

# Mössbauer investigation of the influence of the sea atmosphere on the corrosion of steel constructions in Sochi

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**Abstract** A study of the sea atmosphere influence on the corrosion products of steel constructions near Sochi at difference distances from the sea has been made. The phases and compositions of the corrosion products formed on different sides of steel construction elements were examined by using Mössbauer spectroscopy (at 298 and 78 K). The results show that phases and composition distributions in oxide films are different on different parts of the constructions. The differences depend not only on the distance from the sea, but from their relative orientation to the sea also. The phase structure of the oxide films on different positions is identified.

**Keywords** Mössbauer effect · Steel corrosion · Phase analysis

## 1 Introduction

The corrosion of steel constructions near the Black Sea in the Sochi region is interesting from scientific and applied technical point of view. There are many buildings and constructions which were built more than 50 years ago. It is interesting to investigate the influence of the sea atmosphere during such a long time on steel constructions and buildings that are disposed in different places relatively to the sea in distance and orientation. Mössbauer spectroscopy is used for the identification of the nature of the oxides, as well as of the fraction of each of them in the corrosion products of steel structures on the beach of the Black Sea near Sochi. Such

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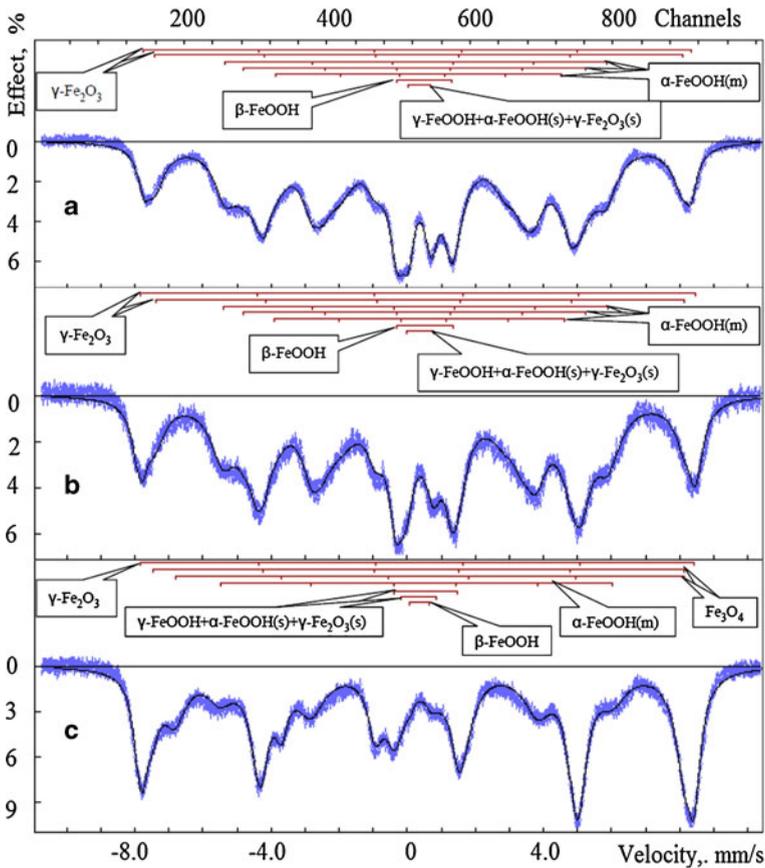
information is useful for a better understanding of the corrosion processes under influence of sea atmosphere and for estimations of the residual durability of the structures. It is necessary to obtain insight in the processes of corrosion and change of oxide phase structure with thickness of the oxide film. In this paper the oxide films, formed on steel structures under influence of sea atmosphere during more than 50 years, are investigated. For investigations the samples were taken from structures that were in periodic contact with water, and the samples from the structures that were under the influence of sea wind only. Bearing columns made from steel were chosen as structures. These square columns supported sun beds on a beach.

## 2 Sample preparation and experimental methods

Samples were taken from different parts of the steel structures. The total thickness of the corrosion layers varies between 2.5 and 3.0 mm. The corrosion products were scraped from the surface of the samples from: a) near surface layers, b) middle layers ( $\sim 1.5$  mm deepness) and c) layers near the metal ( $\sim 3.0$  mm deepness). From the scraped products absorbers with thickness  $\sim 30\div 50$  mg/cm<sup>2</sup> were prepared with using technology described in papers [1, 2]. Mössbauer measurements were performed using a <sup>57</sup>Co(Cr) source with the spectrometer in transmission mode. The spectrometer was calibrated with  $\alpha$ -Fe foil spectrum at room temperature. The spectra were fitted using programs UnivemMS, MSTools [3].

## 3 Results and discussions

The Mössbauer spectra obtained from different corrosion products are shown in Figs. 1 and 2. For the identification of the iron compounds in some cases measurements at liquid nitrogen temperature have been carried out (Fig. 2c). It was observed that surface color and structure of oxide films depend on the sample position in relation to seawater and to its distribution in oxide layer. The comparison of the spectral shapes of oxides from different depths of rust shows changes of the shape with increasing rust depth (Fig. 1a, b, c). It can be seen that the lines of magnetic phases are broadened and change in intensity. This means that the compositions of the iron compounds are not uniform in the oxide film and that there is a change of compound distribution with depth in the oxide film. The spectra in Fig. 1 were fitted to some iron components having broadened Lorentzian lines. The fit parameters agreed with those published by Cook [4–6]. In investigated oxide films the following compounds of iron are identified:  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite),  $\alpha$ -FeOOH (goethite) (m),  $\gamma$ -FeOOH (lepidocrocite),  $\alpha$ -FeOOH (goethite) (s),  $\beta$ -FeOOH (Akaganeite), Fe<sub>3</sub>O<sub>4</sub> (magnetite) (where m-massive, s- superparamagnetic). In the central part of the spectra (Fig. 1) paramagnetic compounds such as  $\alpha$ -FeOOH (s),  $\gamma$ -FeOOH,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> are introduced without identification of their relative components. The existence of those compounds is proven by recordings of Mössbauer spectra at T = 80 K. Most of the spectral area is located in the magnetic lines (Fig. 1). In this case we can assume that the particle size of practically all these compounds are  $> 15$  nm [7] in the investigated oxide films.

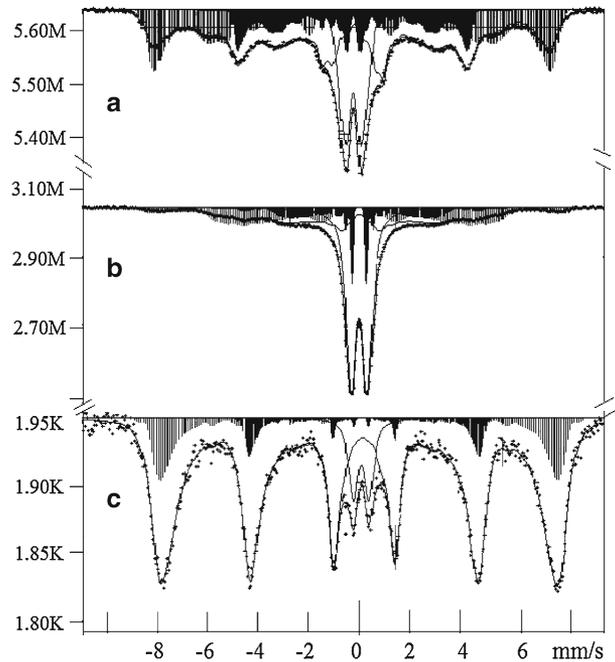


**Fig. 1** Mössbauer spectra of corrosion products formed on a detail of a construction that was in periodic contact with seawater during storms: **a** oxide from surface layer, **b** oxide from middle layer, **c** oxide from layer close to the metal substrate

Spectra of oxide films from details located at a distance of 10 m from the sea are shown in Fig. 2. The spectra of the samples located closer to seawater (Fig. 1) in comparison with those of samples located at the distance of 10 m from the sea (Fig. 2) have distinctions as well in the ratio of the separate compounds of iron as in their distribution along the oxide film thickness. These differences between the spectral shapes in Figs. 1 and 2 show the influence of the distance from the seawater on corrosion processes in steels.

In the case of the distance of 10 m as well as in the case of Fig. 1 the spectra have broadened Lorentzian line shapes as well at room temperature as at liquid nitrogen temperature (Fig. 2). In the last case the following compounds of iron such as  $\gamma$ - $\text{Fe}_2\text{O}_3$  (maghemite),  $\alpha$ - $\text{FeOOH}$  (goethite) (m),  $\gamma$ - $\text{FeOOH}$  (lepidocrocite),  $\alpha$ - $\text{FeOOH}$  (goethite) (s),  $\beta$ - $\text{FeOOH}$  (Akaganeite) (where m-massive, s- superparamagnetic) are identified in samples located at 10 m. It can be seen that at liquid nitrogen temperature (Fig. 2c) there are substantial changes in the shapes of the spectrum in comparison with that obtained at room temperature (Fig. 2b).

**Fig. 2** Mössbauer spectra of corrosion products formed on a detail of a construction that was located at the distance of 10 m from sea. Oxides were scraped from surface layers: **a** side looking at sea ( $T = 298\text{ K}$ ), **b** side opposite to sea ( $T = 298\text{ K}$ ), **c** side opposite to sea ( $T = 80\text{ K}$ )



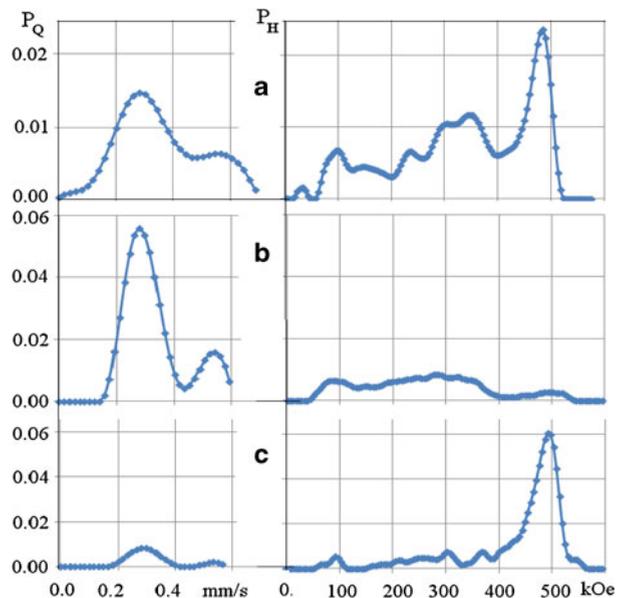
These differences are explained by a transformation particles of goethite,  $\alpha$ -FeOOH, of particle size  $<15\text{ nm}$ , from the superparamagnetic state to the magnetic state. This follows from the analysis of Fig. 2b and c. Figure 2b shows that most of the spectral area is located in the central doublet which was identified by low temperature analysis to be lepidocrocite,  $\gamma$ -FeOOH, and superparamagnetic goethite  $\alpha$ -FeOOH(s) having particle size  $<15\text{ nm}$ . The spectrum recorded at 80 K, Fig. 2c, now shows a much larger component of magnetic goethite resulting from the reduced magnetic relaxation rate at the lower temperature. The doublet remaining at 77 K is comprised of mainly lepidocrocite plus a small fraction of superparamagnetic goethite,  $\alpha$ -FeOOH (s2), estimated to have a particle size  $<8\text{ nm}$  [7].

From the shape of the spectra (Figs. 1, 2) it follows that the magnetic structure of the oxides is not defined by unique hyperfine magnetic fields but rather by a distribution of magnetic fields. It can be clearly seen in Fig. 3.

Figure 3 shows that there are magnetic particles in the rust with low magnetic fields from 10.0 to 33.0 T as well at room temperature as at  $T = 80\text{ K}$ . Identification of these particles is not simple because of the absence of data with such low magnetic fields for iron compounds. Therefore, it can be assumed that some oxide particles with nanodimensions can have small magnetic fields or for some particles of iron compounds there exist a large scale of magnetic fields.

The color of the rust on a sample that was in periodic contact with seawater is brown over the complete thickness. We also observed that they were porous. Doublet lines on these spectra (Fig. 1) are caused generally by the presence of lepidocrocite, maghemite and very small concentrations of goethite. As it was shown [7] the goethite promotes the formation of a protective layer. In oxides formed near the sea there are practically no particles of superparamagnetic goethite. This may

**Fig. 3** Distribution of quadrupole splitting  $P_Q$  and magnetic field  $P_H$  from spectra in Fig. 2: **a** side looking at sea ( $T = 298$  K), **b** side opposite to sea ( $T = 298$  K), **c** side opposite to sea ( $T = 80$  K). The amplitude of the graph is proportional to the contents of iron compounds



explain that the corrosion layer is not protective and that the process of material destruction is continued quickly. It is proven by the presence of phase  $Fe_3O_4$  that it is formed, according to [6], close to the metal and caused by a long influence of a humid environment—in our case by sea water. So we can conclude that this construction from which this specimen was cut is under progressive corrosion.

The color of the rust on the structure located at a distance of 10 m from the sea on the side opposite to the sea is black. Moreover, the presence of superparamagnetic goethite and a low concentration of maghemite in general is typical for the inside layers. As it was mentioned above superparamagnetic goethite promotes formation of a protective layer. It means that the part of the structure located at 10 m from the sea and opposite to the sea is not under progressive corrosion.

#### 4 Conclusion

The influence of the Black Sea water and atmosphere on details of steel beach constructions was investigated.

In oxide films the presence of the phases  $Fe^{2+}$  and  $Fe^{3+}$  in different types of compounds such as  $\gamma$ - $Fe_2O_3$ ,  $Fe_3O_4$ , ( $\alpha$ -,  $\beta$ -,  $\gamma$ -) $FeOOH$  are observed.

It is found that on structures that were in periodic contact with water, a protective layer was not created, in contrast to sides of structures located at 10 m from the sea, where a protective layer was created. In the rust of structures periodically contacted with water the following compounds are found: a phase akaganeite, being formed in conditions of high content of chlorides in the environment, and the phases maghemite and magnetite, caused by a long period of humidity.

In samples located at 10 m from the sea, the presence of superparamagnetic goethite is established and demonstrates the creation of a protective layer.

Akaganeite is found only on a sample that was facing the sea. Magnetite is absent completely, and maghemite is present, but in smaller contents than in a sample contacting with water, which demonstrates a smaller influence of a long time of humidity.

In this study we illustrated the applicability of the Mössbauer effect for corrosion process research and the possibility for controlling the present state of steel structures.

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