

## ON MAGNETITE FORMATION AS A CORROSION PRODUCT OF STEEL

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A Mössbauer study on magnetites formed under the influence of differing concentrations of sulfate and chloride ions and also under the presence Cu, Mn and Cr ions is presented. It is found that different concentrations of sulfate and chloride ions in the synthesis procedure does not influence the physical and chemical properties of the magnetite. On the other hand, the concentrations of these ions in accelerated corrosion tests influence mainly the amount of magnetite formed. Mössbauer results suggest that the physical and crystallographic properties and amounts of the final products can be differently affected by the combined effect of sulfate and chloride ions plus the presence of alloying elements.

### Introduction

In corrosion science it is very important to understand the mechanisms of formation of the different iron oxides as atmospheric rust components. This study includes the understanding of the role played by pollutants and alloying elements on rust formation. One of the main rust components is magnetite, which is very common in steel exposed to chloride rich atmospheres.

The aim of the present study is to look into the magnetite formation under the influence of varying concentrations of chloride and sulfate ions and also under the combined effect of these ions plus cations such as  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$ . The effect of the chloride and sulfate ions was investigated by using two approaches. The first one consisted in preparing magnetites with different types of precursors and the second method, by performing alternating immersion/emersion tests on low carbon steels.

### Experimental procedure

The synthetic pure samples were prepared using a hydrolysis method similar to the one proposed by Schwertmann and Cornell [1], which uses ferrous sulfate and alkaline solutions as precursors. In some instances, the ferrous sulfates were replaced partly or totally with ferrous chlorides, while keeping constant the contribution of ferrous ions (see Table 1). In other cases, the amount of ferrous ions was varied, but without changing the amount of sulfates or chlorides. The first case was achieved by replacing ferrous sulfate by sodium sulfate, and the second case was accomplished by replacing ferrous chloride by sodium chloride.

The effect of pollutants was also studied through accelerated corrosion tests [2,3]. For that purpose, AISI 1008 low carbon steel coupons were subjected periodically to the influence of several combinations of chloride and sulfate ions during 65 days (see Table 2). The coupons rotated continuously over a period of 41 min, 13 min of which they were immersed in the solutions and the remaining time they were outside at a temperature of about 45 °C. The rust obtained was classified into inner (adherent) and outer (loosely bound) layers. The inner rust was investigated by room temperature Mössbauer spectroscopy.

**Table 1.** Some selected examples about the mixture of solutions employed in the preparation of magnetites in pure form and in the presence of the  $\text{Cu}^{2+}$  solutions. The percentages are given in mole %.

In pure Form		With cationic solutions	
Sample	Precursors	Sample	Precursors
1	100% $\text{FeSO}_4$	6	95% $\text{FeCl}_2$ + 5% $\text{CuCl}_2$
2	50% $\text{FeSO}_4$ + 50% $\text{FeCl}_2$	7	95% $\text{FeSO}_4$ + 5% $\text{CuCl}_2$
3	100% $\text{FeCl}_2$	8	95% $\text{FeCl}_2$ + 5% $\text{CuSO}_4$
4	50% $\text{FeCl}_2$ + 50% $\text{Na}_2\text{SO}_4$	9	95% $\text{FeSO}_4$ + 5% $\text{CuSO}_4$
5	50% $\text{Fe SO}_4$ + 50% $\text{NaCl}$	10	99% $\text{FeCl}_2$ + 1% $\text{CuCl}_2$

Magnetites were also prepared in the presence of copper, chromium or manganese sulfate (or chloride) solutions (see Table 1). For this purpose, 1, 5 and 10 mole % of Fe, in the nominal composition, was replaced by Cu, Cr, or Mn [4,5].

Room temperature Mössbauer spectra were obtained in the transmission mode using a constant acceleration drive and a triangular reference signal. A  $^{57}\text{Co/Rh}$  source with initial activity of 25 mCi was used. All absorbers were prepared by mixing the material with pure sugar to achieve a homogeneous thickness of about 10 mg  $\text{Fe}/\text{cm}^2$ .

## Results and discussion

The synthesis methods produce magnetites with relatively good crystallinities and stoichiometries. It has been found that the magnetic hyperfine fields for the A and B sites,  $B_{hf,A}$  and  $B_{hf,B}$  respectively, in samples obtained from sulfate and chloride precursors are the same between the error bars of about  $\pm 0.1$  T. Additionally,  $B_{hf,A}$  and  $B_{hf,B}$  and the other hyperfine parameters were not noticeably affected in the magnetites obtained using sodium chloride or sodium sulfate as secondary precursors. These results suggest that the type and concentration of precursors have little or no effect on the crystallographic, chemical or physical properties of the pure magnetites.

As mentioned in the introduction, the effect of sulfate and chloride ions was also studied through accelerated corrosion tests. The results of these investigations are summarized in Table 2.

**Table 2.** Pollutant concentration for the different corrosion tests, relative amount of magnetite present at the inner most layer in the corrosion products, and the mean corrosion rate after 65 days coupons exposure to the solutions [2].

Corrosion tests	1	2	3	4	5	6
$\text{Cl}^-$ ( $10^{-3}$ M)	1.00	1.00	1.25	1.50	1.75	3.00
$\text{SO}_4^{2-}$ ( $10^{-4}$ M)	1.00	1.25	1.00	1.00	1.00	2.00
Magnetite (%)	9.8	5.6	58	10.2	26.2	42.9
Corrosion rate ( $\mu\text{m}/\text{y}$ )	9.8	5.6	58	10.2	26.2	42.9

Morales et al. [2] have found a correlation between the corrosion rate and the relative magnetite content for coupons exposed during 65 days, i.e. higher corrosion velocities produce a higher