- Depth profiles obtained by RBS confirmed that the retained dose did not exceed 5×10^{16} ions.cm^{-2}. Flat topped and skewed distribution profiles (RBS) were obtained and regarded as indicative of sputtering and saturation doses[4].

- Breakdown and dissolution of Fe-Ta surface alloy layers is localized with preferential dissolution of iron. This is suggested as a result of EDAX analysis in active and passive adjacent zones, in a crevice, where the amount of detected Ta was not significantly different.

- A potential displacement of about 0.5V in the noble direction scale was found as a result of implantation.

ACKNOWLEDGMENTS

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CORROSION PRODUCTS OF LOW ALLOY STEEL UNDER WET-DRY CYCLING CONDITIONS

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Summary

The corrosion products formed on weathering steel and pure iron exposed to a wet-dry cycled SO_2-atmosphere have been studied by means of reflection (CEMS) and transmission Mössbauer spectroscopy and X-ray diffraction. After 48 days of exposure, rusts of both materials exhibit different morphologies. $FeSO_3.3H_2O$, $FeSO_4.nH_2O$ and amorphous ferric oxyhydroxides (probably ferrihydrite and/or α-FeOOH of small particle size) are the constituents of both rusts. The main differences between the corrosion products of both materials are related with the concentration of Fe^{2+} species and the crystallinity and/or particle size of ferric oxyhydroxides. The presence of Fe^{2+} species in 48 day-old rusts is attributed to the effect of the wet-dry cycling conditions.

1. Introduction

The daily change from wet to dry atmosphere, the so-called wet-dry cycle, affects the atmospheric rusting of ferrous materials [1-3]. In this work, the differences between the products formed on pure iron and low alloy steel, both exposed to simulated wet-dry cycles under artificially SO_2-polluted atmospheres, are shown. Mössbauer spectroscopy and X-ray diffraction were the main techniques employed for the analysis of products.

2. Experimental

Samples were polished (Al_2O_3, 0.3 μm) discs of weathering steel (ASTM A-508 gr A) and commercial iron (Comeca, St. Cyr, France, <0.15% Cu; 0.1% C+P+Mn+Si) exposed at 25°C during 48 days to an SO_2-polluted (0.008% by vol.) atmosphere, whose relative humidity (RH) was sequentially maintained 6h at 98% RH and 18h at 15% RH. The artificially SO_2-polluted atmosphere was prepared as described in [4].

Mössbauer spectra of rusts were taken by CEMS using a home made parallel plate avalanche counter [5] and by transmission after rust descaling. A closed-cycle Helium cryogenic generator (Air Products) was employed during the recording of transmission spectra at 78 and 14 K.

X-ray diffractograms of the rusts were taken "in situ", prior to rust descaling, in a Philips PW 1730/10 diffractometer using the Cu K_α line.

3. Results and Discussion

The rusts on the two materials seem very different even at first sight: the corrosion products form white spots and the surface appears roughest for the iron discs, whereas the film on weathering steel (WS) is adherent and more homogeneous than on iron. Weight gain of the corroded samples was 2 and 3 mg.cm^{-2} for WS and Iron, respectively.

The CEMS and transmission spectra were fitted to a maximum of ten Lorentzian lines corresponding to two Fe^{2+} doublets (A and B), two Fe^{3+} doublets (C and D), and two lines corresponding to the peaks 2 and 5 of the α-Fe sextet of the base (fig. 1). Mössbauer parameters, shown in Table 1, allow the following assignments to be made: doublets "A" and "B" to $FeSO_3.3H_2O$ and $FeSO_4.nH_2O$, respectively [6], doublet "C" to amorphous Fe^{3+} oxyhydroxides or ferrihydrite [7, 8], and doublet "D" to superparamagnetic (spm) α-FeOOH, γ-FeOOH, or ferrihydrite [8, 9].

The most significant difference between the CEM spectra of WS and Iron rusts concerns the Fe^{2+} sulphite/sulphate ratio, which is about twenty times higher for the WS than for the Iron samples. However, in the WS transmission spectra this ratio is twice higher than in Iron. This result proves that the relative concentration of the two Fe^{2+} species is analogous for surface and bulk in the WS rust, whereas in the Iron sample the Fe^{2+} sulphite/sulphate ratio is higher in the bulk rust than in the surface rust (see fig. 1).
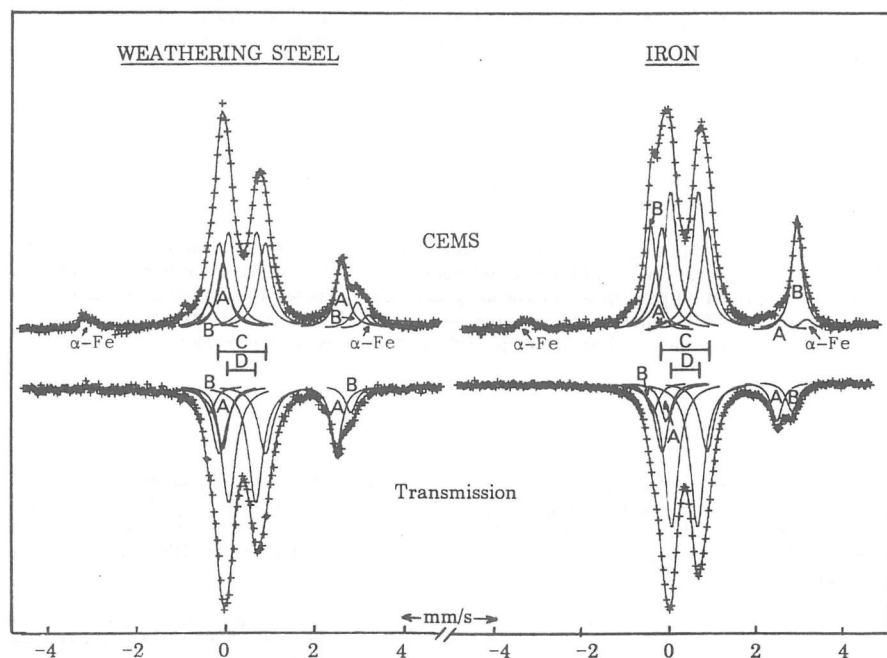

Figure 1.– CEM-spectra of rust samples (top) and transmission-spectra of the descaled rusts (bottom).

Table 1.– Mössbauer parameters of corrosion products (IS referred to α-Fe; Γ = full linewidth at half maximum).

	Compound assigned	IS (mm/s)	QS (mm/s)	Γ (mm/s)
Fe^{2+}(A)	$FeSO_3.3H_2O$	1.23 (2)	2.55 (3)	0.30 (1)
Fe^{2+}(B)	$FeSO_4.nH_2O$	1.26 (3)	3.20 (3)	0.30 (1)
Fe^{3+}(C)	Ferrihydrite	0.39 (2)	1.03 (2)	0.37 (1)
Fe^{3+}(D)	Ferrihydrite spm α-FeOOH γ-FeOOH	0.39 (2)	0.61 (2)	0.37 (1)

Transmission spectra of the descaled rusts taken at 78 and 14 K (fig. 2) show no magnetic splitting of WS products and split partially (24% and 35% at 78 K and 14 K, respectively) for the Iron products. This split part is a broad sextet characteristic of a finely grained material with a particle size distribution. Thus, the sextet was fit using one hyperfine field distribution which yields parameters that can be ascribed to finely divided α-FeOOH.
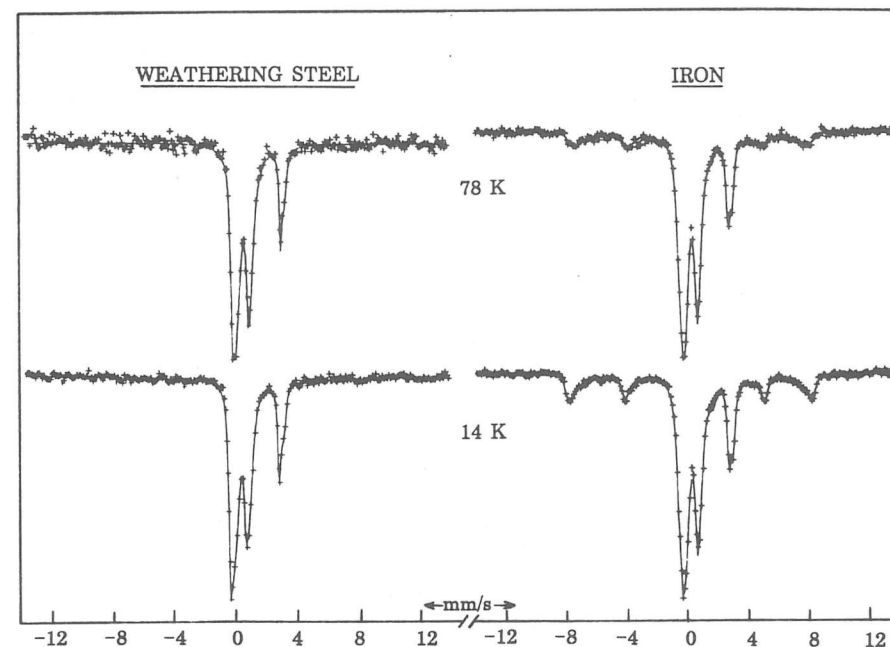

Figure 2.– Transmission-spectra of the descaled rusts at 78 and 14 K.

X-ray diffractograms confirm the presence of $FeSO_3.3H_2O$ and $FeSO_4.nH_2O$ in WS and Iron rusts. Line sets corresponding to α-FeOOH and ferrihydrite, both of low crystallinity [8–10], appear only in the rust of iron discs.

The lack of diffraction lines corresponding to the Fe^{3+}-species present in the WS rust and the lack of magnetic spectrum at 14 K prove the "quasi" amorphous nature of these Fe^{3+}-species and their smaller particle size as compared to those of Iron rust.

Fe^{2+} sulphite and sulphate are formed [11, 12] during the early stages of corrosion in humid SO_2-atmospheres. These Fe^{2+} species remain in the rust as long as 48 days under the present conditions. Thus, the effect of wet-dry cycling is the stabilisation of the Fe^{2+} species, probably because their oxidation to Fe^{3+} is retarded during the dry periods, when the rust is dry enough to precipitate corrosion products from the water layer formed in the preceding wet period [6].

As in previous studies [6, 12], the $FeSO_3.3H_2O$ concentration was higher for the WS (19%) than for the Iron (12%) corrosion products, and also higher in the bulk than in the surface rust, specially for Iron (12% and 3% for bulk and surface, respectively), proving that the oxidation of $FeSO_3.3H_2O$ to $FeSO_4.nH_2O$ progresses more slowly in WS than in Iron.

4. Conclusions

1. Under the cycling conditions used here the rust on weathering steel forms an adherent, compact layer constituted by $FeSO_3.3H_2O$, $FeSO_4.nH_2O$ and amorphous ferric oxyhydroxides, probably ferrihydrite and/or α-FeOOH of very small particle size.

2. For the same conditions both the Fe^{2+}/Fe^{3+} and $FeSO_3.3H_2O/FeSO_4.nH_2O$ ratios are higher in weathering steel than in iron.

3. Ferric oxyhydroxides of iron rust have a higher grade of crystallinity and/or higher particle size than those of weathering steel rust.

Acknowledgements

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INFLUENCE OF IMIDAZOLES IN THE DEPOSITION VELOCITY OF COOPER ON NON CONDUCTORS BY ELECTROLESS.

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ABSTRACT.

The effect of the imidazoles I-III (1) on the deposition velocity of cooper on phenolic and epoxy resins has been studied. It is shown that these substances affect the stability of the cooper electroless baths in the temperature interval 25-52 °C.

EXPERIMENTAL.

The effect of imidazole I-III (1) on electroless copper deposition was studied by the gravimetric method and Tafel plots.

Cooper was deposited by means of the electroless copper plating bath recommended by Pearlstein and Baudrand (2). The epoxy plate samples were activated in $PdCl_2$ solution prior to immersion into the plating solution.

The Tafel plots were measured with a Princeton Applied Research Model 173 potentiostat. The SCE electrode was used as a reference system. The working electrode was on electroless deposited copper plate ($0,25$ cm^2). A $99,5$ % pure copper plate with 3 cm^2 area was used as counter electrode.

The point when the first smal metallic nuclei appeared in the bulk solution was considered as the start of copper electroless bath decomposition. The time at the complete decoloration of the solution was taken as the bath life time (TIL).

RESULTS AND DISCUSSION.

A persistent problem in the use of electroless copper baths has been their tendency to descompose spontaneously. Many