Atmospheric corrosion in the Gulf of México

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The corrosion products on steels exposed at two sites in Campeche, México and one site at Kure Beach, USA, have been investigated to determine the extent to which different marine conditions and exposure times control the oxide formation. The corroded coupons were analyzed by Mössbauer, Raman and infrared spectroscopy as well as X-ray diffraction, in order to completely identify the oxides and map their location in the corrosion coating. The coating compositions were determined by Mössbauer spectroscopy using a new parameter, the relative recoilless fraction ($F$-value) which gives the atomic fraction of iron in each oxide phase from the Mössbauer sub-spectral areas. For short exposure times, less than three months, an amorphous oxyhydroxide was detected after which a predominance of lepidocrocite ($\gamma$-FeOOH), and akaganeite ($\beta$-FeOOH), were observed in the corrosion coatings with the fraction of the later phase increasing at sites with higher atmospheric chloride concentrations. The analysis also showed that small clusters of magnetite (Fe$_3$O$_4$), and maghemite ($\gamma$-Fe$_2$O$_3$), were seen in the micro-Raman spectra but were not always identified by Mössbauer spectroscopy. For longer exposure times, goethite ($\alpha$-FeOOH), was also identified but little or no $\beta$-FeOOH was observed. It was determined by the Raman analysis that the corrosion products generally consisted of inner and outer layers. The protective layer, which acted as a barrier to slow further corrosion, consisted of the $\alpha$-FeOOH and nano-sized $\gamma$-Fe$_2$O$_3$ phases and corresponded to the inner layer close to the steel substrate. The outer layer was formed from high $\gamma$-FeOOH and low $\alpha$-FeOOH concentrations.

1. Introduction

The region surrounding the Gulf of México has one of the harshest, most corrosive environments in the world [1,2]. Recently, it has also been the location of significant economic development with the building of structures, ranging from industrial sites such as refineries and petrochemical processing plants, to homes and schools, and infrastructures including roads and bridges. The lifetime of these structures is severely limited due to atmospheric corrosion. Several research programs are presently underway to determine the atmospheric corrosivity and to evaluate the effects of atmospheric corrosion on steels used for structural applications at sites around the Gulf of México. Specific goals involve improving the overall understanding of the corrosion behavior of the steels being tested, quantifying the harsh conditions in the region, developing data to improve the existing models for predicting the lifetime of

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structures suffering atmospheric corrosion, and improving analytical technics used to investigate corrosion.

Samples of stainless, carbon and weathering steels, produced in México and the US, are being exposed at twelve Méxican and one US sites for periods between one and 36 months in order to provide a better understanding of their corrosion behavior in adverse atmospheric conditions not commonly found at other sites around the world. Some of the findings for short term exposures of carbon steel are presented in this paper and compared with those of some long term exposures recently completed in a separate study [3].

2. **Corrosion conditions in México**

The Gulf of México has recently been shown to have much higher atmospheric corrosion rates [4,5] than any region in the US, including Kure Beach, NC [6]. These result from adverse environmental conditions, including high mean annual temperature, humidity and rainfall, as well as high concentrations of chlorides (due to prevailing Gulf winds) and sulfur dioxide (due primarily to industrial emissions). Since economic development is of recent origin near the Gulf of México, there has been minimal atmospheric corrosion testing and evaluation. Environmental conditions have been monitored at the Méxican exposure sites for three years [1,2], with the data for some of them being presented in table 1 along with estimates of the ISO corrosivity classes [7,8]. The table shows the extreme weather conditions and contaminant levels around the Gulf of México in comparison to popular exposure sites in the United States. Sites at Coatzacoalcos and Veracruz provide high combined pollutant levels and time-of-wetness not experienced in the US.

The system of classification for exposures in the atmosphere (corrosivity parameters \( T, P \) and \( S \)) [7,8], was developed by ISO and ASTM based on the environmental conditions at over 50 standard exposure sites in 11 countries, and from corrosion rate

<table>
<thead>
<tr>
<th>Site</th>
<th>Distance from Gulf/Atlantic (m)</th>
<th>Mean temp. (°C)</th>
<th>Relative humidity (%)</th>
<th>Time of wetness (h/mth)</th>
<th>Pollutants (mg/m²/day)</th>
<th>Corrosion rates (µm/yr)</th>
<th>Corrosion class (ISO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Campeche, Mx</td>
<td>4000</td>
<td>26</td>
<td>72</td>
<td>370 T4</td>
<td>45 S1 4 P0</td>
<td>15</td>
<td>C2</td>
</tr>
<tr>
<td>Campeche, Mx</td>
<td>4</td>
<td>26</td>
<td>72</td>
<td>450 T5</td>
<td>170 S2 4 P0</td>
<td>78</td>
<td>C4</td>
</tr>
<tr>
<td>Veracruz, Mx</td>
<td>1000</td>
<td>25</td>
<td>80</td>
<td>420 T4</td>
<td>326 S3 20 P1</td>
<td>178</td>
<td>C5</td>
</tr>
<tr>
<td>Veracruz, Mx</td>
<td>700</td>
<td>25</td>
<td>80</td>
<td>480 T5</td>
<td>520 S3 20 P1</td>
<td>207</td>
<td>&gt; C5</td>
</tr>
<tr>
<td>Coatzacoalcos, Mx</td>
<td>4000</td>
<td>26</td>
<td>75</td>
<td>500 T5</td>
<td>90 S2 33 P1</td>
<td>300</td>
<td>&gt; C5</td>
</tr>
<tr>
<td>Kure Beach, NC</td>
<td>25</td>
<td>18</td>
<td>79</td>
<td>380 T4</td>
<td>311 S3 12 P1</td>
<td>164</td>
<td>C5</td>
</tr>
<tr>
<td>Kure Beach, NC</td>
<td>250</td>
<td>18</td>
<td>79</td>
<td>380 T4</td>
<td>110 S2 12 P1</td>
<td>46</td>
<td>C3</td>
</tr>
<tr>
<td>Bethlehem, PA</td>
<td>Inland 300 km</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>5 S0 26 P1</td>
<td>76</td>
<td>C4</td>
</tr>
</tbody>
</table>
data generated from the mass loss measurements from corrosion samples exposed at those sites. Unfortunately none of the sites was located in México, Central or South America. The site corrosion classifications, which range from C1 to C5, find nearly all of the sites around the Gulf of México falling into the single and most aggressive class, C5. This classification is not adequate for discerning between the Méxican sites, which have very different environmental conditions, as is shown in table 1. Industries which produce and market structural materials rely on the corrosivity classifications when selecting the type of steel to be used for a given location. In México a subdivision of the C5 may be required pending the findings of the present exposure program.

3. Corrosion product analysis

To understand how the various atmospheric conditions control the formation of corrosion products and the role of these oxides in protecting the steel through increased corrosion resistance, a full analysis of the chemical and phase composition of the coatings 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 Dispersive X-ray analysis (EDS) and Scanning Electron Microscopy (SEM).

Mössbauer spectroscopy alone is able to identify each oxide phase, but spectra need to be recorded at 300 K and 77 K to separate akaganeite, \( \beta \)-FeOOH, and lepidocrocite, \( \gamma \)-FeOOH. Even then, the identification of superparamagnetic maghemite, \( \gamma \)-Fe\(_2\)O\(_3\), is very difficult due to magnetic relaxation effects. The oxide identification should therefore be supported by other techniques. X-ray diffraction is able to identify akaganeite, but cannot easily distinguish between maghemite and magnetite, Fe\(_3\)O\(_4\). Infrared spectrometry easily identifies goethite and lepidocrocite but gives broad patterns akaganeite and magnetite. Raman spectrometry is able to identify all the oxide phases but until recently was susceptible to transforming the oxyhydroxide phases through laser heating, resulting in incorrect phase determination. It is only recently that innovations in the field of Raman spectrometry have allowed the technique to be used for corrosion research at the microscopic level. Low power lasers, low noise CCD detectors and improved optical filters now permit identification of all iron oxides without phase transformation due to laser heating. In addition data acquisition times are now only several seconds, allowing the oxides to be mapped to spatial resolution less than 1 \( \mu \)m, in less than one hour. The location of each oxide, whether it formed as single or mixed phase layers or in clusters, can be mapped in three-dimensions, across the surface of the corrosion coating and in depth profile through the thickness of the coating.

The micro-Raman and Mössbauer techniques together provide complete, in-situ, non-destructive, three-dimensional identification of corrosion products. A summary of the oxide parameters for each technique was recently published by Oh et al. [9].
Table 2
Relative recoilless fractions (F-values), for some iron oxides at 300 K and 77 K [3]. The values were measured relative to hematite (α-Fe₂O₃). Average error is ±0.04.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>α-FeOOH</th>
<th>β-FeOOH</th>
<th>γ-FeOOH</th>
<th>δ-FeOOH</th>
<th>α-Fe₂O₃</th>
<th>γ-Fe₂O₃</th>
<th>Fe₃O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>0.77</td>
<td>0.81</td>
<td>0.80</td>
<td>0.37</td>
<td>1.00</td>
<td>0.74</td>
<td>0.90</td>
</tr>
<tr>
<td>77 K</td>
<td>0.80</td>
<td>0.86</td>
<td>0.82</td>
<td>0.49</td>
<td>1.00</td>
<td>0.75</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Mössbauer spectroscopy is the only technique able to accurately measure the fraction of each oxide in a corrosion coating. In corrosion research, this data is essential for monitoring oxide growth and phase transformations under different exposure conditions. It has been common to quote these fractions in terms of Mössbauer subspectral areas, assuming that the recoil-free fraction, \( f \), of each oxide phase was the same, a fact which has been shown to be incorrect [10]. However, it was recently reported [9], that the subspectral areas can be converted to atomic fraction of iron in each oxide phase, using the experimentally measured relative recoilless fractions, \( F \)-values, given in table 2. The \( F \)-values, measured relative to hematite, \( \alpha \)-Fe₂O₃, at 300 K and 77 K, do not require knowledge of the recoil-free fraction, \( f \), of each oxide, a parameter which is very difficult to determine. Knowing the atomic fraction of iron contained in each oxide phase, permits direct conversion to atomic percent, weight percent or molecular percent of each phase in the coating. If the coating thickness is known, the absolute amount of each phase can be calculated.

4. Experimental procedure

Coupons of Type A36 low carbon mild steel and Type A588 Weathering steel were exposed for times between 1 month and 16 years in marine environments at two sites in Campeche, México, and at the 250 m lot at Kure Beach, North Carolina, USA. In Campeche, one site was 4 m and the other 4000 m from the shoreline of the Gulf of México. The coupons (150 × 100 mm) were attached at 45° to racks facing the water and 1.5 m from the ground. The average annual environmental parameters, corrosion rates and ISO classifications are shown in table 1. The corrosion products were initially studied in-situ, still attached to their steel substrates, using scattering Mössbauer spectroscopy by detecting the re-emitted Gamma radiation (GMS) and the Conversion Electrons (CEMS). The corrosion products were also removed from the steel by scraping, and analyzed by transmission Mössbauer spectroscopy (TMS) at 77 K and 300 K. CEMS spectra were also recorded of the material that remained on the steel substrates following coating removal. Infrared spectra of the corrosion products were recorded with an FTIR spectrometer, using the diffused reflectance technique, in the range of 400–4000 cm⁻¹. Raman spectrometry was used to study metallographic cross-sections of the corroded steel coupons over the range 200–800 cm⁻¹ using a laser beam focused to 2 μm.
5. Results

At the end of 1, 2 and 3 months exposure, the corrosion coatings all contained a predominance of a mixture of amorphous and crystalline lepidocrocite as indicated by both broad and narrow IR peaks at 1020 cm\(^{-1}\). Very small peaks possibly corresponding to akaganeite and goethite were also present. Between 4 and 6 months exposure, the lepidocrocite transformed from the amorphous to the crystalline phase as shown by the sharpening of the IR peak at 1020 cm\(^{-1}\) and the formation of a sharp peak at 750 cm\(^{-1}\). IR spectrometry showed that for exposure times up to 12 months, goethite formed as the second dominant phase in amounts which increased with exposure time. Figure 1 shows the IR pattern of a carbon steel coupon exposed at the inland site at Campeche for 12 months. Well crystallized phases of lepidocrocite (750 and 1020 cm\(^{-1}\)) and goethite (790 and 890 cm\(^{-1}\)) are clearly present. Mössbauer analysis of the same carbon steel coupon identified four oxides after 12 months of exposure. Figure 2(a) shows the GMS spectrum of the attached coating and figure 2(b) the TMS spectra recorded at 300 K and 78 K. Since the corrosion coating on this coupon was thin, the sub-spectrum from the carbon steel substrate is clearly seen. The analysis showed the presence of a predominance of lepidocrocite, nearly equal amounts of goethite and akaganeite, and a small fraction of magnetite. Table 3 summarizes the fraction of each oxide identified by TMS. The akaganeite was identified by low temperature Mössbauer analysis and confirmed by X-ray diffraction. The GMS analysis of the intact coating identified smaller amounts of goethite and magnetite compared to the TMS analysis, indicating layering of the oxides, which was confirmed by Raman spectrometry.

![FTIR pattern of corrosion products on carbon steel exposed in Campeche, México, for 12 months. Lepidocrocite and goethite are the two predominant oxides.](image)
Figure 2. Mössbauer spectra of the corrosion coatings on carbon steel coupons exposed in Campeche, México, for (a) and (b) 12 months at the 4000 m site and (c) and (d) 7 months at the 4 m site.

Comparing steel coupons exposed at both sites in Campeche, it was determined by Mössbauer spectroscopy and Raman spectrometry that each contained the same four oxides. However the coupons exposed at the 4 m site contained a greater fraction of akaganeite and a smaller fraction of lepidocrocite than found at the 4000 m site. The GMS and TMS spectra of the carbon steel coupon exposed for 7 months at
Table 3
Percentage of each iron oxide phase in the corrosion coatings of carbon steel coupons exposed at Campeche, México, and Kure Beach, USA. The values are given as atomic fraction of iron identified in each phase by Mössbauer spectroscopy. The goethite components in the form of bulk micron-sized (m) and superparamagnetic nano-sized (n) particles are also listed. Average error is ±1%.

<table>
<thead>
<tr>
<th></th>
<th>Campeche, Mx 4000 m site, 12 months</th>
<th>4 m site, 7 months</th>
<th>Kure Beach, NC 250 m lot, 16 years</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-FeOOH</td>
<td>28</td>
<td>23</td>
<td>58</td>
</tr>
<tr>
<td>β-FeOOH</td>
<td>24</td>
<td>42</td>
<td>0</td>
</tr>
<tr>
<td>γ-FeOOH</td>
<td>43</td>
<td>27</td>
<td>3</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>5</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>γ-Fe₂O₃</td>
<td>0</td>
<td>0</td>
<td>39</td>
</tr>
</tbody>
</table>

the 4 m site are shown in figures 2(c) and (d), respectively. The corrosion rate was higher at the shoreline site, table 1, and the corrosion coatings thicker than those formed at the inland site for the same exposure time. This can be observed in the GMS spectrum of figure 2(c) in which less carbon steel substrate signal is observed. The fractions of the oxides formed, table 3, were different from those formed at the inland site. Approximately twice the relative fraction of akaganeite formed closer to the shoreline and in about half the time. It was estimated that the thickness of the corrosion coating for the coupon exposed at the shoreline, 12 μm, was twice that for the inland exposure. The Mössbauer data of table 3 therefore predict that about the same total amount of lepidocrocite formed on both coupons while the amount of goethite was doubled and the amounts of akaganeite and magnetite tripled. The significant increase in the amount of akaganeite which formed at the shoreline was attributed to the much higher atmospheric chloride concentration closer to the Gulf. Further investigations of this correlation are presently underway. Comparison of the GMS and TMS spectra again indicated that the oxides were to some extent layered and that goethite formed closer to the surface of the corrosion coating while magnetite formed closer to the steel substrate.

As exposure time increased the structure of the corrosion coatings changed significantly. Distinct layers of mixed oxide phases formed with the composition of each layer being different. Mössbauer analysis of five different carbon and Weathering steels exposed at the Kure Beach site for times greater than 11 years always identified only goethite, lepidocrocite and maghemite in the corrosion products. The fraction of each phase varied with exposure location, time and steel type [3]. For most coupons, the goethite was present only as nano-sized particles exhibiting magnetic relaxation effects in the Mössbauer spectra. The fraction of goethite in each corrosion coating increased with increasing corrosion resistance [3,11]. Interestingly, Mössbauer spectroscopy did not identify akaganeite or magnetite on the long term exposure coupons. The fraction of each oxide phase on a carbon steel coupon exposed at Kure Beach for
16 years, as determined by TMS, is listed in table 3. Goethite and maghemite were the two predominant oxides with much less lepidocrocite being present compared to the coupons with short exposure times. For carbon steel, the goethite was found to consist of a mixture of both nano and micron-sized particles whereas for the Weathering steel coupons more nano-sized goethite particles were identified.

Micro-Raman spectrometry through oxide mapping, provided detailed information on the corrosion products and their layering. The Raman analysis agreed well with the Mössbauer analysis in identifying the main oxides as goethite, lepidocrocite and maghemite after long exposures. The goethite contribution to the patterns exhibited broad linewidths for most coatings, confirming the nanometer particle size. For carbon steel, the goethite contribution was a superposition of broad and narrow peaks con-
firming the presence of mixed particle size. Distinct mixed oxide layers were found to be present in all samples. Some coupons contained two main layers and others more than two. However only two different types of layers were identified. The oxide layering, labeled A and B, is shown in figure 3(a) for a corrosion coating consisting of three distinct layers. Figures 3(b)–(d) show the micro-Raman spectra of various regions in the coating. Layer A, figure 3(b), consisted of a mixture of goethite and lepidocrocite. On all coupons studied this "outer layer" was never detected adjacent to the steel but mostly closer to the top of the corrosion coating. Layer B, figure 3(c), the "inner layer" consisted of a mixture of goethite and maghemite and was always found next to the steel substrate and often above layer A and close to the coating surface. For exposure times of 16 years, no more than three distinct layers were observed over the 14 coupons studied. The oxides in each of layers A and B were always the same, as listed above, although the fraction of each varied with steel type and exposure site. On many coupons, small clusters, 5 μm diameter, of pure magnetite or nearly pure maghemite were identified, and then only in the inner layer. Regions C on figure 3(a) indicate islands of pure magnetite with the Raman spectrum being shown in figure 3(d). The magnetite islands, which appeared to be well crystalline, were only observed on the inner layer closer to the steel substrate. Islands of nearly pure maghemite formed in any of the inner layers and were present only as nano-sized particles.

6. Discussion

Exposure of steels to environments of high humidity, which increased the time-of-wetness, resulted in amorphous lepidocrocite being one of the earliest corrosion products to form. Continued exposure led to the formation of crystalline lepidocrocite and goethite after which magnetite also formed, most likely from the lepidocrocite in times of highest time-of-wetness. High fractions of akaganeite also formed in coatings from the Gulf of México. Its presence is interesting since it is known to form mainly in chloride containing environments and the analysis showed an increase in its fraction in regions of higher atmospheric chloride concentration. The belief that chlorides are trapped in its tetragonal structure suggests that the presence of akaganeite could increase the corrosion rate of the steel. Akaganeite is also unstable and is known to transform to hematite [12], although none was observed in the exposed samples. Although possible transformation of akaganeite has not been studied under environmental exposure conditions, it is apparent from the analysis that a transformation must occur since akaganeite was not observed after long exposures. The transformation presents a problem concerning the effect that deposition of the trapped chlorides in the vicinity of the steel substrate, has on long term corrosion rates of the steel. Measurement of actual chloride concentrations in the corrosion coatings would provide valuable information for understanding the increased corrosion rates in marine environments.

The observed layering of the corrosion products begins to provide some insight into the protective mechanism of the coating. Their formation is not believed to be
seasonal since no more than three layers formed after 16 years exposure. Detailed investigation of the oxide concentration variations, which are thought to occur within each layer, would be helpful in explaining environmental influence on oxide formation from year to year. The fact that there is a direct relationship between the amount of nano-sized goethite and the corrosion resistance of the steels investigated, suggests that the goethite reduced the porosity of the coating and decreased the amount of oxygen and water reaching the steel substrate. Electrochemical measurements will soon begin to measure coating porosity in the samples.

7. Conclusions

Atmospheric exposure conditions suggest that regions around the Gulf of México that have undergone recent economic development, will experience higher corrosion rates than observed in most other regions in the world. Careful study of the degradation of steel in México will help evaluate the problems, lead to improved selection of materials and increase the overall understanding of the corrosion processes at the microscopic level. Complete identification of the corrosion products formed on steels requires more than one and most likely three analytical techniques. In the marine environments around the Gulf of México, akaganeite formed in large fractions for short exposure times but was not identified after long term exposures when the corrosion process appeared to be stable. Very distinct layers of mixed oxides were commonly observed after long exposure times and the presence of large fractions of nano-sized goethite suggested that one type of layer found in all coupons studied, may contribute to the protection of steel from further corrosion.

References
