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Formation of Rust During the Corrosion of Steel in Water and $(\text{NH}_4)_2\text{SO}_4$ Solutions. Part II*

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Chemical and structural properties of the rust formed by corrosion of steel in water and $(\text{NH}_4)_2\text{SO}_4$ solutions at 20 °C for time periods up to 6 months were investigated by X-ray diffraction, Fourier transform IR spectroscopy and ^{57}Fe Mössbauer spectroscopy. Three oxide phases, $\gamma\text{-FeOOH}$ (lepidocrocite), Fe_3O_4 (magnetite) and $\alpha\text{-FeOOH}$ (goethite) were detected in the rust samples. The distribution of these phases in the rust was dependent on the time of corrosion and the concentration of $(\text{NH}_4)_2\text{SO}_4$. ^{57}Fe Mössbauer spectroscopy indicated the substoichiometric character of magnetite ($\text{Fe}_{3-x}\text{O}_4$). Magnetite was not observed in the rust generated in 2M $(\text{NH}_4)_2\text{SO}_4$ solution. Fourier transform IR spectroscopy was particularly useful in the detection of very small amounts of goethite and lepidocrocite in the rust. The strong influence of $(\text{NH}_4)_2\text{SO}_4$ electrolyte on the corrosion of steel in aqueous medium was explained as a cumulative effect of two aggressive ions, NH_4^+ and SO_4^{2-} .

INTRODUCTION

Corrosion of steel surfaces depends on the nature and concentration of inorganic electrolytes in aqueous media. Atmospheric corrosion of steel is also known to depend on the type of inorganic pollutant: for instance, it is accelerated² in the presence of SO_2 pollutant. The akaganeite ($\beta\text{-FeOOH}$) phase can be found in the rust generated in a marine atmosphere. It is assumed that chlorides play an important

* Part I, Ref. 1

role in the formation of akaganeite. The phase composition of rust also depends on other corrosion parameters, such as temperature, pH, oxygen content, the nature of steel, etc. The crystallinity, stoichiometry and particle size of the oxide components, as well as limitations of the experimental techniques used are the factors that must be taken into account in the chemical and structural analysis of rust. X-ray diffraction has been traditionally used in the phase analysis of rust generated in aqueous medium or in atmospheric corrosion processes. Spectroscopic techniques, such as Mössbauer, Auger, ESCA, IR and Raman, also found an important application in analyses of the chemical and structural properties of rust.

In a previous work,¹ we investigated the early stages of the formation of rust by corrosion of steel in water and $(\text{NH}_4)_2\text{SO}_4$ solutions using X-ray diffraction and FT-IR spectroscopy. The present investigation was undertaken to obtain further information about the effect of $(\text{NH}_4)_2\text{SO}_4$ electrolyte on the corrosion of steel in aqueous medium. The time of corrosion was extended up to six months. Mössbauer spectroscopy was applied as a complementary technique to X-ray diffraction and FT-IR spectroscopy. The application of Mössbauer spectroscopy in corrosion science has already been discussed in the literature.³⁻⁹

The $(\text{NH}_4)_2\text{SO}_4$ electrolyte was chosen (a) because NH_4^+ and SO_4^{2-} ions belong to the group of aggressive ions with respect to corrosion and (b) because there are certain similarities between the formation of rust in the presence of SO_4^{2-} ions and the precipitation of oxide phases from FeSO_4 solutions.¹⁰⁻¹³ Also, NH_4^+ ions are characterized by complexing activity, which is not the case of Na^+ ions in corrosion processes in aqueous media. Ammonium sulphate can be present in aerosol particles in the atmosphere¹⁴ and, due to this fact, it can influence the atmospheric corrosion of metals.

EXPERIMENTAL

Ammonium sulphate, p. a., obtained from Kemika (Zagreb), doubly distilled water, and cold rolled low carbon steel JUS-ČO146 ($C_{\text{max}} = 0,12\%$, $Mn_{\text{max}} = 0.50\%$, $P_{\text{max}} = 0.04\%$, $S_{\text{max}} = 0.04\%$) were used. A commercial steel foil was cut into 60 mm x 100 mm coupons. These coupons were polished and cleaned using a standard procedure. The experiments were carried out at 20 °C in glass beakers sealed with polyethylene foils to prevent direct contact of the corrosion system with air oxygen. The steel coupons were completely immersed into the aqueous medium. The experimental conditions for the preparation of rust samples S_1 to S_{20} are given in Table I. The corrosion products were cleaned from mother liquor with doubly distilled water. A Sorvall RC2-B ultraspeed centrifuge (up to 20 000 r.p.m.) was used for separation of corrosion products from the aqueous phase.

pH-measurements were performed with a pHM-26 instrument and the corresponding electrodes produced by Radiometer.

X-ray powder diffraction measurements were performed at room temperature using a Philips diffractometer with a proportional counter and monochromatized Cu $K\alpha$ radiation (graphite monochromator).

FT-IR spectra were recorded at room temperature using a spectrometer produced by Perkin-Elmer (model 2000). This spectrometer was coupled with a personal computer loaded with the IR Data Manager (IRDM) program. Rust samples were pressed into disc using spectroscopically pure KBr.

⁵⁷Fe Mössbauer spectra were recorded at room temperature with a WISSEL spectrometer. Mathematical deconvolution of the Mössbauer spectra was performed using the SIRIUS program.

TABLE I
Experimental conditions for the preparation of the corrosion products
of steel at 20 °C

Sample	Solution	Time of corrosion ^(*)	pH of mother liquor
S ₁	H ₂ O	1 d	5.50
S ₂	H ₂ O	3 d	5.35
S ₃	H ₂ O	7 d	5.50
S ₄	H ₂ O	21 d	5.40
S ₅	H ₂ O	3 m	5.90
S ₆	0.1 M (NH ₄) ₂ SO ₄	1 d	7.15
S ₇	0.1 M (NH ₄) ₂ SO ₄	3 d	7.45
S ₈	0.1 M (NH ₄) ₂ SO ₄	7 d	7.35
S ₉	0.1 M (NH ₄) ₂ SO ₄	21 d	7.40
S ₁₀	0.1 M (NH ₄) ₂ SO ₄	3 m	7.70
S ₁₁	2 M (NH ₄) ₂ SO ₄	1 d	7.85
S ₁₂	2 M (NH ₄) ₂ SO ₄	3 d	7.90
S ₁₃	2 M (NH ₄) ₂ SO ₄	7 d	8.25
S ₁₄	2 M (NH ₄) ₂ SO ₄	21 d	8.05
S ₁₅	2 M (NH ₄) ₂ SO ₄	3 m	6.80
S ₁₆	H ₂ O	6 m	8.00
S ₁₇	0.05 M (NH ₄) ₂ SO ₄	6 m	7.65
S ₁₈	0.1 M (NH ₄) ₂ SO ₄	6 m	7.50
S ₁₉	0.5 M (NH ₄) ₂ SO ₄	6 m	7.50
S ₂₀	2 M (NH ₄) ₂ SO ₄	6 m	6.50

(*)d = day, m = month

RESULTS AND DISCUSSION

Table II shows the phase composition of corrosion products (samples S₁ to S₂₀), as determined by X-ray diffraction. Lepidocrocite was the dominant component in samples S₁ to S₅, which were generated by corrosion of steel in doubly distilled water over a period up to 3 months. Magnetite was an additional component; its relative content increased from sample S₁ to sample S₅. In sample S₅, a small amount of goethite was detected by FT-IR spectroscopy.

After a period of 7 days, corrosion of steel in 0.1 M (NH₄)₂SO₄ solution generated lepidocrocite as a single phase (samples S₆ to S₈), and after 21 days magnetite was detected as an additional component in sample S₉. After 3 months of corrosion, magnetite, lepidocrocite and goethite were present in sample S₁₀.

Corrosion of steel in 2 M (NH₄)₂SO₄ solution, for up to 3 months, generated lepidocrocite (samples S₁₁ to S₁₅), as shown by X-ray diffraction. The XRD lines of lepidocrocite, observed for samples S₁₁ to S₁₄ were broadened. The FT-IR spectra of samples S₁₁ to S₁₅ confirmed the presence of lepidocrocite as a single phase, while a small amount of goethite was detected in sample S₁₅.

A strong effect of (NH₄)₂SO₄ concentration on the phase composition of rust was also observed after 6 months of steel corrosion (Table II, samples S₁₆ to S₂₀). The characteristic results, obtained by FT-IR spectroscopy for samples S₁₆ to S₂₀, are

TABLE II
The results of XRD phase analysis of corrosion products

Sample	Phase composition (approximate molar fraction)	Sample	Phase composition (approximate molar fraction)
S ₁	$\gamma\text{-FeOOH} + \text{Fe}_3\text{O}_4$ (1/8)	S ₁₁	$\gamma\text{-FeOOH}^{(**)}$
S ₂	$\gamma\text{-FeOOH} + \text{Fe}_3\text{O}_4$ (1/6)	S ₁₂	$\gamma\text{-FeOOH}^{(**)}$
S ₃	$\gamma\text{-FeOOH} + \text{Fe}_3\text{O}_4$ (1/5)	S ₁₃	$\gamma\text{-FeOOH}^{(**)}$
S ₄	$\gamma\text{-FeOOH} + \text{Fe}_3\text{O}_4$ (1/4)	S ₁₄	$\gamma\text{-FeOOH}^{(**)}$
S ₅ ^(*)	$\gamma\text{-FeOOH} + \text{Fe}_3\text{O}_4$ (1/4)	S ₁₅ ^(*)	$\gamma\text{-FeOOH}$
S ₆	$\gamma\text{-FeOOH}$	S ₁₆	$\gamma\text{-FeOOH} + \text{Fe}_3\text{O}_4 + \alpha\text{-FeOOH}$ (dominant)
S ₇	$\gamma\text{-FeOOH}$	S ₁₇	$\text{Fe}_3\text{O}_4 + \alpha\text{-FeOOH} + \gamma\text{-FeOOH}$ (small) (very small)
S ₈	$\gamma\text{-FeOOH}$	S ₁₈	$\text{Fe}_3\text{O}_4 + \alpha\text{-FeOOH} + \gamma\text{-FeOOH}$
S ₉	$\gamma\text{-FeOOH} + \text{Fe}_3\text{O}_4$ (1/8)	S ₁₉	$\alpha\text{-FeOOH} + \gamma\text{-FeOOH} + \text{Fe}_3\text{O}_4$
S ₁₀	$\text{Fe}_3\text{O}_4 + \gamma\text{-FeOOH} + \alpha\text{-FeOOH}$ (1/4) (1/4)	S ₂₀	$\gamma\text{-FeOOH} + \alpha\text{-FeOOH}$ (very small)

(*) A small amount of $\alpha\text{-FeOOH}$ phase was detected by FT-IR spectroscopy

(**) Broadened diffraction lines

Remark: A small amorphous fraction may be present in the early stages of corrosion. The presumption is that the amorphous fraction contained iron oxides and/or oxyhydroxides.

summarized in Figures 1 and 2. In sample S₁₆, lepidocrocite was determined by the characteristic bands at 1023 and 745 cm^{-1} , while magnetite could be recognized only on the basis of the band at 555 cm^{-1} . However, the presence of magnetite cannot be determined with certainty only on the basis of this IR band since it could also be ascribed to hematite. The presence of a small amount of goethite was indicated by the IR bands at 894 and 795 cm^{-1} .

The FT-IR spectrum of sample S₁₇ suggested, on the basis of a very strong band at 585 cm^{-1} , that magnetite was the prevailing component. The bands at 894 and 796 cm^{-1} indicated the presence of a small amount of goethite, while lepidocrocite was determined by the band at 1023 cm^{-1} . The FT-IR spectra of the rust formed on the steel surface in 0.1 and 0.5 M $(\text{NH}_4)_2\text{SO}_4$ solutions (samples S₁₈ and S₁₉) showed an increase in the relative intensities of the bands corresponding to goethite and lepidocrocite, and a decrease in the band at 577 – 561 cm^{-1} corresponding to magnetite. The FT-IR spectrum of sample S₂₀ indicated that lepidocrocite was the prevailing component (bands at 1023 and 746 cm^{-1}), while the presence of a very small amount of goethite was suggested by weak bands at 895 and 798 cm^{-1} .

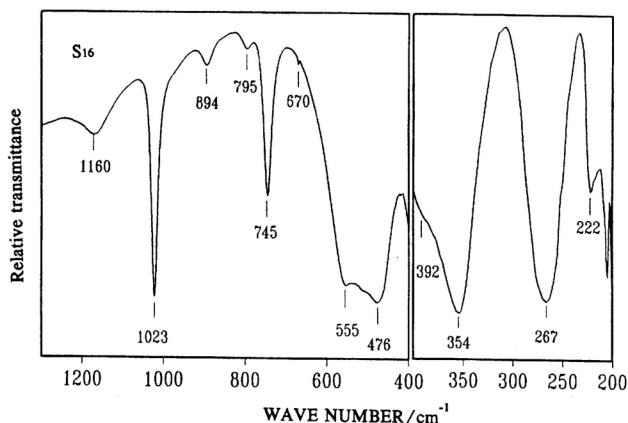


Figure 1. Fourier transform IR spectrum of sample S₁₆ recorded at RT.

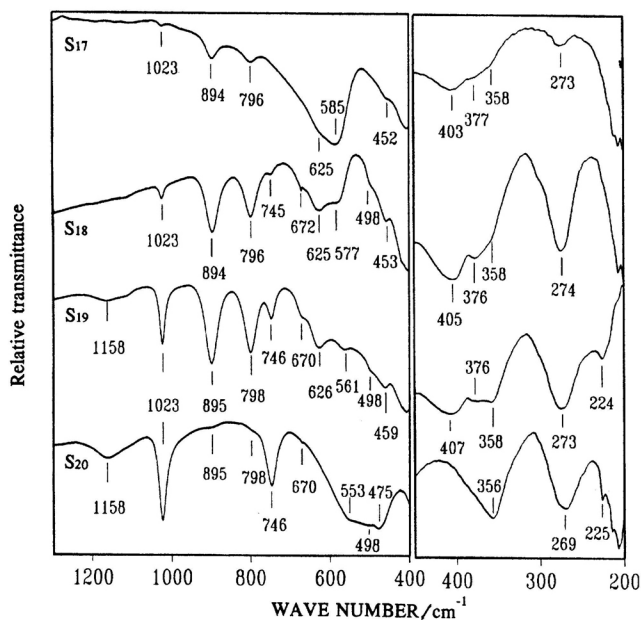


Figure 2. Fourier transform IR spectra of samples S₁₇ to S₂₀ recorded at RT.

The Mössbauer spectra of samples S₁₆ to S₂₀ are shown in Figures 3 to 5, and the calculated parameters of the hyperfine interactions for these samples are given in Table III. The spectrum of sample S₁₆ indicated that the dominant components in this sample were lepidocrocite and substoichiometric magnetite, Fe_{3-x}O₄. The hyperfine magnetic fields, HMF(M₁) = 492 kOe and HMF(M₂) = 460 kOe, were meas-

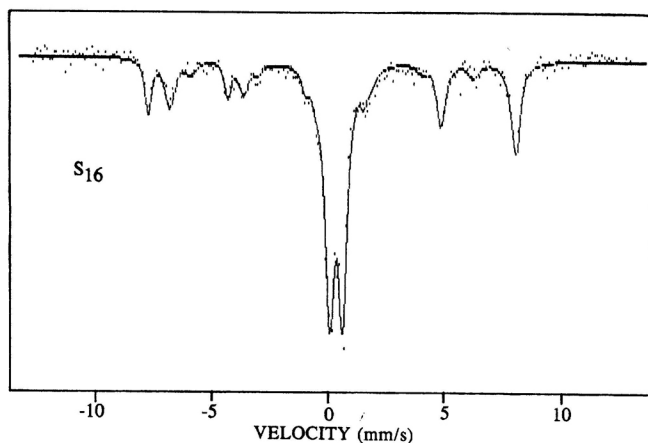


Figure 3. ^{57}Fe Mössbauer spectrum of sample S₁₆ recorded at RT.

ured for $\text{Fe}_{3-x}\text{O}_4$ in sample S₁. The small amount of goethite was characterized by magnetic field $\text{HMF}(M_3) = 378$ kOe. The central quadrupole doublet, Q, was characterized by splitting, $\Delta = 0.55$ mm/s, which is in agreement with the known Δ value for lepidocrocite.³ Addition of $(\text{NH}_4)_2\text{SO}_4$ electrolyte in doubly distilled water caused significant changes in the composition of the rust (samples S₁₇ to S₂₀), as illustrated

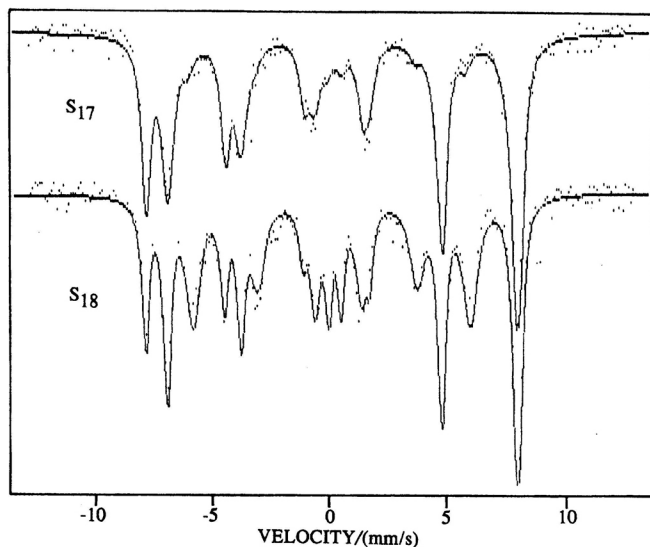


Figure 4. ^{57}Fe Mössbauer spectra of samples S₁₇ and S₁₈ recorded at RT.

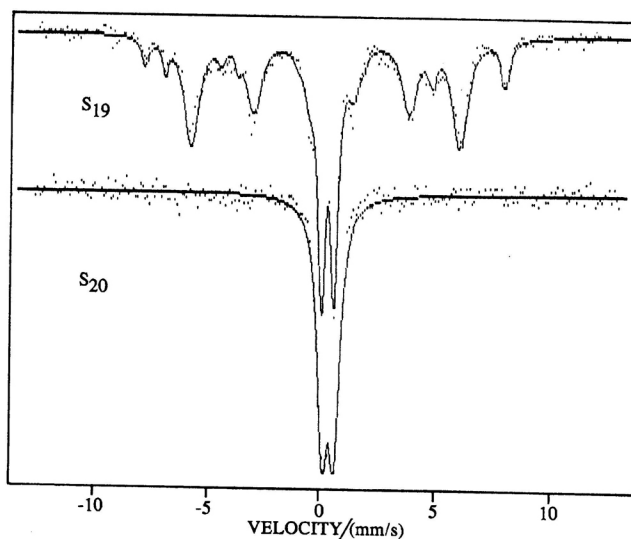


Figure 5. ^{57}Fe Mössbauer spectra of samples S_{19} and S_{20} recorded at RT.

by the corresponding Mössbauer spectra. In sample S_{17} , the dominant component was $\text{Fe}_{3-x}\text{O}_4$. The Mössbauer spectrum of sample S_{17} also indicated the presence of small amounts of goethite and lepidocrocite. The spectrum of sample S_{18} indicated that the stoichiometry of magnetite in this sample was close to the Fe_3O_4 composition. With an increase in the $(\text{NH}_4)_2\text{SO}_4$ concentration from 0.05 to 2 M, a gradual increase in the intensity of the central quadrupole doublet was observed. The Mössbauer spectrum of sample S_{20} , recorded at room temperature, was fitted for one doublet with $\delta_{\text{Fe}} = 0.35$ mm/s and $\Delta = 0.54$ mm/s, and these parameters could be ascribed to lepidocrocite. X-ray diffraction and FT-IR spectroscopy pointed to the presence of a very small amount of goethite in sample S_{20} , and when the Mössbauer spectrum of the same sample was taken into account, it could be concluded that goethite particles were of superparamagnetic (SPM) dimensions.

The present study undoubtedly indicated the presence of a maximum of three crystalline oxide phases in one rust sample. The X-ray measurements point to the conclusion that a small amorphous fraction can be also present in the rust in the early stages of corrosion. The presence of lepidocrocite, magnetite or goethite in the rust depended on the time of corrosion and the concentration of $(\text{NH}_4)_2\text{SO}_4$. The experiments clearly demonstrated regularities in the phase composition of rust in dependence on time, and showed that the concentration of $(\text{NH}_4)_2\text{SO}_4$ had the decisive influence on phase composition. For instance, all rust samples that were generated in doubly distilled water within a period of 6 months contained magnetite, while in the rust samples generated in 2 M $(\text{NH}_4)_2\text{SO}_4$ solutions within the same corrosion time magnetite was not observed. The possible mechanisms of lepidocrocite, magnetite or goethite formation in corrosion processes were discussed in a previous paper.¹

TABLE III

⁵⁷Mössbauer parameters calculated for selected corrosion products, S₁₆ to S₂₀

Sample	Lines	Isomer shift $\delta^*/(\text{mm/s})$	Quadrupole splitting $\Delta E_q/(\text{mm/s})$	Hyperfine magnetic field HMF/kOe	Line width $\Gamma/(\text{mm/s})$
S ₁₆	Q	0.40	0.55		0.47
	M ₁	0.29	0.04	492	0.33
	M ₂	0.68	0.04	460	0.53
	M ₃	0.40	0.32	378	0.55
S ₁₇	Q	0.33	0.61		0.60
	M ₁	0.30	0.03	491	0.47
	M ₂	0.65	-0.02	458	0.59
	M ₃	0.21	0.32	367	0.60
S ₁₈	Q	0.35	0.52		0.37
	M ₁	0.27	-0.02	494	0.36
	M ₂	0.65	0.01	461	0.38
	M ₃	0.36	0.25	366	0.74
S ₁₉	Q	0.37	0.54		0.38
	M ₁	0.26	0.00	492	0.41
	M ₂	0.65	0.08	460	0.31
	M ₃	0.38	0.26	360	0.78
S ₂₀	Q	0.35	0.54		0.72

*Isomer shifts are given relative to α -FeErrors: ± 0.01 mm/s and ± 1 kOe

The strong influence of $(\text{NH}_4)_2\text{SO}_4$ electrolyte on the corrosion of steel in aqueous medium can be considered as a cumulative effect of two aggressive ions, NH_4^+ and SO_4^{2-} . The presence of SO_4^{2-} ions, at given pH values, can create corrosion conditions similar to the precipitation processes of oxyhydroxides and oxides from FeSO_4 solutions. On the other hand, the presence of NH_4^+ ions may promote the dissolution of iron (steel) in the solution,¹⁵ thus accelerating the corrosion reactions. Goethite was detected in the rust formed by corrosion of steel in water or $(\text{NH}_4)_2\text{SO}_4$ solutions at 20 °C over a longer period of time. However, in this case, goethite was not the dominant component of the rust. An opposite situation was found in the rust samples obtained² after the corrosion of steel at 90 °C. It can be suggested that lepidocrocite was the main material source for the formation of goethite. It appears that γ -FeOOH was converted to α -FeOOH *via* a dissolution/precipitation mechanism. A gradual increase in the goethite content of the rust was observed at 20 °C with a prolonged time of corrosion. Formation of α -FeOOH in a more significant amount at 90 °C than at 20 °C can be explained by an increased rate of γ -FeOOH dissolution and increased concentration of Fe^{3+} ions.

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SAŽETAK

Stvaranje hrđe tijekom korozije čelika u vodi i otopinama (NH₄)₂SO₄. II.

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Kemijska i strukturna svojstva hrđe, stvorene korozijom čelika u vodi i otopinama (NH₄)₂SO₄ pri 20 °C u vremenskom periodu do 6 mjeseci, istraživana su difrakcijom X-zraka, FT-IR spektroskopijom i ⁵⁷Fe Mössbauerovom spektroskopijom. U uzorcima hrđe detektirane su tri oksidne faze: lepidokrokrit, magnetit i getit. Raspodjela tih faza u uzorcima hrđe ovisila je o vremenu korozije i o koncentraciji (NH₄)₂SO₄. ⁵⁷Fe Mössbauerova spektroskopija pokazala je nestehiometrijski karakter magnetita (Fe_{3-x}O₄). Magnetit nije opažen u hrđi koja je stvorena u otopini 2M (NH₄)₂SO₄. FT-IR spektroskopija pokazala se posebno pogodnom za određivanje malih količina getita i lepidokrokita u hrđi. Snažan utjecaj koncentracije (NH₄)₂SO₄ na fazni sastav hrđe objašnjen je kumulativnim efektom iona NH₄⁺ i SO₄²⁻ agresivnih u korozijskom smislu.