The Effect of Bicarbonate/Carbonate Ions on the Formation of Iron Rust

Musić, Svetozar; Nowik, Israel; Ristić, Mira; Orehovec, Zvonko; Popović, Stanko

Source / Izvornik: **Croatica Chemica Acta, 2004, 77, 141 - 151**

Journal article, Published version
Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

CROATICA CHEMICA ACTA
CCACAA **77** (1–2) 141–151 (2004)

ISSN-0011-1643
CCA-2911
Original Scientific Paper

The Effect of Bicarbonate/Carbonate Ions on the Formation of Iron Rust*

Svetozar Musić,[a] Israel Nowik,[b] Mira Ristić,[a,] Zvonko Orehovec,[a] and Stanko Popović[c]**

[a]*Ruđer Bošković Institute, P. O. Box 180, HR-10002 Zagreb, Croatia*

[b]*Racah Institute of Physics, The Hebrew University, IL-91094 Jerusalem, Israel*

[c]*Department of Physics, Faculty of Science, University of Zagreb, P. O. Box 331, HR-10002 Zagreb, Croatia*

RECEIVED MARCH 12, 2003; REVISED JULY 18, 2003; ACCEPTED AUGUST 12, 2003

The effect of bicarbonate/carbonate ions on the formation of iron rust in an aqueous medium has been investigated using XRD, Mössbauer and FT-IR spectroscopies. Corrosion of carbon steel in doubly distilled water was monitored as a reference process. Lepidocrocite as the dominant phase and magnetite were detected in rust generated in doubly distilled water in a period from three weeks to one year at room temperature. At 90 °C, magnetite and small amounts of hematite/goethite were formed in a period from one day to three weeks. In these rust samples, FT-IR spectroscopy detected a very small amount of lepidocrocite, which dissolves and thus occurs in overall phase transformations in rust. On the other hand, goethite was found as the dominant phase in rust formed in natural water containing a significant amount of bicarbonate ions, whereas magnetite and lepidocrocite were minor phases. In 0.005 M Na_2CO_3, goethite and magnetite were generated at room temperature, and after one month of corrosion, magnetite was present only in traces. Corrosion in 0.005 M Na_2CO_3 at 90 °C generated $Fe_2(OH)_2CO_3$ and magnetite. A certain analogy between the precipitation of Fe^{III}-oxyhydroxides from iron-salt solutions containing carbonates and the formation of goethite and lepidocrocite in rust was shown. Mössbauer spectroscopy showed that microstructural properties of the oxide phases also varied. Magnetite showed substoichiometry ($Fe_{3-x}O_4$) and in some cases it was difficult to distinguish between $Fe_{3-x}O_4$ and maghemite (γ-Fe_2O_3). Mössbauer spectra, recorded as a function of temperature, showed poor crystallinity and/or superparamagnetic behavior of goethite particles. Also, the Mössbauer spectra of the rust formed in carbonate solutions provided evidence of the amorphous fraction, which is in agreement with XRD. The difference between the results of the present investigation and those obtained by other researchers can be attributed to the electrochemical stimulation of steel (iron) surfaces in bicarbonate/carbonate aqueous media and the shorter corrosion times used in their experiments.

Key words
iron rust
carbon steel
bicarbonate/carbonate ions
lepidocrocite
goethite
hematite
magnetite
basic iron carbonate
Mössbauer
FT-IR
XRD

INTRODUCTION

Iron oxyhydroxides and oxides are typical constituents of rust, generated by the corrosion of steel surface in contact with water. All polymorphs of iron(III) oxyhydroxide, such as α-, β-, γ- and δ-FeOOH, as well as oxides such as Fe_3O_4, γ-Fe_2O_3 and α-Fe_2O_3 were found in iron rust. The phase composition of the rust depends on the physicochemical factors of the corrosion process, such as elec-

---

* Dedicated to Professor Nenad Trinajstić on the occasion of his 65th birthday.

** Author to whom correspondence should be addressed. (E-mail: ristic@rudjer.irb.hr) trolyte composition, pH, type of steel, temperature and time of rusting. $Fe(OH)_2$ produced at the surface of corroding steel undergoes complex phase transformations, starting from its first appearance up to the time of rust sampling. Many examples showed that $Fe(OH)_2$ is not always formed in the early stages of iron (steel) corrosion in an aqueous medium. Iron(III) oxyhydroxides, or mixtures of iron oxyhydroxides and oxides are formed instead. In specific cases, rust may contain a significant amount of amorphous fraction and/or very fine oxide particles. Investigations of phase composition of rust and the corresponding phase transformations in rust are very important in studying the mechanism of steel corrosion.

The present work is focused on the formation and phase composition of rust produced in the presence of bicarbonate/carbonate ions in an aqueous medium in order to obtain more data about steel rusting in laboratory conditions. However, the importance of this work is not merely academic. Bicarbonate/carbonate ions are present in natural, service and waste waters and therefore they may influence the corrosion process in practice (iron/steel facilities, pipelines, *etc.*). Mössbauer and FT-IR spectroscopies and X-ray powder diffraction were used in rust analysis. Mössbauer spectroscopy is a specifically useful technique in the investigation of corrosion processes, for example, the formation of atmospheric rust[1] and rust in a water medium,[2] corrosion inhibition,[3] metal/organic coatings,[4] and metal/metal coatings.[5] More details about the application of Mössbauer spectroscopy in corrosion science and engineering are given in a book by Ujihira and Nomura.[6]

EXPERIMENTAL

Carbon steel was chosen in the corrosion experiments because it has a suitable corrosion rate and yields a suitable amount of rust for Mössbauer measurements in transmittance mode. Rusting was monitored in natural water with a high content of bicarbonate ions, in solutions with dissolved sodium carbonate, as well as in doubly distilled water used as a reference corrosion medium. The aqueous medium used was not deaerated before contact with steel. However, when the carbon steel specimens were immersed in an aqueous medium, the vessels were hermetically closed to eliminate the influence of atmospheric oxygen during the corrosion experiments. The chemical composition of natural water is given in Table I.

TABLE I. Chemical composition of natural water(a)

Cation or anion	Concentration / mg dm^{-3}
Sodium (Na^+)	158.2
Potassium (K^+)	5.3
Lithium (Li^+)	(b)
Calcium (Ca^{2+})	86.7
Magnesium (Mg^{2+})	33.6
Strontium (Sr^{2+})	(b)
Iron (Fe^{2+})	(b)
Manganese (Mn^{2+})	0.2
Aluminium (Al^{3+})	(b)
Chloride (Cl^-)	60.1
Fluoride (F^-)	(b)
Bromide (Br^-)	(b)
Iodide (I^-)	(b)
Bicarbonate (HCO_3^-)	734.3
Sulfate (SO_4^{2-})	27.8

(a) The content of not dissociated H_2SiO_3 is 13.5 mg dm^{-3}.
(b) Concentrations are 0.1 mg dm^{-3} or less.

Alloying metals (copper is a typical example) may influence the steel corrosion rate. For this reason, elemental composition of the investigated steel was determined using the Proton Induced X-ray Emission (PIXE) facility at the Ruđer Bošković Institute, Zagreb. Protons of 3.0 MeV were used. PIXE analysis is a fast and non-destructive analytical technique, providing simultaneous determination of most elements ($Z > 13$) with detection limits in ppm range depending on the element analyzed. Since the penetration of protons into steel is ~35 microns, it can be supposed that PIXE analysis represents also the bulk composition of the material. The results of PIXE analysis for ten qualitatively known metals in carbon steel are given in Table II. The concentrations of metals measured in ppm were recalculated in w / %.

TABLE II. Analysis of ten metals on steel surface, as determined with PIXE(a)

Element	w / %
Fe	98.695
Mn	0.565
Cu	0.174
Ni	0.137
Zn	0.080
Ca	0.074
Ti	0.043
K	0.035
V	0.018
Cr	0.015
	Total amount 100 %

(a) The w/% of a particular metal is calculated against the total amount of the ten metals measured.

After the required corrosion time elapsed, rust was scraped, then analyzed by ^{57}Fe Mössbauer and FT-IR spectroscopies and X-ray powder diffraction.

^{57}Fe Mössbauer spectroscopic measurements were performed using a ^{57}Co/Rh source (50 mCi) and the conventional constant acceleration Mössbauer drive. Spectra of the samples were collected in transmittance mode at 300 and 90 K, and in specific cases also at 4.2 K. The spectra were analyzed by the least-square fit program, which allows a sum of magnetic sextets with the distribution of hyperfine fields

TABLE III. Phase composition of rust samples produced in doubly distilled water and natural water at rt, as found by XRD

Corrosion medium	Corrosion time	Phase composition (approx. molar fractions)	Estimated crystallite size of the dominant component / nm (a)
doubly distilled water	1 w	L + M (0.30)	25(7)
doubly distilled water	3 w	L + M (0.30)	30(8)
doubly distilled water	6 m	L + M (0.35)	30(7)
doubly distilled water	1 y	L + M (0.40)	35(8)
natural water	3 w	G + L (0.05) + M (?)	18(5)
natural water	4 m	G + M (0.25) + L (0.05)	15(4)
natural water	9 m	G + M (0.20) + L (0.10)	13(4)
natural water	1 y	G + L (0.30) + M (0.05)	10(3)

Key: w = week; m = month; y = year; L = lepidocrocite; G = goethite; M = magnetite.
(a) Numbers in brackets: estimated standard deviations of the last significant figure.

and quadrupole doublets subspectra. The analysis enabled a reduction in the hyperfine interaction parameters and the relative intensities of various subspectra.

FT-IR spectra were recorded at room temperature using a Perkin-Elmer spectrometer (model 2000). The FT-IR spectrometer was operated with the IRDM (IR Data Manager) program. Specimens were pressed into a spectroscopically pure KBr matrix.

X-ray powder diffraction measurements were performed at room temperature using a Philips counter diffractometer (model MPD 1880, Cu*K*α radiation, proportional counter, graphite monochromator).

RESULTS

Corrosion of Carbon Steel in Doubly Distilled Water at Room Temperature

Table III shows the composition of rust samples produced in doubly distilled water at room temperature (rt), as found by XRD. Rust formed after one week of corrosion in doubly distilled water contained lepidocrocite, as the dominant component, and magnetite. These two phases were also present in rust after one year of corrosion in the same corrosion medium; however, the fraction of magnetite was slightly increased. During that time the crystallite size of lepidocrocite increased from 25(7) to 35(8) nm. Crystallite size of the dominant component in rust samples was determined using the Scherrer method (Table III).

Figures 1 and 2 show the Mössbauer spectra of the corrosion products formed at room temperature in doubly distilled water after one week, three weeks and six months. The spectra were recorded at 300 K (Figure 1) and 90 K (Figure 2). At 300 K, the spectra showed superposition of a central quadrupole doublet and two sextets. The central quadrupole doublet present in the spectrum of the rust, formed after 1 week of corrosion, with parameters δ_{Fe} = 0.35 mm s^{-1} and Δ = 0.56 mm s^{-1}, can be assigned to lepidocrocite (γ-FeOOH). In reference literature,[7] the following Mössbauer parameters at 294 K are given for lepidocrocite: δ_{Fe} = 0.37 mm s^{-1} and Δ = 0.53 mm s^{-1}. Mössbauer parameters calculated for the two sextets M1 and M2 can be assigned to magnetite. In reference literature,[7] the values of 49.0 T for A-sites (tetrahedral) and 46.0 T for B-sites (octahedral) at 295 K are given for the two magnetite sextets. In the inverse spinel structure of magnetite, one-third of iron as Fe^{3+} ions occupy all the available A-sites, whereas one-third of iron as Fe^{3+} ions occupy one-half of B-sites, and one third of iron as Fe^{2+} ions occupy the other half of B-sites. On the basis of the intensity ratios recorded for M1 and M2 subspectra, it can be concluded that the magnetite phase in

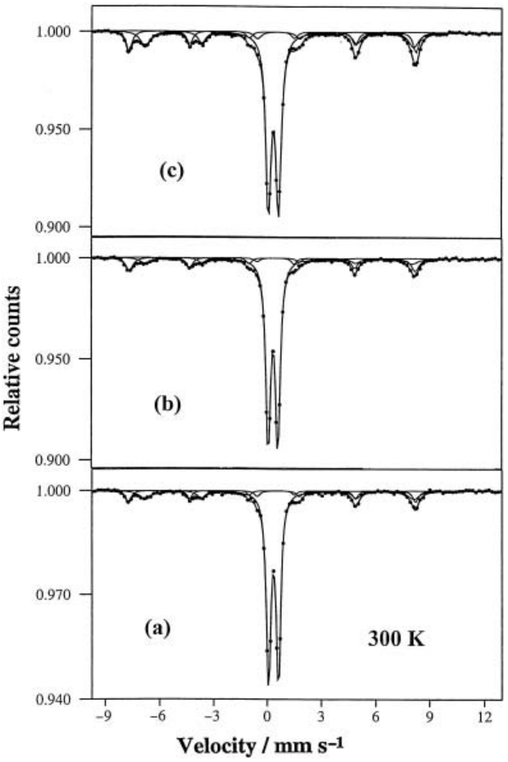

Figure 1. ^{57}Fe Mössbauer spectra at 300 K of rust formed after (a) one week, (b) three weeks and (c) six months of corrosion in doubly distilled water.

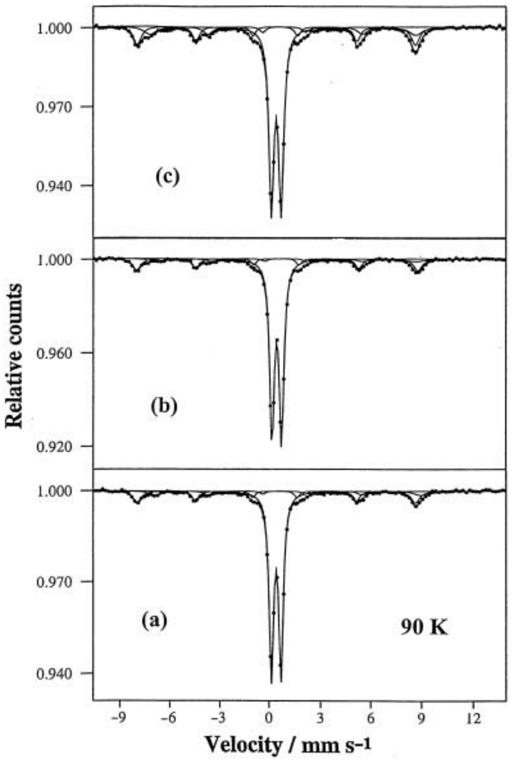

Figure 2. ^{57}Fe Mössbauer spectra at 90 K of rust formed after (a) one week, (b) three weeks and (c) six months of corrosion in doubly distilled water.

rust is substoichiometric ($Fe_{3-x}O_4$). The Mössbauer spectra recorded at 90 K confirmed the presence of a mixture of lepidocrocite and magnetite in rust. Integral intensities of the Mössbauer subspectra corresponding to lepidocrocite and magnetite are in agreement with the corresponding molar fractions (Table III) measured by XRD.

Figure 3 shows the FT-IR spectra of rust collected after one week, three weeks and six months of corrosion in doubly distilled water. The spectra indicate that lepidocrocite, characterized by its typical IR bands at 1021 and 745 cm^{-1}, is the dominant phase in these samples.

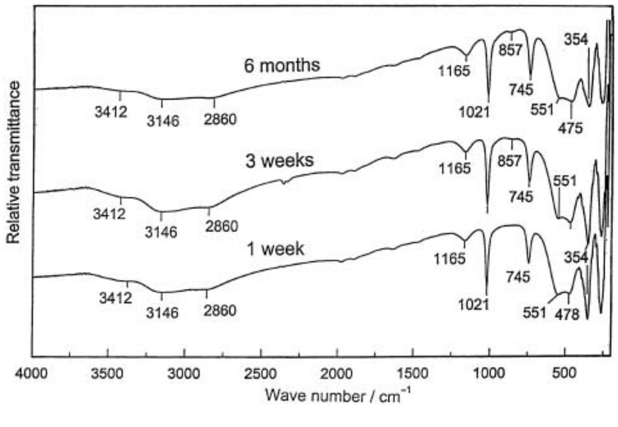

Figure 3. FT-IR spectra of rust formed after one week, three weeks and six months of corrosion in doubly distilled water.

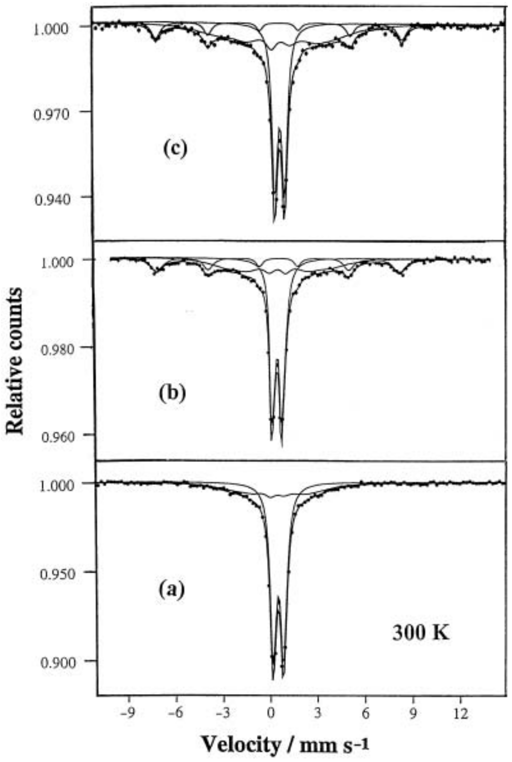

Figure 4. ^{57}Fe Mössbauer spectra at 300 K of rust formed after (a) three weeks, (b) four months and (c) nine months of corrosion in natural water.

On the basis of an IR band at 551 cm^{-1}, it could be concluded that a significant fraction of magnetite is also present in these samples. However, this band must be taken with caution when identifying magnetite only on the basis of FT-IR spectroscopy because hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) also exhibit their dominant IR bands in this spectral region.

Corrosion of Carbon Steel in Natural Water at rt

Corrosion of carbon steel in natural water at rt strongly influenced the phase composition of rust, as shown in Table III. XRD analysis showed goethite (α-FeOOH) as the dominant fraction in all rust samples collected during a period from 3 weeks to 1 year. Two additional phases, magnetite and lepidocrocite, were also present in all these samples; however, their fractions differed in dependence on the corrosion time. A decrease in the crystallite size of goethite from 18(5) to 10(3) nm during the corrosion between 3 weeks and 1 year was measured. It is realistic to suppose that bicarbonate ions present in significant quantities in natural water play a dominant role in the formation of rust.

Figures 4 and 5 show the Mössbauer spectra of corrosion products formed in natural water after 3 weeks, 4 and 9 months at room temperature. The spectra were recorded at 300 K (Figure 4) and 90 K (Figure 5). Mössbauer spectra in Figure 4 show superposition of a central

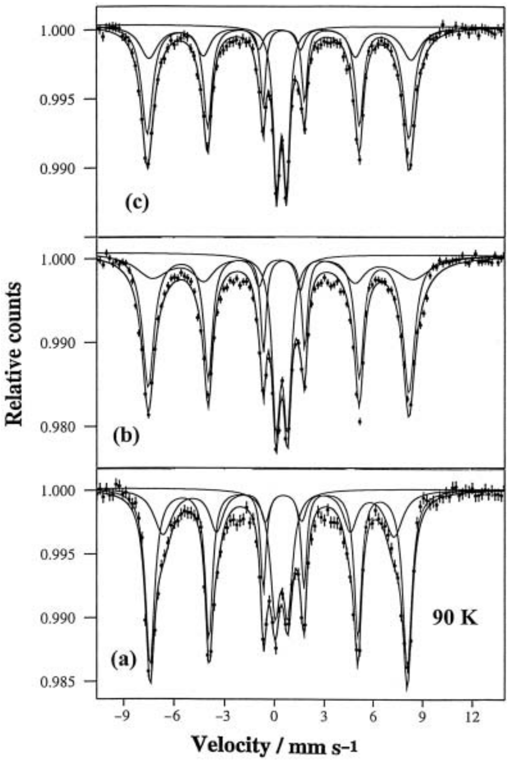

Figure 5. ^{57}Fe Mössbauer spectra at 90 K of rust formed after (a) three weeks, (b) four months and (c) nine months in natural water.

quadrupole doublet and a poorly defined sextet(s). For example, the spectrum at 300 K of rust isolated after three weeks consists of a central quadrupole doublet (δ_{Fe} = 0.45 mm s^{-1} and Δ = 0.66 mm s^{-1}) and a collapsing sextet (average HMF = 17.0 T). With the corrosion time prolonged up to one year, an additional sextet is observed. This additional sextet of small relative intensity with HMF = 48.4 or 48.5 T can be assigned to very substoichiometric $Fe_{3-x}O_4$ and/or maghemite. The HMF (average) of the collapsing sextet changed from 17.0 to 23.0 T, which can be ascribed to improved crystallinity of one portion of goethite particles with prolonged corrosion time. On the other hand, the second portion of superparamagnetic goethite particles contributes to the central quadrupole doublet. The splittings, Δ, of the central quadrupole doublet, from 0.66 to 0.62 mm s^{-1}, were calculated and these values were higher than those for lepidocrocite, thus indicating that some other factors also contribute to the central quadrupole doublet, such as superparamagnetic fraction and possibly an amorphous fraction. This conclusion is in line with the Mössbauer results obtained at 90 K (Figure 5 and Table IV), which showed a significant decrease in the integral intensity for the Q component from 69 to 16 % in rust collected after 3 weeks of corrosion. This effect is also observed for rust samples collected after 4 and 9 months of corrosion. The integral intensities for the Q component decreased from 49 to 21 % and from 51 to 21 % at 300 and 90 K.

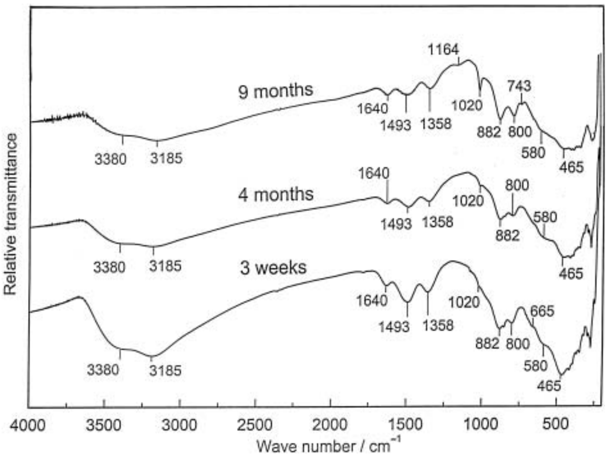

Figure 6. FT-IR spectra of rust formed after three weeks, four months and nine months of corrosion in natural water.

Influence of the chemistry of the corrosion medium was also observed in the FT-IR spectra of the rust samples, as shown in Figure 6. The presence of goethite can be monitored using two typical IR bands at 882 and 800 cm^{-1}. In this case, the two bands are very broadened due to tiny goethite crystallites. The presence of lepidocrocite can be monitored following the IR band at 1020 cm^{-1} up to 4 months of corrosion, whereas rust formed after 9 months of corrosion showed the bands typical of lepidocrocite at 1164, 1020 and 743 cm^{-1}. The shoulder at 580 cm^{-1} can be assigned to magnetite only if we know the phase composition of rust determined by other techniques. The IR bands at 3380 and 3185 cm^{-1} are due to the stretching modes of H_2O molecules and OH groups, whereas the band at 1640 cm^{-1} is due to bending vibrations of H_2O molecules. The pronounced IR bands at 1493 and 1358 cm^{-1} are due to the bicarbonates, which were originally present in natural water used in our experiments.

Corrosion of Carbon Steel in Doubly Distilled Water at 90 °C and in Aqueous Solutions of Na_2CO_3 at rt and 90 °C

Corrosion of carbon steel in doubly distilled water at 90 °C and in sodium carbonate solution at rt and 90 °C was also investigated. The results of XRD phase analysis of rust samples collected in these experiments are given in Table V. Corrosion in 0.005 M Na_2CO_3 solution at rt yielded goethite, as the dominant phase, and magnetite. The molar fraction of magnetite significantly decreased during a period from one week to one month. The corrosion rate in doubly distilled water was accelerated with the increase in temperature. After one day of corrosion at 90 °C rust contained a mixture of magnetite as the dominant phase and hematite, whereas after three days of corrosion a small amount of goethite also appeared. Magnetite remained the dominant phase in rust formed in doubly distilled water during a period from one day to three weeks. Corrosion of

TABLE IV. Hyperfine interaction parameters calculated for the rust samples produced in doubly distilled water and in natural water at rt

Corrosion medium	Corrosion time	Mössbauer experiment temperature / K	Spectral lines	Isomer shift / mm s^{-1}	Quadrupole splitting / mm s^{-1}	Hyperfine magnetic field / T	Intensity / %
doubly distilled water	1 w	300	Q	0.35	0.28		72
			M1	0.26	0	49.4	11
			M2	0.64	0	46.2	17
doubly distilled water	3 w	300	Q	0.35	0.27		73
			M1	0.27	0	49.1	16
			M2	0.63	0	45.8	11
doubly distilled water	6 m	300	Q	0.37	0.28		62
			M1	0.27	0	49.3	17
			M2	0.65	0	46.2	21
doubly distilled water	1 w	90	Q	0.43	0.29		73
			M1	0.34	0	51.6	18
			M2	0.9	0.1	49.2	9
doubly distilled water	3 w	90	Q	0.47	0.29		73
			M1	0.41	0	52.0	18
			M2	0.9	0	48.0	9
doubly distilled water	6 m	90	Q	0.44	0.29		62
			M1	0.34	0	51.5	22
			M2	0.8	–0.1	49.2	16
natural water	3 w	300	Q	0.45	0.33		69
			M	0.24	0	17.0av.	31
natural water	4 m	300	Q	0.39	0.32		49
			M1	0.37	0	48.4	19
			M2	0.34	0	20.5av.	32
natural water	9 m	300	Q	0.45	0.31		51
			M1	0.38	0	48.5	14
			M2	0.32	–0.16	23.0av.	45
natural water	3 w	90	Q	0.44	0.38		16
			M1	0.46	–1.2	48.0	56
			M2	0.45	–1.2	43.0	28
natural water	4 m	90	Q	0.46	0.34		21
			M1	0.46	–1.3	48.7	53
			M2	0.45	1.2	48.6	26
natural water	9 m	90	Q	0.44	0.31		21
			M1	0.44	–1.4	48.9	53
			M2	0.41	0.4	48.9	26

Key: isomer shifts are given relative to α-Fe at 300 K; quadrupole interaction is given by expression Eq = –eqQ/4; w = week; m = month; av. = average. Errors: intensity = 2 %; I.S. = 0.05 mm s^{-1}; Eq for paramagnetic site = 0.03 mm s^{-1}; Eq for magnetic site = 0.01 mm s^{-1}; HMF = 0.5 T.

TABLE V. Phase composition of rust samples, produced in doubly distilled water at 90 °C and in sodium carbonate solutions at rt as found by XRD

Corrosion medium	Corrosion time	Temperature / °C	Phase composition (approx. molar fraction)	Note
0.005 M Na_2CO_3	1 w	rt	G (0.7) + M (0.3)	BDL, A
0.005 M Na_2CO_3	3 w	rt	G (0.9) + M (0.1)	LBDL, A
0.005 M Na_2CO_3	1 m	rt	G + M (<< 0.1)	BDL, A
doubly distilled water	1 d	90	M (0.8) + H (0.2)	LBDL
doubly distilled water	3 d	90	M + H (< 0.1) + G (< 0.1)	LBDL
doubly distilled water	1 w	90	M + H (< 0.1) + G (< 0.1)	LBDL
doubly distilled water	3 w	90	M + G (< 0.1) + H (< 0.1)	LBDL
0.005 M Na_2CO_3	1 w	90	$Fe_2(OH)_2CO_3$ + M	BDL, A
0.005 M Na_2CO_3	3 w	90	$Fe_2(OH)_2CO_3$ + M	BDL, A

Key: d = day; w = week; m = month; G = goethite; M = magnetite; H = hematite; A = amorphous fraction; BDL = broadened diffraction lines; LBDL = little broadened diffraction lines.

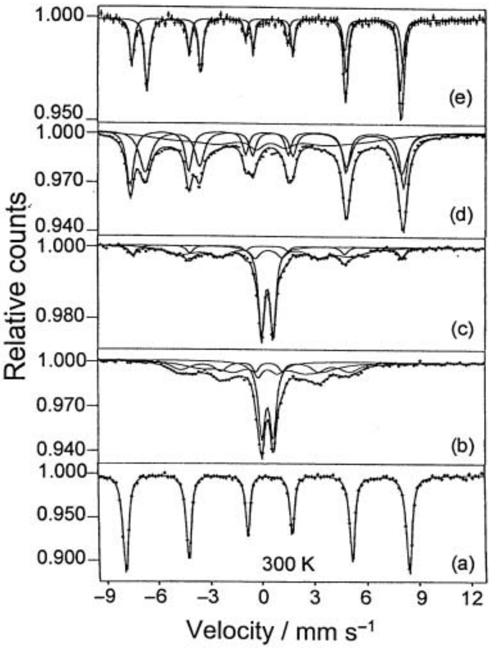

Figure 7. ^{57}Fe Mössbauer spectra at 300 K of (a) α-Fe_2O_3, (b) rust formed in 0.005 M Na_2CO_3 at rt in one month, (c) rust formed in 0.005 M Na_2CO_3 at rt in one week, (d) rust formed in doubly distilled water at 90 °C in 3 weeks, and (e) Fe_3O_4. α-Fe_2O_3 and Fe_3O_4 used as reference materials.

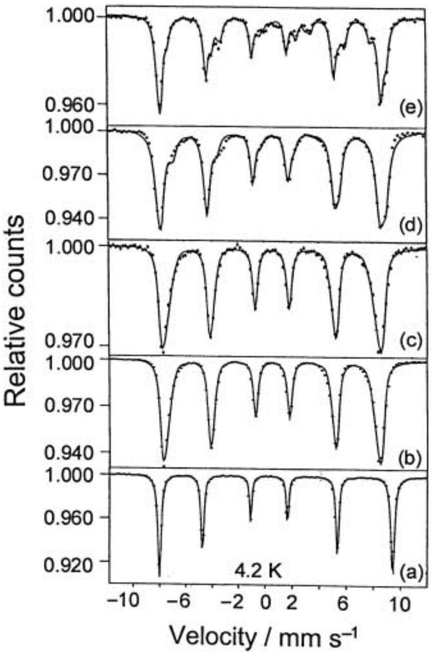

Figure 9. ^{57}Fe Mössbauer spectra at 4.2 K of (a) α-Fe_2O_3, (b) rust formed in 0.005 M Na_2CO_3 at rt in one month, (c) rust formed in 0.005 Na_2CO_3 at rt in one week, (d) rust formed in doubly distilled water at 90 °C in three weeks and (e) Fe_3O_4. α-Fe_2O_3 and Fe_3O_4 used and reference materials.

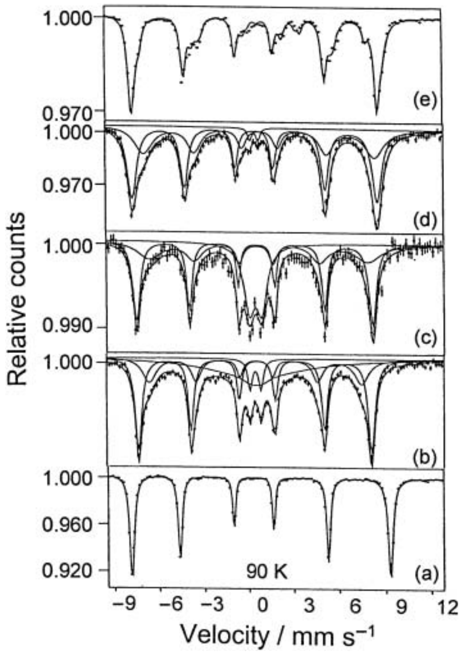

Figure 8. ^{57}Fe Mössbauer spectra at 90 K of (a) α-Fe_2O_3, (b) rust formed in 0.005 M Na_2CO_3 at rt in one month, (c) rust formed in 0.005 M Na_2CO_3 at rt in one week, (d) rust formed in doubly distilled water at 90 °C in three weeks, and (e) Fe_3O_4. α-Fe_2O_3 and Fe_3O_4 are used as reference materials

carbon steel in 0.005 M Na_2CO_3 solution at 90 °C yielded a mixture of basic iron carbonate and magnetite during a period from one to three weeks. The XRD pattern of basic iron carbonate showed data similar to those of green rust defined in Powder Diffraction File, cards No. 46-0098 for $Fe_6(OH)_{12}CO_3$ and No. 50-1380 for $Fe_6(OH)_{12}CO_3 \cdot 2H_2O$.[8] A good agreement of our XRD pattern was found with the data contained in card No. 33-0650 for $Fe_2(OH)_2CO_3$.[8]

Figures 7, 8 and 9 show Mössbauer spectra of selected rust samples produced in 0.005 M Na_2CO_3 solutions at rt for one week and one month, as well as in doubly distilled water at 90 °C for 3 weeks. The reference spectra of α-Fe_2O_3 and Fe_3O_4 were also measured are shown for comparison. These spectra were measured at 300 K (Figure 7), 90 K (Figure 8) and 4.2 K (Figure 9). Hyperfine interaction parameters calculated for these selected rust samples are given in Table VI.

Mössbauer spectrum at 300 K of rust generated in 0.005 M Na_2CO_3 solution at rt for one week (Figure 7c) shows superposition of a strong central quadrupole doublet and two sextets, M1 and M2, of weak relative intensities. The splitting of the central quadrupole doublet, $\Delta = 0.68$ cm^{-1}, can be assigned to the presence of amorphous and superparamagnetic particles. Hyperfine magnetic splitting component M1 can be assigned to very substoichiometric $Fe_{3-x}O_4$ and/or γ-Fe_2O_3, whereas sextet M2 can be assigned to superparamagnetic and/or poor crystalline goethite. At 90 K (Figure 8c), the integral intensity of the central quadrupole doublet is significantly decreased (from 42 to 25 %), whereas at 4.2 K (Figure 9c) this doublet is not present. The average hyperfine field of 522 kOe is measured at 4.2 K, and the shape of this

TABLE VI. Hyperfine interaction parameters calculated for the selected rust samples produced in 0.005 M Na_2CO_3 and in doubly distilled water

Corrosion medium	Corrosion time	Corrosion temperature	Mössbauer experiments temp. / K	Spectral lines	Isomer shift mm s^{-1}	Quadrupole interaction mm s^{-1}	Hyperfine magnetic field / T	Intensity %
0.005 M Na_2CO_3	1 w	rt	4.2	M	0.48	–0.07	52.2	100
			90	M1	0.47	–0.10	48.4	44
				M2	0.62	0.05	44.8	31
				Q	0.49	0.42		25
			300	M1	0.32	0	47.9	13
				M2	0.35	–0.1	30.2	45
				Q	0.36	0.34		42
0.005 M Na_2CO_3	1 m	rt	4.2	M	0.48	–0.08	49.9	100
			300	M1	0.21	–0.18	21.5	39
				M2	0.35	–0.12	30.2	27
				Q	0.37	0.34		34
doubly distilled water	3 w	90 °C	4.2	M1	0.41	–0.04	50.7	55
				M2	0.50	–0.04	52.8	29
				M3	0.96	0	49.0	16
			90	M1	0.44	–0.03	50.2	57
				M2	0.78	–0.06	47.2	41
				Q	0.47	0.28		2
			300	M1	0.64	0	45.5	34
				M2	0.29	–0.02	48.6	29
				M3	0.42	–0.12	32.8	37

Key: w = week; m = month; Isomer shifts are given relative to α-Fe at 300 K; Quadrupole interaction is given by expression $Eq = -eqQ/4$; The error bars at the isomer shift, quadrupole interaction and magnetic hyperfine field values are 0.05 mm s^{-1}, 0.05 mm s^{-1} and 5 kOe, respectively.

spectrum actually shows the distribution of hyperfine magnetic interactions.

Mössbauer spectrum at 300 K of rust generated in 0.005 M Na_2CO_3 solution at rt for 1 month (Figure 7b) shows superposition of a strong central quadrupole doublet and a collapsing hyperfine magnetic splitting. This spectrum is fitted for one quadrupole doublet ($\Delta = 0.68$ mm s^{-1}) and two collapsing sextets M1 (HMF = 21.5 T) and M2 (HMF = 30.2 T). At 90 K, the Mossbauer spectrum (Figure 8b) was considered a superposition of the central quadrupole doublet and three sextets, M1 (47.8 T), M2 (43.6 T) and M3 (15.0 T; smeared subspectrum). The spectrum recorded at 4.2 K (Figure 9b) showed hyperfine magnetic splitting with the parameters $\delta_{Fe} = 0.48$ mm s^{-1}, $\Delta Eq = -0.16$ mm s^{-1} and HMF = 49.9 T. These parameters can be assigned to goethite.

The Mössbauer spectrum at 300 K of rust generated in doubly distilled water at 90 °C for 3 weeks (Figure 7d) was fitted for three sextets. The sextets M1 and M2 can be assigned to substoichiometric $Fe_{3-x}O_4$. In the fitting procedure, the contribution of the poorly shaped sextet M3 with HMF = 32.8 T was also taken into account. The spectrum recorded at 4.2 K (Figure 9d) was fitted for three sextets, M1, M2 and M3, and the corresponding HMF values of 50.7, 52.8 and 49.0 T were calculated for these sextets. For the Fe_3O_4 reference spectrum (Figure 9e), the following HMF values at 4.2 K were calculated: M1 = 51.0 T, M2 = 52.9 T and M3 = 47.0 T. Differences in the integral intensities and increased M3 values (49.0 T) calculated for rust in relation to the reference Fe_3O_4 can be explained by the presence of minor phases, hematite and Fe^{III} oxyhydroxide, in that rust sample.

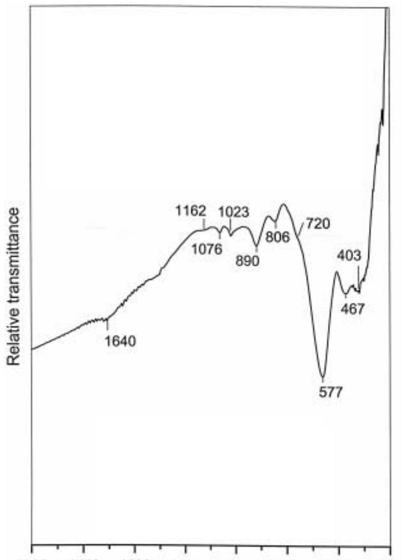

Fig 10. FT-IR spectrum of rust formed in doubly distilled water at 90 °C in 3 weeks.

FT-IR spectra of rust samples generated in doubly distilled water at 90 °C in a period from one day to three weeks showed a weak intensity band at 1023 cm^{-1}, which can be assigned to lepidocrocite. The FT-IR spectrum, recorded for rust formed after three weeks of corrosion, illustrates this situation (Figure 10). This spectrum shows IR bands at 890 and 806 cm^{-1} due to the presence of goethite, whereas the bands at 1162 and 1023 cm^{-1} can be assigned to lepidocrocite. However, one of the prominent IR bands of lepidocrocite at ~745 cm^{-1} is masked by a very strong band centered at 577 cm^{-1}. The IR band at 403 cm^{-1} can be assigned to magnetite. The IR band at 467 cm^{-1} may appear as a result of magnetite substoichiometry. However, the contributions to the IR bands at 467 and 577 cm^{-1} may also be due to associated hematite. The IR band at 1640 cm^{-1} is due to the bending vibration of H_2O molecules. Interpretation of the measurements performed with this sample gives a nice example of how the complementary techniques such as XRD, Mössbauer and FT-IR spectroscopies can be used in rust analysis.

DISCUSSION

In the present investigation, the corrosion rate observed for doubly distilled water medium was high. Rapid delamination of outer layers was observed. However, a black and compact layer of magnetite was formed in the vicinity of the steel surface.

Experimental results of the present investigation clearly showed differences between the corrosion processes in doubly distilled water and bicarbonate/carbonate solutions. The effect of temperature on the phase composition of rust was also markedly strong. In general, corrosion of steel (iron) in pure water starts with the oxidation of Fe^0 to Fe^{2+}, which is usually present in the solution as a $FeOH^+$ complex. In the next step the $FeOH^+$ complex is oxidized to Fe^{3+}, which further forms Fe^{III} hydroxy complexes and/or Fe^{III} hydroxy polymers as precursors of the γ-FeOOH precipitate.[9,10] Fe^{3+} ions can also be generated by dissolution of an unstable hydrous oxide phase, for example γ-FeOOH.

Formation of Fe_3O_4 as the corrosion product in pure water is often described by the following reaction:

$$3\ Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2 \qquad (1)$$

However, if corrosion of steel takes place in slightly acidic solutions, it is more likely that the $Fe(OH)^+$ complex and Fe^{III} hydroxy complexes or amorphous iron(III) hydroxide will be involved in the formation of Fe_3O_4. The reductive dissolution of γ-FeOOH may generate Fe^{2+} and Fe^{3+} ions in the form of hydroxy complexes, which can be precursors of Fe_3O_4. The formation of Fe_3O_4 from γ-FeOOH during the corrosion process in an aqueous medium can be illustrated[11,12] by the following chemical reactions:

$$\gamma\text{-FeOOH} + H^+ + e^- \rightarrow Fe(OH)_2, \qquad (2)$$

$$2\ \gamma\text{-FeOOH} + Fe(OH)_2 \rightarrow Fe_3O_4 + 2\ H_2O, \qquad (3)$$

or

$$3\ \gamma\text{-FeOOH} + H^+ + e^- \rightarrow Fe_3O_4 + 2\ H_2O. \qquad (4)$$

Our corrosion experiments in doubly distilled water at rt during a period from one week to one year showed the formation of lepidocrocite as the dominant phase and magnetite in rust, whereas with prolonged corrosion time a slight increase in the magnetite fraction was observed. With an increase in temperature, the corrosion rate in doubly distilled water was significantly increased. The phase composition of rust was different compared to that generated at rt. Magnetite was the dominant phase (molar fraction > 0.8) in rust samples in a period from one day to three weeks. Hematite and goethite were found in small amounts. FT-IR spectroscopy showed the presence of lepidocrocite traces in these rust samples. Lepidocrocite dissolves and thus takes place in the phase transformation of rust.

A strong influence of the chemical composition of natural water on the phase composition of rust was also observed and this effect can be attributed to the bicarbonate ions present in natural water and, to a much smaller extent, to the presence of other anions and cations. In the case of natural water, rust generated at rt contained goethite as the dominant phase and lepidocrocite and magnetite as minor phases. Corrosion in 0.005 M Na_2CO_3 at rt yielded goethite as the dominant phase and magnetite in rust, whereas lepidocrocite was not found. At 90 °C, basic iron carbonate, $Fe_2(OH)_2CO_3$, and magnetite were present in rust. It is evident that bicarbonates, as well as carbonates, play a prominent role in corrosion in an aqueous medium, influencing the phase composition of corrosion products as well as the corrosion rate. In a previous work,[13] we observed that the γ-FeOOH formation was strongly suppressed or totally eliminated by high amounts of bicarbonate ions. At a very early stage of corrosion carbonates may be structurally incorporated into rust (hydroxycarbonates), whereas over a longer time of corrosion they can modify phase transformations in rust by mechanisms of preferential adsorption. There is certain analogy between the precipitation of iron^{III} oxyhydroxides from solutions containing carbonates[14–16] and the formation of α-FeOOH and γ-FeOOH during the corrosion process in solutions containing carbonates. The authors of these works[14–16] suggested that carbonate anions directed the polymerization of the double bonds of $FeO_3(OH)_3$ octahedra common to both compounds towards a corner-sharing arrangement, and thereby to α-FeOOH, whereas chlorides permitted edge-sharing as in γ-FeOOH. At 90 °C, the formation of basic iron carbonate $Fe_2(OH)_2CO_3$ is favored, as shown in the present work.

The effects of bicarbonate/carbonate ions on corrosion of steel (iron) were also investigated by other researchers. For example, the formation of corrosion layers on low-alloy carbon steels in $CO_2(g)$ saturated solutions was investigated by Mössbauer spectroscopy.[17] The corrosion process was electrochemically stimulated. Siderite ($FeCO_3$), faulted cementite (Fe_3C^*) and Fe–C* were the phases detected in corrosion products. Formation of $FeCO_3$ and Fe–C* phases was attributed to the presence of ~1 % Cr in steel. On the other hand, Legrand *et al.*,[18,19] investigating the oxidation of iron in bicarbonate/carbonate solutions, observed the formation of siderite, am-FeOOH (am = amorphous) and GR1(CO_3), (GR1 = green rust formed in the presence of carbonate anions). Bonin *et al.*[20] used Raman spectroscopy to investigate the formation of carbonate-containing green rust on iron electrodes in solutions simulating groundwater. Differences between the results of the present investigation and those obtained by other researchers[17–20] can be attributed to the arrangement of their experiments. In their experiments[17–20] they used electrochemical stimulation of steel (iron) during the corrosion process in an aqueous medium containing bicarbonate/carbonate ions. Their experimental arrangements made it possible to investigate shorter times of corrosion of steel (iron).

REFERENCES

1. H. Leidheiser, Jr. and S. Musić, *Corrosion Sci.* **22** (1982) 1089–1096.
2. H. Leidheiser, Jr., S. Musić, and J. F. McIntyre, *Corrosion Sci.* **24** (1984) 197–208.
3. H. Leidheiser, Jr., G. W. Simmons, S. Nagy, and S. Musić, *J. Electrochem. Soc.* **129** (1982) 1658–1662.
4. H. Leidheiser, Jr., S. Musić, and G. W. Simmons, *Nature* **297** (1982) 667–669.
5. H. Leidheiser, Jr., S. Musić, A. Vértes, H. Herman, and R. A. Zatorski, *J. Elecrochem. Soc.* **131** (1984) 1348–1349.
6. Y. Ujihira and K. Nomura, *Analyses of Corrosion Products of Steels by Conversion Electron Mössbauer Spectrometry*, Research Signpost, 1996, Trivandrum 695 008, India.
7. E. Murad and J. H. Johnston, in: Gary J. Long (Ed.) *Iron Oxides and Oxyhydroxides in Mössbauer Spectroscopy Applied to Inorganic Chemistry,* Chapter 12, Vol. 2, Plenum Publishing Corporation, 1987, p. 507.
8. Powder Diffraction File, International Center for Diffraction Data, Newtown Square, 19073–3273, USA, Pa.
9. J. Kassim, T. Baird, and J. F. Fryer, *Corrosion. Sci.* **22** (1982) 147–158.
10. L. May, *Latvijas PSR Zinatnu Akademijas Vestis,* 1983, pp. 131–139.
11. M. Stratmann, K. Bonnenkamp, and H.-J. Engell, *Corrosion Sci.* **23** (1983) 969–985.
12. A. Kuch, *Corrosion Sci.* **28** (1988) 221–231.
13. S. Musić, Đ. Dragčević, I. Czakó-Nagy, and S. Popović, *Croat. Chem. Acta* **70** (1997) 689–702.
14. L. Carlson and U. Schwertmann, *Clay Miner.* **25** (1990) 65–71.
15. E. Murad and R. M. Taylor, *Clay Miner.* **19** (1984) 77–83.
16. E. Murad and R. M. Taylor, *The Oxidation of Hydroxycarbonate Green Rust,* in: G. J. Long and J. G. Stevens (Eds.) *Industrial Applications of the Mössbauer Effect,* Plenum Publ. Corp., 1986, pp. 585–593.
17. I. Raspini, E. Chung, and C. Saragovi, *Corrosion Sci.* **56** (2000) 832–838.
18. L. Legrand, S. Savoye, A. Chausse, and R. Messina, *Electrochim. Acta* **46** (2000) 111–117.
19. L. Legrand, M. Abdelmoula, A. Géhin, A. Chausse, and J.-M. R. Genin, *Electrochim. Acta* **46** (2001) 1815–1822.
20. P. M. L. Bonin, M. S. Odziemkowski, E. J. Reardon, and R. W. Gillham, *J. Solution Chem.* **29** (2001) 1061–1074.

SAŽETAK

Utjecaj iona HCO_3^-/CO_3^{2-} na nastajanje željezove hrđe

Svetozar Musić, Israel Nowik, Mira Ristić, Zvonko Orehovec i Stanko Popović

Utjecaj iona HCO_3^-/CO_3^{2-} na nastajanje željezove hrđe u vodenoj otopini istraživan je primjenom rentgenske difrakcije, Mössbauerove i FT-IR spektroskopije. Nastajanje željezove hrđe u dva puta destiliranoj vodi motreno je kao referentni proces. Korozijom ugljikova čelika u dva puta destiliranoj vodi pri sobnoj temperaturi, u vremenu od tri tjedna do jedne godine, nastaje lepidokrokit kao dominantna faza te magnetit. Korozijski produkti dobiveni u vremenu od jednoga do tri tjedna pri 90 °C sadrže magnetit i male udjele hematita i/ili getita. FT-IR spektroskopija je potvrdila prisutnost manje količine lepidokrokita u ovim uzorcima. Na temelju ovoga može se zaključiti da korozijom ugljikova čelika u dva puta destiliranoj vodi nastaje lepidokrokit koji se zatim otapa i na taj način sudjeluje u faznim prijelazima u hrđi. Getit je dominantna faza u hrđi nastaloj korozijom ugljikova čelika u prirodnoj vodi koja sadrži značajnu količinu bikarbonatnih iona, dok se magnetit i lepidokrokit javljaju kao dodatne faze. Getit i magnetit su produkti korozije ugljikova čelika u vodenoj otopini

0.005 M Na_2CO_3 pri sobnoj temperaturi, dok je magnetit prisutan u tragovima nakon jednoga mjeseca korozije. Korozija u vodenoj otopini 0.005 M Na_2CO_3 pri 90 °C uzrokovala je nastajanje $Fe_2(OH)_2CO_3$ i magnetita. U radu je pokazano da postoji određena analogija između procesa taloženja Fe^{III} oksihidroksida u otopinama Fe^{III} soli koje su sadržavale karbonatne ione te nastajanje getita i lepidokrokita u hrđi. Mössbauerova spektroskopija ukazala je na promjenu mikrostrukture oksidnih faza u uzorcima hrđe. Uzorci hrđe sadržavali su podstehiometrijski magnetit ($Fe_{3-x}O_4$), a u nekim uzorcima bilo je teško razlikovati $Fe_{3-x}O_4$ od maghemita (γ-Fe_2O_3). Mössbauerovi spektri hrđe snimljeni pri različitim temperaturama pokazali su slabu kristalnost i/ili superparamagnetsko ponašanje čestica getita. Isto tako, Mössbauerovi spektri hrđe nastale u karbonatnim otopinama ukazali su na prisutnost amorfne frakcije, što je u suglasnosti s rezultatima rentgenske difrakcije. Rezultati dobiveni u ovom radu razlikuju se u odnosu na podatke dostupne u literaturi, a koji opisuju utjecaj iona HCO_3^-/CO_3^{2-} na koroziju elektrokemijski stimulirana čelika (željeza). Razlog tome je razlika u načinu izvođenja eksperimenta korozije željeza (čelika).