FT-IR and Mössbauer Study of Corrosion of Steel in Tap and Mineral Water

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The influence of carbonates on the process of corrosion of steel in aqueous media has been studied. The corrosion of steel in tap water and mineral water of three different chemical compositions (all for human use) was monitored for up to 6 months. Rust samples were analyzed using Fourier transform infrared (FT-IR) spectroscopy and ^{57}Fe Mössbauer spectroscopy. Some selected samples were also analyzed by X-ray powder diffraction (XRD). It was shown that the concentration of carbonates plays an important role in the corrosion of steel in aqueous media, both during short (days), and long times (months) of corrosion. For short times of corrosion in the presence of a high content of carbonates, the rust was found amorphous for XRD. It was proved that γ-FeOOH was absent in amorphous rust. The possible presence of ferrihydrite in this amorphous fraction is discussed taking into account the FT-IR and Mössbauer spectroscopic results. At a very high concentration of carbonates, after 6 month of corrosion, γ-FeOOH was not found in the rust. Formation of α-FeOOH and Fe_3O_4 in corrosion products was also monitored. It was suggested that, in the very early stages of corrosion, carbonates can be structurally incorporated in the rust in the form of hydroxycarbonates, while in the later stages, they can modify the phase transformation by the mechanism of specific adsorption.

INTRODUCTION

The phase composition of the rust generated by corrosion of steel in aqueous media depends on different factors, such as temperature, pH, oxygen content, presence of inorganic or organic ions, *etc.*[1–4] The type of steel has more influence on the kinetics of rusting than on the phase composition of the rust. In the case of atmospheric corrosion of steel, important factors are the wet/dry cycles which influence the composition of the rust.[5–6] Numerous investigations have shown the presence of different oxide phases in the rust, such as $Fe(OH)_2$, amorphous $Fe(OH)_3$, α-FeOOH, β-FeOOH, γ-FeOOH, δ-FeOOH, α-Fe_2O_3, γ-Fe_2O_3, and Fe_3O_4. Many researchers have described an intermediate corrosion product, called »green rust«. In these works, significant differences in the chemical and crystallographic characterization of »green rust« were found because of the different conditions of its formation. The crystallinity, stoichiometry, particle size and morphology of the oxide phases in the rust may also vary significantly. XRD has been traditionally used in the characterization of corrosion products. With the advancement of spectroscopic techniques (Mössbauer, Auger, E.S.C.A., Raman), corrosion scientists and engineers have recognized the capabilities of these techniques in the characterization of rust and the study of the corrosion mechanism.

This paper describes new results obtained during an investigation of the corrosion of steel in tap water and mineral water of three different chemical compositions (all for human use). These four kinds of water were used as corrosion media because: (a) steel pipe-lines play an important role in the transport of water, (b) the chemical composition of tap water and mineral water can vary significantly, and (c) the literature data on this subject are not numerous. One of the aims of the present work was also to correlate the capabilities of FT-IR spectroscopy and Mössbauer spectroscopy in the characterization of rust.

EXPERIMENTAL

The experimental procedure for the preparation of corrosion products and the type of steel used were described in previous papers.[2–4] The chemical compositions of water, used in the present experiments, are given in Table I. The experiments were performed at room temperature (RT). The corrosion products were sampled after a corrosion time of 1 day to 6 months for tap water and mineral water A, and after a corrosion time of 21 days to 6 months for mineral water B and mineral water C. For short corrosion times, the yield of corrosion products was small, and they were of colloidal nature. For this reason, an ultraspeed centrifuge (operational range up to 20 000 r.p.m.) was used to separate the corrosion products from the mother liquor. Corrosion products were characterized at RT by FT-IR spectroscopy (Perkin-Elmer spectrometer, Model 2000, KBr matrix), and also by ^{57}Fe Mössbauer spectroscopy (WISSEL spectrometer) at RT and 80 K. The Mössbauer spectra were fitted

TABLE I

Chemical composition (mg/l) of the water used in the corrosion experiments

Ions and CO_2	Tap water*	Mineral water A	Mineral water B	Mineral water C
Na^+		144	468	480
K^+		30	60	75
Ca^{2+}	10.65	87.3	118.1	219.5
Mg^{2+}	2.49	31.4	53.7	95.1
F^-		0.30	1.98	0.42
Cl^-	16.2		67.0	47.5
SO_4^{2-}	45.12		6.4	89.2
HCO_3^-	164.5	779	1852	2370
CO_2	44		3130	4460

* City of Zagreb (average composition)

using the SIRIUS program.[7] X-ray powder diffraction (Philips diffractometer, Model MPD 1880) was used as a complementary technique to spectroscopic techniques in the analysis of selected samples.

RESULTS AND DISCUSSION

FT-IR Spectroscopy

The results of FT-IR spectroscopic measurements are summarized in Figures 1, 2 and 4. The FT-IR spectra of the corrosion products formed in tap water (Figure 1) showed the following characteristics. After 1 day of corrosion, very broad bands at 888 and 802 cm^{-1} were observed and ascribed to fine particles of α-FeOOH (goethite) of, apparently, poor crystallinity. A small amount of γ-FeOOH (lepidocrocite) could be suggested only on the basis of the shoulder at 1023 cm^{-1}. Bands at 1512 and 1383 cm^{-1} are due to the presence of carbonates, while the band at 1637 cm^{-1} corresponds to water molecules. After 21 days of corrosion, bands at 892 and 797 cm^{-1} corresponding to α-FeOOH were well pronounced, and the intensity of the bands of γ-FeOOH at 1024 and 749 cm^{-1} increased. The weak band at 553 cm^{-1} observed after 6 months of corrosion could not be ascribed to Fe_3O_4 (magnetite) with certainty, because the dominant band of α-Fe_2O_3 (hematite) also appears in this spectral region. XRD confirmed the existence of Fe_3O_4 (Table II).

The FT-IR spectra of the rust formed in mineral water A (Figure 2), showed differences in relation to the spectra of the rust formed in tap water
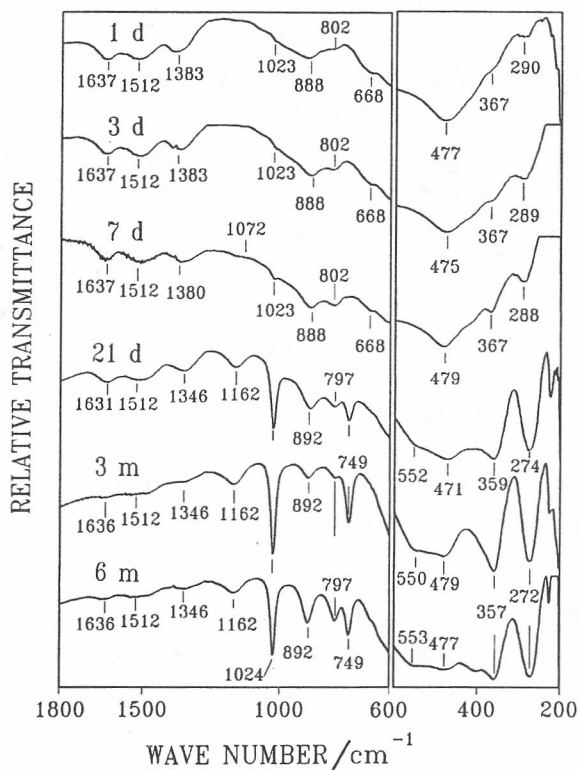
Figure 1. FT-IR spectra (RT) of the corrosion products generated in tap water after a corrosion time of 1 day to 6 months.

during the same corrosion time. A very broad and strong band at 948 cm^{-1} was observed for the rust formed after 1 to 7 days of corrosion. Also, very strong bands corresponding to carbonates were visible. The band at 948 cm^{-1}

TABLE II

Phase analysis of selected rust samples determined by XRD

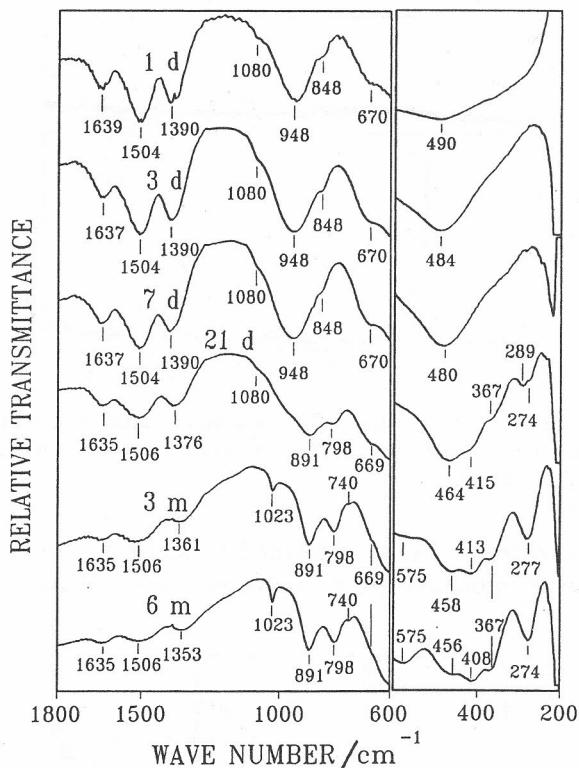| Sample	Time of corrosion	Phase analysis
Tap water	6 months	γ-FeOOH + α-FeOOH + Fe$_3$O$_4$
Mineral water A	1 day	amorphous + calcite (traces)
	3 days	amorphous + calcite (traces)
	7 days	amorphous + calcite (traces)
	6 months	α-FeOOH + Fe$_3$O$_4$ + γ-FeOOH
Mineral water B	6 months	α-FeOOH + Fe$_3$O$_4$
Mineral water C	6 months	α-FeOOH

Figure 2. FT-IR spectra (RT) of the corrosion products generated in mineral water A after 1 day to 6 months of corrosion.

could be ascribed to ferrihydrite according to the conclusions made in our previous paper.[2] In order to check the presence of ferrihydrite in the rust formed after 1 to 7 days of corrosion in mineral water A, the corresponding samples were also analyzed by XRD. These samples were found dominantly amorphous, as illustrated by the XRD pattern taken for the rust generated after 1 day of corrosion (Figure 3). However, the presence of small particles of ferrihydrite, which are not detectable by XRD, could not be excluded. XRD also showed traces of $CaCO_3$ (calcite) in the rust, formed in the early stages of corrosion, due to the high calcium and carbonate content of mineral water A. After 21 days of corrosion, weak bands at 891 and 798 cm^{-1}, corresponding to α-FeOOH, were visible, while after 3 months of corrosion bands at 1023 and 740 cm^{-1}, corresponding to γ-FeOOH, appeared. The band at 575 cm^{-1}, recorded after 3 and 6 months of corrosion, could be ascribed to Fe_3O_4. XRD (Figure 3 and Table II) and Mössbauer spectroscopy were used, as complementary techniques to FT-IR spectroscopy, for positive assignation of this phase (Fe_3O_4) in the rust.
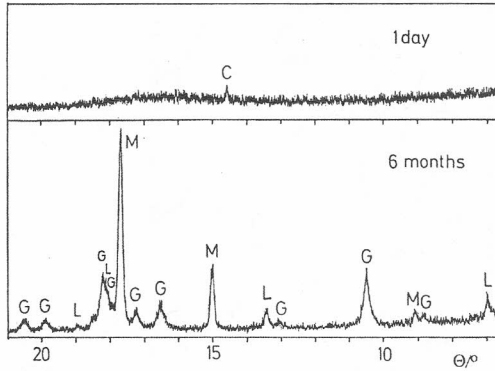
Figure 3. Characteristic parts of the XRD patterns of rust formed in mineral water A (monochromatized radiation Cu-Kα). Descriptions: G = α-FeOOH, M = Fe_3O_4, L = = γ-FeOOH and C = $CaCO_3$.

The FT-IR spectra of the rust formed in mineral water B and mineral water C (Figure 4) indicated the presence of α-FeOOH as a single phase in
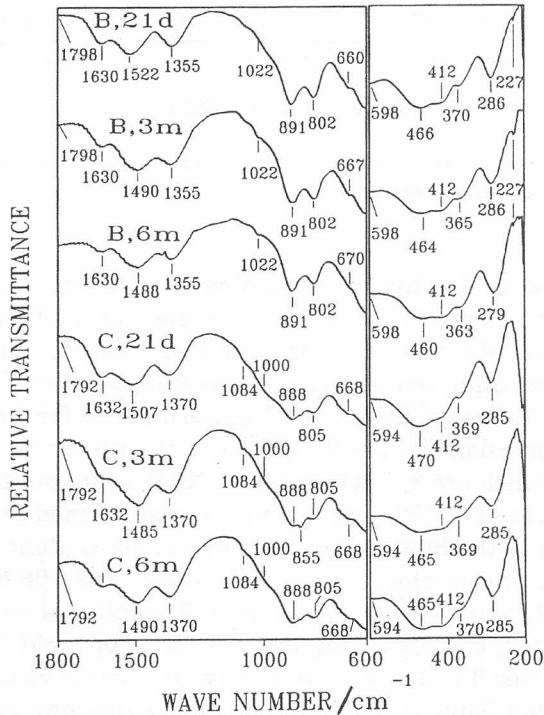

Figure 4. FT-IR spectra (RT) of the corrosion products generated in mineral water B and C after 21 days to 6 months of corrosion.

the rust after 21 days of corrosion. The rust formed after 3 months of steel corrosion in mineral water B contained α-FeOOH (bands at 891 and 802 cm^{-1}) and γ-FeOOH (band at 1022 cm^{-1}), whereas in the rust formed in mineral water C for the same time of corrosion only α-FeOOH (bands at 888 and 805 cm^{-1}) was detected. γ-FeOOH was not detected by FT-IR spectroscopy in the rust formed in mineral water C, even after 6 months of corrosion. FT-IR measurements undoubtedly indicated that the high content of carbonates in mineral water had a dominant influence on the presence of γ-FeOOH in the rust. The formation of γ-FeOOH was gradually suppressed with increasing concentrations of HCO_3^- (CO_2).

Mössbauer Spectroscopy

Corrosion products were also characterized using Mössbauer spectroscopy, and we shall discuss the specific results obtained by this technique (Figures 5 to 8 and Table III). Figure 5 shows the Mössbauer spectra of the rust formed in tap water after 1 day, 7 days and 6 months of corrosion, re-
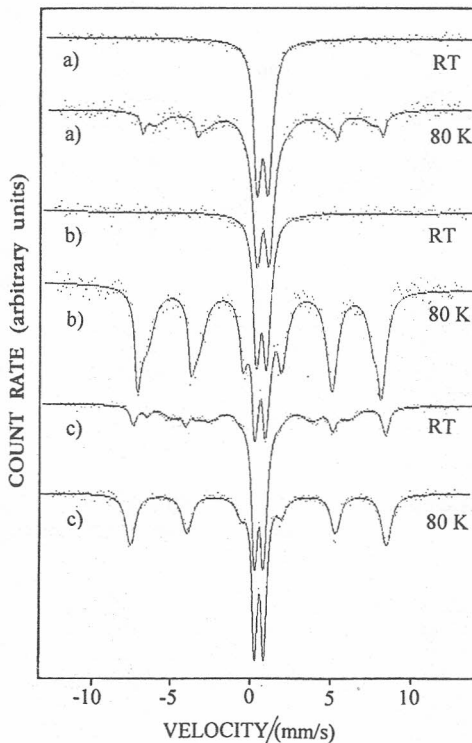

Figure 5. ^{57}Fe Mössbauer spectra of the corrosion products generated in tap water (a = 1 day, b = 7 days and c = 6 months of corrosion).

TABLE III

^{57}Mössbauer parameters calculated for the corrosion products

Tap water

Time of corrosion	Temp. of spectra recording	Component	Isomer shift, δ/mm s^{-1}	Quadrupole splitting, Δ or E_q mm s^{-1}	Hyperfine magnetic field, H/kOe	Line width, Γ/mm s^{-1}
1 d	RT	Q	0.35	0.68		0.60
	80 K	Q	0.44	0.75		0.68
		M_1	0.56	−0.32	473	0.31
		M_2	0.62	−0.21	433	1.55
7 d	RT	Q	0.36	0.62		0.56
	80 K	Q	0.49	0.66		0.54
		M_1	0.45	−0.15	478	0.51
		M_2	0.51	−0.22	445	1.02
21 d	RT	Q	0.37	0.58		0.58
	80 K	Q	0.48	0.59		0.49
		M_1	0.48	−0.23	482	0.42
		M_2	0.50	−0.26	452	0.92
3 m	RT	Q	0.36	0.56		0.47
		M	0.37	−0.04	487	0.94
	80 K	Q	0.47	0.56		0.44
		M_1	0.49	0.03	516	0.31
		M_2	0.51	−0.07	479	0.96
6 m	RT	Q	0.36	0.55		0.47
		M_1	0.29		488	0.47
		M_2	0.70		460	0.56
		M_3	0.38		342	1.35
	80 K	Q	0.47	0.57		0.39
		M	0.47	−0.20	499	0.71

Mineral water A

Time of corrosion	Temp. of spectra recording	Component	Isomer shift, δ/mm s^{-1}	Quadrupole splitting, Δ or E_q mm s^{-1}	Hyperfine magnetic field, H/kOe	Line width, Γ/mm s^{-1}
1 d	RT	Q	0.33	0.79		0.66
	80 K	Q	0.44	0.86		0.61
21 d	RT	Q	0.37	0.70		0.63
	80 K	Q	0.45	0.79		0.65
		M_1	0.47	−0.25	477	0.42
		M_2	0.47	−0.21	443	1.08

Mineral water B

Time of corrosion	Temp. of spectra recording	Component	Isomer shift, δ/mm s^{-1}	Quadrupole splitting, Δ or E_q mm s^{-1}	Hyperfine magnetic field, H/kOe	Line width, Γ/mm s^{-1}
21 d	RT	Q	0.37	0.63		0.61
	80 K	M	0.47	−0.23	468	0.78
3 m	RT	Q	0.35	0.63		0.64
	80 K	Q	0.47	0.69		0.56
		M_1	0.46	−0.22	477	0.45
		M_2	0.49	−0.28	452	0.91
6 m	RT	Q	0.38	0.60		0.56
		M	0.44	−0.07	473	1.89

Mineral water C

Time of corrosion	Temp. of spectra recording	Component	Isomer shift, δ/mm s^{-1}	Quadrupole splitting, Δ or E_q mm s^{-1}	Hyperfine magnetic field, H/kOe	Line width, Γ/mm s^{-1}
21 d	RT	Q	0.37	0.63		0.58
	80 K	Q	0.43	0.65		0.50
		M	0.48	−0.23	455	0.91
3 m	RT	Q	0.35	0.66		0.61
	80 K	Q	0.42	0.83		0.82
		M_1	0.47	−0.06	477	0.49
		M_2	0.48	−0.06	444	0.88
6 m	RT	Q	0.36	0.63		0.56
	80 K	Q	0.46	0.79		0.72
		M_1	0.48	−0.06	476	0.44
		M_2	0.49	−0.06	446	0.85

Isomer shift, δ, is given relative to α-Fe
Descriptions: d = day, m = month, Q = quadrupole doublet and M = hyperfine magnetic splitting
Errors: ± 0.01 mm s^{-1} for isomer shift and quadrupole splitting
± 2 kOe for hyperfine magnetic splitting

spectively. The Mössbauer spectrum at RT of the rust formed after 1 day of corrosion showed a quadrupole doublet (δ_{Fe} = 0.35 mm s^{-1}, Δ = 0.68 mm s^{-1}, Γ = 0.60 mm s^{-1}), while at 80 K superposition of a quadrupole doublet (Δ = = 0.75 mm s^{-1}) and two sextets with hyperfine magnetic fields, H_1 = 473 and H_2 = 433 kOe, was observed. After 7 days of corrosion, the Mössbauer spectrum at RT of the rust showed a quadrupole doublet (δ_{Fe} = 0.36 mm s^{-1}, Δ = 0.62 mm s^{-1}, Γ = 0.56 mm s^{-1}) and superposition of a quadrupole doublet and two sextets with hyperfine magnetic fields, H_1 = 478 and H_2 = 445 kOe at 80 K. These spectra pointed to the superparamagnetic behaviour of α-FeOOH

particles. The Mössbauer spectrum at RT recorded for the rust after 6 months of corrosion was deconvoluted into four spectral components, *i.e.*, a quadrupole doublet (δ_{Fe} = 0.36 mm s^{-1}, Δ = 0.55 mm s^{-1}, Γ = 0.47 mm s^{-1}) and three sextets with hyperfine magnetic fields, H_1 = 488, H_2 = 459 and H_3 = 342 kOe. Hyperfine magnetic fields H_1 and H_2 can be ascribed to $Fe_{3-x}O_4$ (substochiometric magnetite), while the inner sextet, H_3, is due to the presence of α-FeOOH. At 80 K, the same sample showed superposition of a quadrupole doublet and one sextet having the following parameters: δ_{Fe} = 0.47 mm s^{-1}, E_q = –0.20 mm s^{-1}, H = 499 kOe and Γ = 0.71 mm s^{-1}. Evidently, the sextet observed at 80 K is the superposition of several hyperfine magnetic subspectra with similar Mössbauer parameters, and due to this fact they are not separable. The decrease of quadrupole splitting Δ from 0.68 mm s^{-1} to 0.55 mm s^{-1} at RT, during 6 months of corrosion, can be ascribed to the increased fraction of γ-FeOOH phase in the rust.

Mössbauer spectroscopy also showed the influence of the chemical composition of mineral water A on the phase composition of the rust. Figure 6 shows the Mössbauer spectra of the rust formed in mineral water A after 1 day and after 21 days of corrosion. The Mössbauer spectra of the rust formed after 1 day of corrosion showed a quadrupole doublet at RT and 80 K with splitting of 0.80 and 0.86 mm s^{-1}, respectively. These values of quadrupole splitting could be ascribed to ferrihydrite. However, this interpretation was
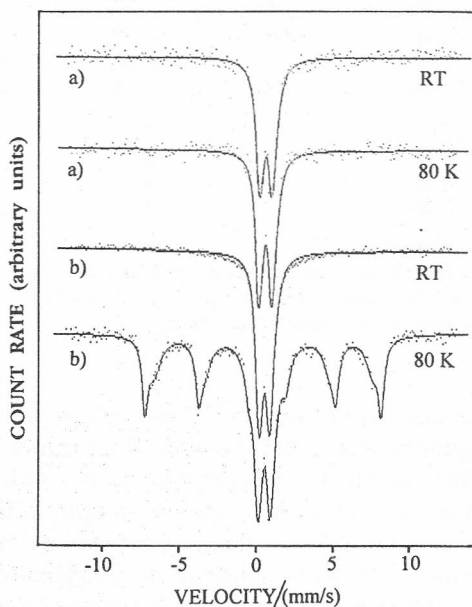

Figure 6. ^{57}Fe Mössbauer spectra of the corrosion products generated in mineral water A (a = 1 day, b = 21 days of corrosion).

not confirmed by XRD. As mentioned above, the Fe-bearing component in the rust formed in mineral water A after 1 day of corrosion was amorphous for XRD. After 21 days of corrosion, the Mössbauer spectrum of the rust at RT showed a quadrupole doublet with a collapsing sextet, and the spectrum recorded at 80 K a quadrupole doublet and two sextets, with $H_1 = 477$ and $H_2 = 443$ kOe, corresponding to superparamagnetic goethite. For longer corrosion times (3 months and more) magnetically splitted component was observed at room temperature.

Figure 7 shows the Mössbauer spectra of the rust formed in mineral water B after 21 days and 3 months of corrosion. The room temperature spectra showed a quadrupole doublet with a collapsing sextet. The spectrum at 80 K, recorded for the rust after 21 days of corrosion, was fitted assuming one sextet with $H = 468$ kOe. After 3 months of corrosion, the spectrum showed superposition of a quadrupole doublet and of two sextets with hyperfine magnetic fields $H_1 = 477$ and $H_2 = 452$ kOe, which can be ascribed to two kinds of α-FeOOH particles. The quadrupole splittings measured for
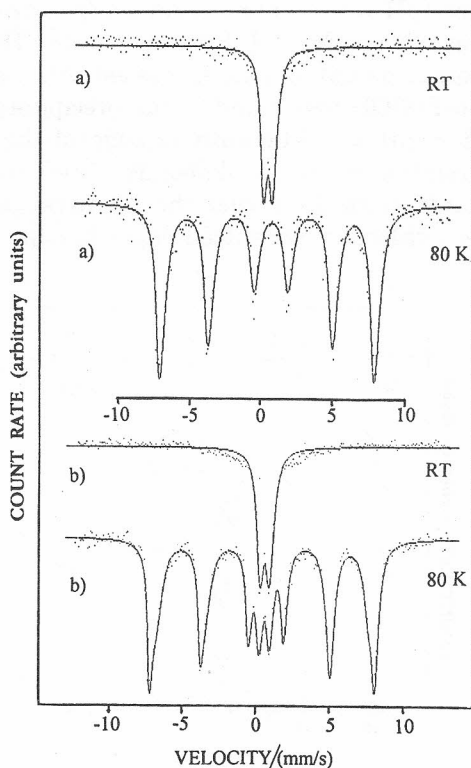

Figure 7. ^{57}Fe Mössbauer spectra of the corrosion products generated in mineral water B (a = 21 days, b = 3 months of corrosion).

the rust formed after 3 months of corrosion were 0.63 and 0.69 mm s^{-1}, as measured at RT and 80 K, respectively. These values are greater than those typical of γ-FeOOH.

Finally, a very strong effect of carbonates on the phase composition of the rust formed by corrosion of steel in mineral water C was observed. Figure 8 shows the RT spectra of the rust generated in mineral water C after 21 days, and 3 and 6 months of corrosion. The spectra are characterized by quadrupole splitting of 0.63, 0.65 and 0.63 mm s^{-1}, respectively. As discussed above, these values cannot be ascribed to γ-FeOOH. XRD analysis of the rust samples formed after 6 months of corrosion (Table II) confirmed the conclusion concerning γ-FeOOH, which was made on the basis of FT-IR and Mössbauer spectroscopic measurements.

The effect of carbonates on the corrosion of steel in aqueous media has not been investigated extensively enough, and literature data on this subject are not numerous. We would like to draw the reader's attention to several publications that could be brought into connection with the present research. For example, Carlson and Schwertmann[8] oxidized $FeCl_2$ solutions with air/CO_2 gas mixtures (pH = 6 or 7) at room temperature. The fraction of γ-FeOOH in mixtures with α-FeOOH decreased as the HCO_3^- content in the solution and the average oxidation rate increased. Also, at given concentrations (HCO_3^-), more α-FeOOH was found in the precipitate formed at pH = 6 than in that formed at pH = 7. The authors suggest that carbonate anions directed the polymerization of the double bonds of $FeO_3(OH)_3$ octaedra, common to both compounds, toward a corner sharing arrangement, and thereby to α-FeOOH, whereas chlorides permitted edge-sharing as in γ-FeOOH.
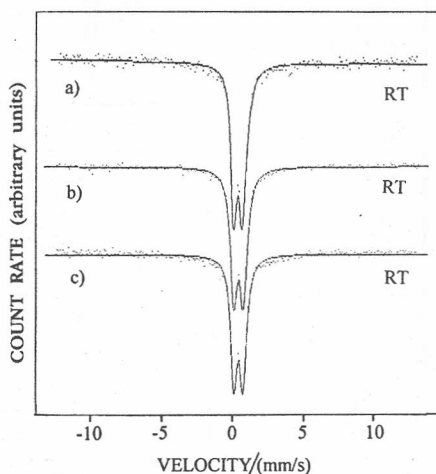

Figure 8. ^{57}Fe Mössbauer spectra (RT) of the corrosion products generated in mineral water C (a = 21 days, b = 3 months and c = 6 months of corrosion).

Markov *et al.*[9] investigated the thermal decomposition mechanism of iron(III) hydroxide carbonate to α-Fe_2O_3 *via* α-FeOOH. The phase transformations were interpreted as a collective rearrangement of structural units due to structural similarities between iron(III) hydroxycarbonate, α-FeOOH and α-Fe_2O_3.

Murad and Taylor[10–11] prepared Fe(II)/Fe(III)-hydroxycarbonate green rust by adding Fe^{3+} as soluble nitrate or ferrihydrite to iron(III) carbonate in aqueous medium. These samples were subjected to oxidation and then analyzed by Mössbauer spectroscopy. It was concluded that Mössbauer spectroscopy is suitable for identification of intermediate phases, which can be formed in nature and in the course of corrosion processes in the presence of carbonates.

CONCLUSION

Our work strongly indicates that carbonates play an important role in the corrosion of steel in aqueous media, both during short (days), and long times (months) of corrosion. For short times of corrosion in the presence of a high content of carbonates, an amorphous phase and total absence of γ-FeOOH were observed. The possible presence of ferrihydrite in this amorphous phase cannot be excluded, taking into account the FT-IR and Mössbauer spectroscopic results. After long-lasting corrosion, the γ-FeOOH formation was strongly suppressed or totally eliminated by high contents of carbonates. In the very early stages of corrosion, carbonates can be structurally incorporated into the rust (hydroxycarbonates), while in the later stages they can modify the phase transformation by the mechanism of preferential adsorption. It appears, therefore, that there is a similarity between the corrosion process in the presence of carbonates and the phase transformations observed during the precipitation of iron hydrous oxides from iron salts in the presence of carbonates.

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SAŽETAK

Studij korozije čelika u vodovodnoj i mineralnoj vodi primjenom FT-IR i Mössbauerove spektroskopije

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Proučavan je utjecaj karbonata na proces korozije čelika u vodovodnoj i mineralnoj vodi tijekom šest mjeseci. Sve vode su bile za humanu upotrebu i različita kemijskog sastava. Uzorci hrđe analizirani su primjenom FT-IR i ^{57}Fe Mössbauerove spektroskopije, a neki su uzorci bili analizirani i rentgenskom difrakcijom. Pokazano je da koncentracija karbonata ima važnu ulogu u procesu korozije čelika u vodenom mediju, kako za kratka vremena (dani), tako i za duga vremena korozije (mjeseci). Pri kratkim vremenima i uz velik sadržaj karbonata hrđa je bila amorfna za rentgensku difrakciju. U tim uzorcima hrđe γ-FeOOH nije bio prisutan. Na osnovi rezultata FT-IR i Mössbauerove spektroskopije razmatrana je moguća prisutnost ferihidrita u amorfnoj hrđi. γ-FeOOH nije nađen u hrđi pri vrlo velikoj koncentraciji karbonata ni nakon šest mjeseci korozije. Praćeno je također stvaranje α-FeOOH i Fe_3O_4. Na osnovi postignutih rezultata zaključeno je da u početnom stupnju korozijskog procesa karbonati mogu biti strukturno ugrađeni u hrđi kao hidroksikarbonati, dok u kasnijoj fazi karbonati mogu modificirati fazni prijelaz mehanizmom specifične adsorpcije.