH (s2) (<8 nm)	Goethite nanophase α-FeOOH (s1 + s2)	Goethite total α-FeOOH (m + s1 + s2)	Lepidocrocite γ-FeOOH	Maghemite γ-Fe_2O_3	Akaganeite β-FeOOH
Weathering steel, Test sites, 16 years, Protective patina	27	46	8	54	81	14	5	0
Carbon steel, Test sites, 16 years, Non-protective patina	33	20	5	25	58	3	39	0
Weathering steel, Bridge, High time-of-wetness, Non-protective patina	50	10	0	10	60	3	37	0
Weathering steel, Bridge, High chloride, Non-protective patina	13	19	5	24	37	0	0	63

[a] α-FeOOH(m): magnetic goethite (>15 nm) exhibiting magnetic sextet at 300 K.
[b] α-FeOOH(s1): superparamagnetic goethite (<15 nm) exhibiting superparamagnetic doublet at 300 K and magnetic sextet at 77 K.
[c] α-FeOOH(s2): superparamagnetic goethite (<8 nm) exhibiting superparamagnetic doublet at 300 K and at 77 K.

particles of the same oxide phases also in the coating. The nanophase component has often been incorrectly referred to as amorphous, due to its previous lack of X-ray identification. Past XRD measurements have lead to the general acceptance that weathering steel has formed a protective patina if the ratio of goethite to lepidocrocite, α-FeOOH/γ-FeOOH designated (α/γ), is greater than 2 [28,29]. However, extensive Mössbauer analysis has shown that through the identification of the nanophase goethite, the value of (α/γ) = 5 is more accurate. A correlation between the Mössbauer and XRD data can be made only if the fraction of large particle goethite, >15 nm, is taken into account, as is measured by XRD. Mössbauer spectra recorded at 300 K and <80 K permit measurement of the fractions of lepidocrocite as well as the goethite components, m, s1 and s2, as described above. The goethite component that is magnetic at 300 K, α-FeOOH(m), is the component that is easily identified by the sharp peaks in the XRD patterns. By Mössbauer spectroscopy, the ratio (α_m/γ) = 2 in weathering steel having a protective coating, agrees with XRD.

Fig. 4(a) shows the X-ray diffraction pattern (CuK$_\alpha$) of the weathering steel coupon exposed at the Bethlehem test site for 15 years. The most prominent and non-overlapping peaks of the goethite (1 1 0), and lepidocrocite (2 1 0) are shown. The measured fractions of these two oxides give (α/γ) = 1.4, whereas the Mössbauer analysis of the same sample, Fig. 3, gives the ratios (α/γ) = 4.9, and (α_m/γ) = 1.0 [30]. Fig. 4(b) shows the extent to which nanophase goethite is not identified by X-ray diffraction. The XRD pattern is of the corrosion coating on weathering steel exposed in the mild marine test site, CP2, at Campeche, Mexico for 3 months [31–34]. After this exposure time, the protective patina has not yet formed. The XRD pattern shows the corrosion products to consist of nearly only lepidocrocite. A broad (1 1 0) diffraction peak at 21.29° shows in fact that a very small amount of goethite is present. It is estimated from this data that (α/γ) < 0.1, in agreement with previously published XRD expectations for short-term exposures [28,29]. The Mössbauer spectra of the same coating are shown in Fig. 5. The room temperature spectrum, Fig. 5(a), shows only a very small magnetic component that, in addition to the steel substrate, is identified as goethite that is exhibiting collective magnetic excitation, CME, [35], and is fitted to a magnetic field distribution. The amount of magnetic goethite, α-FeOOH(m), in the spectrum, after subtracting the iron substrate component, is 6%. The spectrum recorded at 80 K, Fig. 5(b), now shows a large magnetic component, in addition to the steel substrate. The fit, using a magnetic field distribution, shows the magnetic goethite, α-FeOOH(m + s1), to have increased 10-fold to 59%. The central doublet is comprised of lepidocrocite (37%) and the second nanophase goethite component, α-FeOOH(s2) (4%). Therefore, in comparison to the XRD analysis that identifies very little goethite, <10%, the Mössbauer analysis identifies 63% goethite of which 57% is nanophase having particle size <15 nm. Given that the nanophase goethite is known to be critical in the formation of the protective patina on weathering steel, Mössbauer spectroscopy, through its ability to measure magnetic relaxation, from which particle volume can be calculated, is a necessary analytical method to accurately characterize rust coatings.
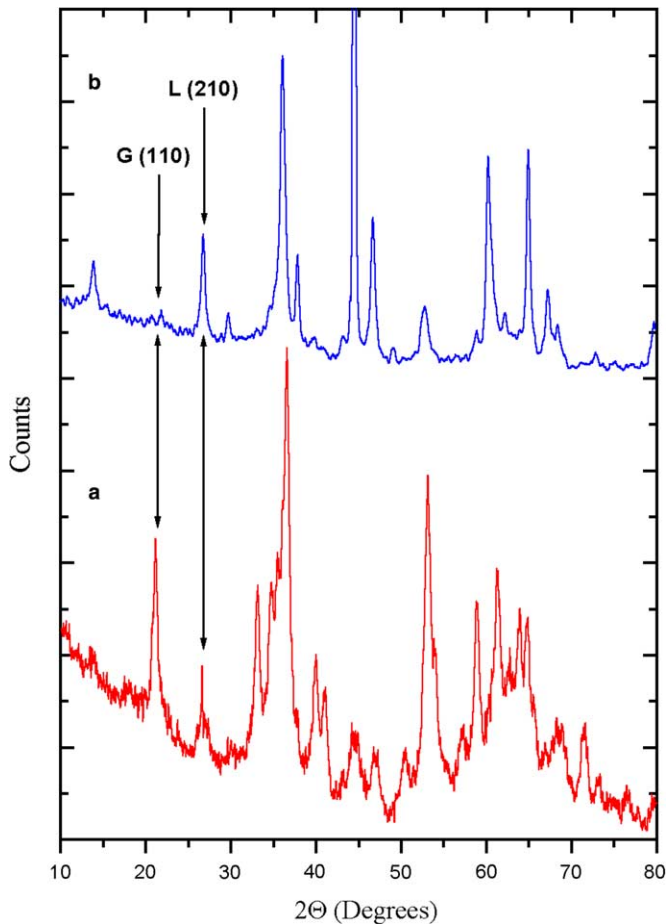
Fig. 4. X-ray diffraction patterns of (a) the protective corrosion coating formed on the weathering steel coupon exposed for 15 years and having $(\alpha/\gamma) = 1.4$, and (b) the corrosion coating formed on weathering steel exposed for 3 months and showing very little goethite content, $(\alpha/\gamma) = 0.1$.

5. Atmospheric corrosion: Non-protective corrosion coatings

The corrosion coatings that form on unpainted carbon steel are generally not very adherent or protective against further corrosion. This commonly results in the build-up of sheets of thick rust as the steel continues to corrode. Eventually the sheets become detached and the exfoliated rust exposes the steel again to the atmosphere. Carbon steel structures therefore need to be painted to protect them from the environment. Spectroscopic analysis of unpainted carbon steel coupons exposed for 16 years at the above-mentioned rural and industrial test sites showed that, although the same iron oxides had formed, the rust compositions were significantly different from those found on the weathering steel coupons [20]. In general, about 50% less
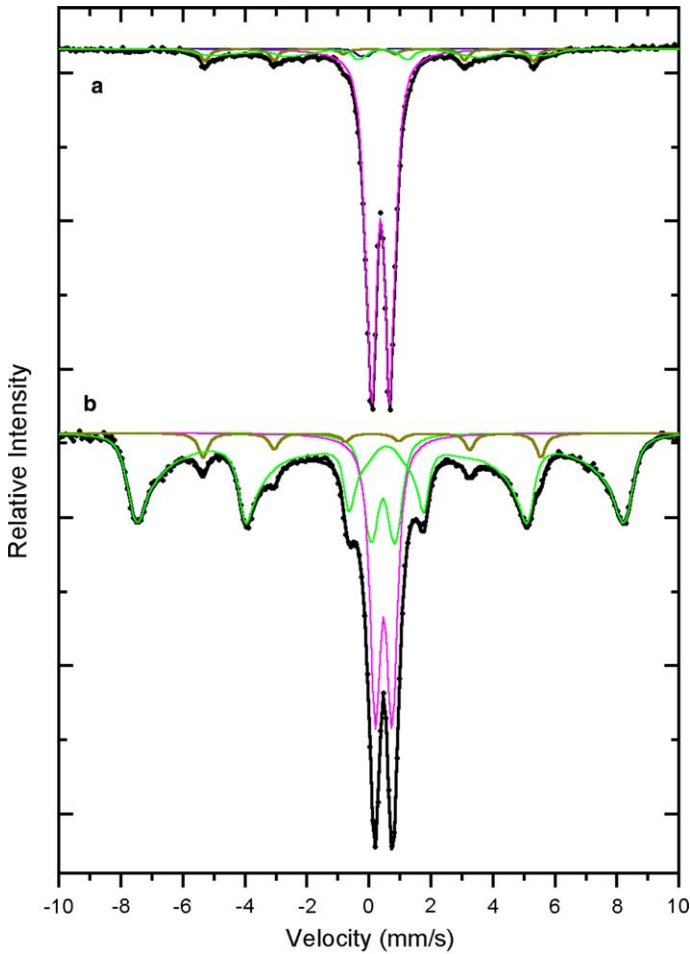
Fig. 5. Mössbauer spectra recorded at (a) 300 K and (b) 77 K, of the corrosion coating on a weathering steel coupon exposed in Mexico for 3 months, and showing a composition of 63% goethite of which 57% is nanophase.

nanophase goethite formed while a significant increase in the fraction of maghemite was measured. Table 2 summarizes the oxide components measured on the carbon steel coupons. It was concluded that the decrease in the amount of nanophase goethite was responsible for increased coating porosity and time-of-wetness at the steel surface. This in turn led to the formation of maghemite in the less-aerobic environment close to the steel.

It has also been observed that non-protective corrosion coatings can form on weathering steel structures exposed in locations that are more adverse than the standard test sites. Two such locations include environments of high time-of-wetness, and high chloride concentrations. The former locations include tropical regions

having long periods of high humidity, and structures that are not well drained or remain wet due to poor air circulation. The latter locations include marine environments, and regions where road de-icing salts are used.

The Luling Bridge is a cable-stayed box-girder bridge that crosses the Mississippi River 18 miles west of New Orleans, Louisiana. Constructed in 1983, the main span of the bridge is 376 m (1222 ft) long and is supported by cables that run to two A-shaped towers or piers set in the river-bed. Each of the two main piers is about 130 m (400 ft) high and consists of two vertical towers joined by a horizontal section at the top [27]. The towers are comprised of 24 nearly cubic box-sections, of size 4 m, prefabricated of type A588 weathering steel, stacked vertically, and welded together. The southern coast of Louisiana, including New Orleans and the lower Mississippi River delta, is one of the most humid regions in the United States with monthly average relative humidity greater than 80% for 4 months of the year and greater that 70% during the other months. The time-of-wetness for the region would therefore be about 33%. The exterior surfaces of the bridge are covered with the tight patina expected to form on weathering steel. However, the interiors of the 24 box-sections show large amounts of exfoliated corrosion products that have flaked from the walls, often in large sheets [27]. The amount of corrosion material was higher in the uppermost, >90 m, and lowest, <40 m, boxes. In order to investigate the cause of the formation of the non-protective rust, spectroscopic analysis was undertaken to identify the corrosion products and to relate them to the environmental conditions inside the piers. Each box-section is nearly completely enclosed except for the ladder openings. Inside, the air circulation is limited and the conditions are very hot and humid. In the evenings, as the bridge cools, moisture condenses on the interior walls, [27], resulting in a time-of wetness estimated to be greater than 80%. Chemical analysis did not identify any chlorides inside the box-sections.

Mössbauer spectroscopy, X-ray diffraction, and micro-Raman spectrometry showed that the compositions of the exfoliated corrosion products from inside the box-sections, were very different to that of the adherent and protective patina discussed above [20,30]. The Mössbauer spectra recorded at 300 K and 77 K are shown in Fig. 6. The room temperature spectrum consists of 85% magnetic oxides identified as goethite and maghemite, and a doublet comprising the other 15%. This shows that only a small fraction of nanophase material is present. At 77 K, the non-magnetic component was only 5% and was identified as lepidocrocite. The complete composition of the non-protective coating is given in Table 2. The amount of large particle, goethite, >15 nm, and maghemite, >25 nm, was 50% and 37% respectively. Only 10% of the material was nanophase goethite and this accounts for the lack of adherence and protection offered the weathering steel by the rust. The rust composition is similar to that of the non-protective and exfoliating corrosion products identified on unpainted carbon steel. Although the amount of large particle maghemite and goethite varied for each box-section, it has been concluded that the formation of the maghemite was due to the very high time-of-wetness on the interior steel walls. Improved air-flow up the piers inside the boxes would eliminate condensation, reduce the corrosion rate, and allow the protective patina to form.
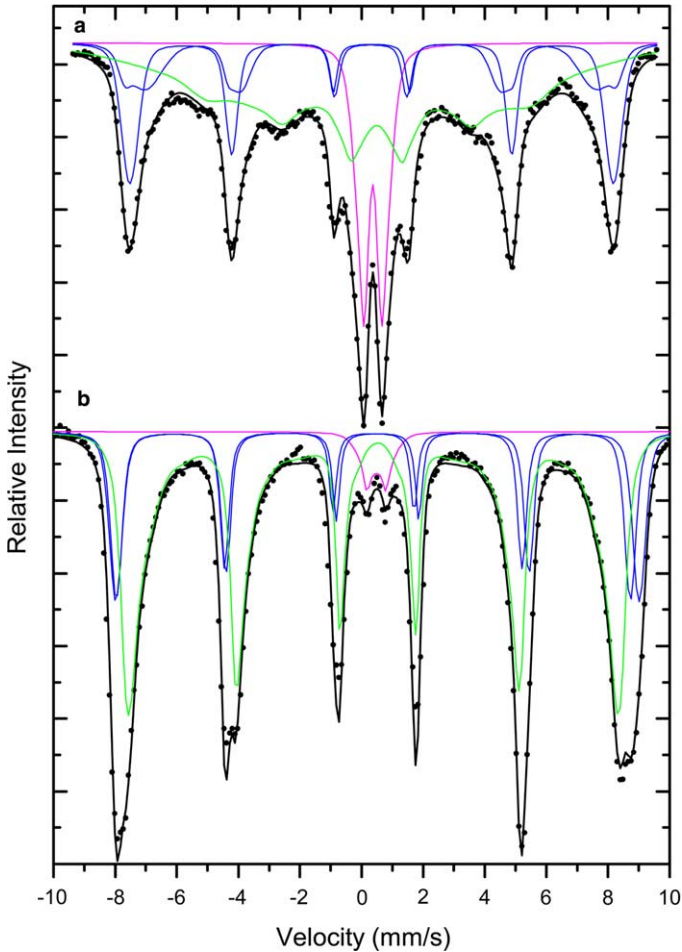
Fig. 6. Mössbauer spectra of the exfoliated corrosion products from the interior weathering steel box-sections of the Luling Bridge. The high fractions of maghemite (37%) and large particle goethite (50%), have formed due to the high time-of-wetness. The coating is not adherent or protective.

Mössbauer spectroscopy is also being extensively used to analyze the corrosion products formed on weathering steel bridges that have been built in locations exposed to high concentrations of chloride. Although typically associated with marine environments, sodium chloride is actually more prevalent in the environment from the use of road de-icing salt. Heavy use of road de-icing salt, as much as 20 tons per lane mile per year, is common throughout regions of the snow-belt in the northern states of the US. The salt deposited by road traffic on the underside of overpass bridges has lead to very high corrosion rates on the girders, and exfoliation of large sheets of non-adherent rust, often greater than 6 mm in thickness. Bridges do not appear to form the adherent rust patina in the presence of the salt. In general a bridge

may be anywhere between 5- and 20-year-old before the exfoliating rust is observed, depending on the amount of salt deposited on the girders. To measure the corrosion rate of a bridge under inspection, it is common to measure the thickness of the cleaned girder sections using a calibrated ultrasonic probe. The thickness of the steel is typically measured at several locations along each girder. However the original thickness at each girder location is needed to determine the thickness loss over the age of the bridge. These original thickness measurements are rarely performed on newly constructed bridges, resulting in inaccurate estimates of bridge corrosion rates. The acceptable limit of thickness loss for weathering steel exposed in a marine environment for 20 years is approximately 0.12 mm/surface [36]. This represents an average thickness loss of 0.5 mil per year (mpy) or 12 μm/yr, for the web or flange sections of a girder. Several US weathering steel bridges exposed to road de-icing salt and showing signs of significant corrosion and exfoliated rust, have recently been investigated to identify the corrosion products that have formed, determine girder thickness losses, and to measure chloride concentrations in the rust [37]. Mössbauer spectroscopy and X-ray diffraction have shown that very large fractions of akaganeite, β-FeOOH, as high as 95%, are present in the corrosion products that have formed on the girders directly above the roadways that are regularly de-iced during winter. In these locations, thickness losses of the steel girders have been measured at about 1.5 mm over 20 years, averaging 1.5 mpy per surface. This is six times higher than is recommended for weathering steel structures. Very high chloride concentrations of 1.5 wt.% have been measured in the rust above the roadway. Variations in corrosion loss and chloride concentration were detected for sections facing towards and away from the traffic directions, showing that under-bridge micro-environments, likely controlled by traffic flow and bridge design, are important for determining corrosion characteristics. The corrosion loss and chloride concentration decreased at larger distances from the road and on exterior sections of the outside girders washed by rainwater and exposed to sunlight that reduces the time-of-wetness.

Fig. 7 shows the Mössbauer spectra of the non-protective rust scraped from a girder exposed to de-icing salt for 20 years. At 300 K, the doublet component comprises 87% of the spectrum with magnetic goethite, α-FeOOH(m) showing CME, making up the other 13%. At 77 K the magnetic ordering of the doublet shows the presence of akaganeite, 63% that was fitted to three iron sites whose parameters agree with published data [38,39]. Magnetic goethite α-FeOOH(m + s1) now makes up 32% of the spectrum and the remaining doublet, 5%, is allocated to superparamagnetic goethite α-FeOOH(s2). Table 2 summarizes the components of the non-adherent rust formed in the presence of the chlorides. It has been determined that the protective patina never forms on weathering steel exposed to high concentrations of chloride. Additionally, very little lepidocrocite was observed on these bridges. The Mössbauer analysis showed that the akaganeite fractions in the different girder rusts varied with traffic direction and distance from the roadway. Ongoing analysis indicates a strong dependence between akaganeite fraction, steel thickness loss and chloride concentration. Investigations are underway to determine the accuracy of Mössbauer spectroscopy for evaluating the corrosion rates of chloride covered weathering steel bridges through the measurement of akaganeite.
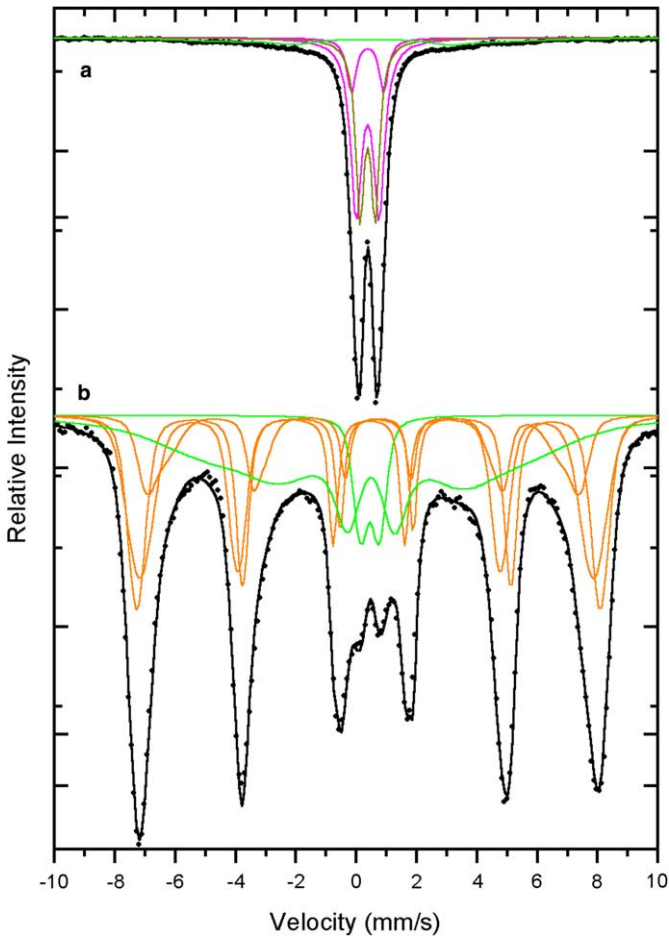
Fig. 7. Mössbauer spectra of the exfoliated corrosion products formed on a 20-year-old weathering steel bridge. The high fraction of akaganeite (63%), is due to the deposition of NaCl from the road de-icing salts used on the roadway beneath the bridge. The coating is not adherent or protective.

6. Conclusion

Mössbauer spectroscopy has demonstrated itself as an accurate, sensitive, and non-destructive analytical technique for the identification of corrosion products formed on structural steel exposed to the atmosphere. Its strength lies in the identification of the nanophase components of the rust through the measurement of their magnetic relaxation at different temperatures. It is able to calculate the fraction of each iron oxide present in rust more accurately than X-ray diffraction, which is restricted to identifying the larger crystallites. In conjunction with micro-Raman spectrometry, that can map the location of each iron oxide in a rust coating to better than 1 μm spatial resolution, Mössbauer spectroscopy can evaluate whether the rust

is protective to the steel or will delaminate from the steel surface. Together the Möss-bauer and micro-Raman techniques provide complete, in situ, non-destructive, three-dimensional identification of corrosion products. This makes Mössbauer spectroscopy the most important analytical technique for quantifying the corrosion properties of steel in different environments. Sufficient Mössbauer data now exists for permit characterization of rusts that have formed in wet environments or regions where chlorides are present in high concentrations. The evaluation as to whether or not a protective rust layer will form on steel exposed in a given environment is now available, resulting in the possibility of Mössbauer spectroscopy being used to measure corrosion rates through the composition of the rust that has formed.

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