Formation of Magnetite in Highly Alkaline Media in the Presence of Small Amounts of Ruthenium*

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The effect of small amounts of ruthenium on the formation of magnetite in highly alkaline media was investigated using X-ray powder diffraction (XRD), Mössbauer and FT-IR spectroscopies, field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS). Acicular $\alpha$-FeOOH particles precipitated in a highly alkaline medium with the addition of tetramethylammonium hydroxide (TMAH) were used as a reference material. Initial addition of small amounts of Ru(NO)(NO3)3 to that precipitation system had a drastic effect on the formation of iron oxide phases and their properties. The addition of Ru(NO)(NO3)3 favoured the formation of stoichiometric Fe3O4. With an increase of the initial Ru(NO)(NO3)3 concentration in the precipitation systems less time was needed for the formation of Fe3O4 as a single Fe-bearing phase in the precipitates. Ruthenium ions made solid solutions $\alpha$-(Fe,Ru)OOH; however, there was no indication of the formation of solid solutions with $\alpha$-Fe2O3 and Fe3O4.

Mössbauer and FT-IR spectroscopies supported the conclusion on the formation of solid solutions $\alpha$-(Fe,Ru)OOH. FE-SEM showed the formation of octahedral Fe3O4 particles of a mm range size. Ruthenium particles ($\approx 20$ nm in size) were deposited onto the surfaces of Fe3O4 particles. They were also present in the form of clusters containing octahedral Fe3O4 particles in the nanosize range ($\approx 100$ nm or less). The formation of Fe3O4 was interpreted as a combining effect of the thermal decomposition products of TMAH under autoclaving conditions and the catalytic action of ruthenium. In such a way strong reductive conditions in the investigated precipitation system were created.

INTRODUCTION

Magnetite (Fe3O4) shows unique magnetic and electrical properties and due to that it has been the subject of many investigations. Verwey and De Boer1 solved the crystal structure of magnetite and Fleet2,3 further refined it. Magnetite has the inverse-spinel structure with space group Fd3m and lattice constant $a = 8.394(5)$ Å.4 Fleet2 measured $a = 8.3941(7)$ Å for natural magnetite. Iron ions occupy two distinct structural positions in magnetite: Fe3+ ions are at tetrahedral sites, whereas Fe2+ and Fe3+ ions are equally distributed at octahedral sites of the spinel-type structure. Fe3O4 undergoes a sharp phase transition near $= 120$ K,5 which phenomenon is often cited in reference literature as the Verwey transition. This transition is related to an abrupt decrease in electric conductivity and a specific heat anomaly. $^{57}$Fe Mössbauer spectrum of Fe3O4 is characterized by two hyperfine magnetic fields (two sextets) at room temperature (RT). In the region of

* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

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Verwey transition and temperatures below it, the Mössbauer spectrum starts to be very complicated. Hargrove and Kündig\textsuperscript{6} reported more than two sextets present in the region of Verwey transition, and later investigations\textsuperscript{7–10} confirmed this finding. Moreover, the Mössbauer spectrum of Fe\textsubscript{3}O\textsubscript{4} was interpreted as the superposition of several sextets. However, there are still uncertainties about the origin of these sextets.

Synthetic magnetite is a very important material in various applications where its chemical or magnetic properties are exploited. Fe\textsubscript{3}O\textsubscript{4} and substoichiometric Fe\textsubscript{3–}\textsubscript{x}O\textsubscript{4} are the typical products of iron (steel) rusting under different conditions.\textsuperscript{11,12} Magnetite can be prepared in the laboratory using different synthesis methods. The common way to prepare Fe\textsubscript{3}O\textsubscript{4} particles is the oxidation of an aqueous Fe(OH)\textsubscript{2} suspension precipitated from Fe\textsubscript{II}-salt solutions.\textsuperscript{13,14} Magnetite can be obtained by adding alkali to the aqueous solutions of Fe\textsuperscript{III}/Fe\textsuperscript{II}-salts.\textsuperscript{15} The phase composition of thus obtained precipitates depends on the pH and temperature. Magnetite particles were also formed by a reaction of ferric oxyhydroxides with ferrous species,\textsuperscript{16,17} or by the reduction of hematite in a H\textsubscript{2} stream at higher temperature, with the retention of the original hematite particle shape.\textsuperscript{18} Thermal decomposition of iron-organic salts is a very simple method for the preparation of magnetite.\textsuperscript{19} On the other hand, the disadvantages of this method are a difficult control of the size and morphology of the particles and the presence of additional unwanted phases such as maghemite (γ-Fe\textsubscript{2}O\textsubscript{3}) and hematite (α-Fe\textsubscript{2}O\textsubscript{3}). A similar situation occurs in the pyrolysis of aerosol droplets containing an Fe-bearing component, where additional phases, γ-Fe\textsubscript{2}O\textsubscript{3} and α-Fe\textsubscript{2}O\textsubscript{3}, can also be formed. Very small magnetite particles can be obtained by combining the microemulsion method with γ-irradiation.\textsuperscript{20} The product of these synthesis methods is usually substoichiometric magnetite (Fe\textsubscript{3–}xO\textsubscript{3}). Recently, Krehula and Music\textsuperscript{21} have found that stoichiometric magnetite can precipitate in alkaline aqueous media when ruthenium ions are present. In this work we have extended our investigations to much lower concentrations of ruthenium ions than those used in the previous work,\textsuperscript{21} with an aim to obtain more data about that precipitation system, as well as about the corresponding precipitation mechanism.

**EXPERIMENTAL**

**Preparation of Samples**

Analytical reagents FeCl\textsubscript{3}, 6H\textsubscript{2}O and Ru(NO)(NO\textsubscript{3})\textsubscript{3} were used. Tetramethylammonium hydroxide solution (25 %, mass fraction, w, electronic grade 99.9999 %) supplied by Alfa Aesar was used. Twice-distilled water prepared in our own laboratory was used in all experiments. The experimental conditions for the preparation of G- and R-samples are given in Table I. In the preparation of R-samples a predetermined volume of the TMAH solution (10 mL) was added to the mixed FeCl\textsubscript{3} + Ru(NO)(NO\textsubscript{3})\textsubscript{3} solutions. The total volume of each precipitation system was 40 mL. The suspensions so formed were vigorously shaken for approximately 10 min, then heated at 160 °C, using the general-purpose bomb by Parr (model 4744), comprising the vessel and cup made of Teflon. Reference sample G was synthesised without the Ru(NO)(NO\textsubscript{3})\textsubscript{3} component. After a proper heating time the precipitates were cooled to room temperature (mother liquid pH = 13.5–13.8). The precipitates were separated from the mother liquid using an ultra-speed centrifuge Sorvall RC2-B, then subsequently washed with twice-distilled water to remove the »neutral electrolyte«.

**Instrumentation**

\textsuperscript{57}Fe Mössbauer spectra were recorded at RT in the transmission mode using a standard WissEl (Starnberg, Germany) instrumental configuration. The \textsuperscript{57}Co/Rh Mössbauer source was used. The velocity scale and all data refer to the metallic \textalpha-Fe absorber at RT. A quantitative analysis of the recorded spectra was made using the MossWinn program.

Fourier transform infrared (FT-IR) spectra were recorded at RT using a Perkin-Elmer spectrometer (model 2000).

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**TABLE I.** Conditions for the preparation of the samples by autoclaving at 160 °C (total volume of the each precipitation system is 40 mL)

<table>
<thead>
<tr>
<th>Sample</th>
<th>[FeCl\textsubscript{3}]/mol dm\textsuperscript{-3}</th>
<th>[Ru(NO)(NO\textsubscript{3})\textsubscript{3}]/mol dm\textsuperscript{-3}</th>
<th>( r = [\text{Ru}] / ([\text{Ru}]+[\text{Fe}] ) )</th>
<th>Volume 25 % w TMAH/mL</th>
<th>Autoclaving time/hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>G1</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>72</td>
</tr>
<tr>
<td>R1</td>
<td>0.1</td>
<td>1.0 × 10\textsuperscript{-5}</td>
<td>1.0 × 10\textsuperscript{-4}</td>
<td>10</td>
<td>72</td>
</tr>
<tr>
<td>R2</td>
<td>0.1</td>
<td>2.5 × 10\textsuperscript{-5}</td>
<td>2.5 × 10\textsuperscript{-4}</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>R3</td>
<td>0.1</td>
<td>1.0 × 10\textsuperscript{-4}</td>
<td>1.0 × 10\textsuperscript{-3}</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>R4</td>
<td>0.1</td>
<td>2.5 × 10\textsuperscript{-4}</td>
<td>2.5 × 10\textsuperscript{-3}</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>R5</td>
<td>0.1</td>
<td>2.5 × 10\textsuperscript{-4}</td>
<td>2.5 × 10\textsuperscript{-3}</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>R6</td>
<td>0.1</td>
<td>5.0 × 10\textsuperscript{-4}</td>
<td>5.0 × 10\textsuperscript{-3}</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>R7</td>
<td>0.1</td>
<td>5.0 × 10\textsuperscript{-4}</td>
<td>5.0 × 10\textsuperscript{-3}</td>
<td>10</td>
<td>24</td>
</tr>
</tbody>
</table>
The FT-IR spectrometer was linked to a PC with an installed IRDM (IR Data Manager) program to process the recorded spectra. The specimens were pressed into small discs using a spectroscopically pure KBr matrix.

X-ray powder diffractometer APD 2000 (Cu Kα radiation, graphite monochromator, NaI-Tl detector) manufactured by ItalStructures (Riva Del Garda, Italy) was used.

A thermal field emission scanning electron microscope (FE-SEM, model JSM-7000F, manufactured by JEOL Ltd.) was used. FE-SEM was linked to the EDS/INCA 350 (energy dispersive X-ray analyser) manufactured by Oxford Instruments Ltd. The specimens were not coated with an electrically conductive surface layer.

RESULTS AND DISCUSSION

X-ray Powder Diffraction

The results of XRD phase analysis are given in Table II, whereas selected XRD patterns are shown in Figures 1 and 2. Crystal phases were determined from XRD patterns using JCPDS PDF cards No. 29–713 for α-FeOOH, No. 13–534 for α-Fe₂O₃ and No. 19–629 for Fe₃O₄.²²

α-FeOOH was obtained as a single phase by hydrothermal heating at 160 °C for 2 h (sample G) and 72 h (sample G1) of the suspensions without ruthenium ions. However, we have found that the adding of small amounts of ruthenium in the form of Ru(NO)(NO₃)₃ had a drastic effect on that precipitation process. Ru(NO)(NO₃)₃ was chosen as a very convenient ruthenium salt which does not undergo hydrolysis in the solid state and dissolves into a transparent solution. On the other hand, ageing of the ruthenium salt RuCl₃ · xH₂O for a prolonged time results in oxidation and the formation of a Ru(IV)-(hydrour)oxide. At the concentration ratio $r = \frac{[\text{Ru}]}{([\text{Ru}]+[\text{Fe}])}$, a significant change in the precipitation system was observed upon 72 h of autoclaving. A mixture of α-FeOOH + α-Fe₂O₃ was obtained. With an increase in the ruthenium concentration to obtain $r = 2.5 \times 10^{-4}$ (sample R2) the phase composition of the precipitate showed the presence of α-FeOOH, Fe₃O₄ and α-Fe₂O₃ (24 h of autoclaving). With a further increase in $r$ to $1 \times 10^{-3}$, Fe₃O₄ was detected as a single phase in the precipitate (sample R3). The same

![Figure 1. XRD patterns of samples G1, R1 and R2, recorded at RT.](image1)

![Figure 2. XRD patterns of samples R3, R6 and R7, recorded at RT.](image2)

TABLE II. Phase composition of the samples, as found by X-ray powder diffraction

<table>
<thead>
<tr>
<th>Sample</th>
<th>$r = \frac{[\text{Ru}]}{([\text{Ru}]+[\text{Fe}])}$</th>
<th>Autoclaving time / hours</th>
<th>Phase composition by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>0</td>
<td>2</td>
<td>α-FeOOH</td>
</tr>
<tr>
<td>G1</td>
<td>0</td>
<td>72</td>
<td>α-FeOOH</td>
</tr>
<tr>
<td>R1</td>
<td>$1.0 \times 10^{-4}$</td>
<td>72</td>
<td>α-FeOOH + α-Fe₂O₃</td>
</tr>
<tr>
<td>R2</td>
<td>$2.5 \times 10^{-4}$</td>
<td>24</td>
<td>α-FeOOH + Fe₃O₄ + α-Fe₂O₃</td>
</tr>
<tr>
<td>R3</td>
<td>$1.0 \times 10^{-3}$</td>
<td>24</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>R4</td>
<td>$2.5 \times 10^{-3}$</td>
<td>2</td>
<td>α-FeOOH</td>
</tr>
<tr>
<td>R5</td>
<td>$2.5 \times 10^{-3}$</td>
<td>24</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>R6</td>
<td>$5.0 \times 10^{-3}$</td>
<td>2</td>
<td>α-FeOOH</td>
</tr>
<tr>
<td>R7</td>
<td>$5.0 \times 10^{-3}$</td>
<td>24</td>
<td>Fe₃O₄</td>
</tr>
</tbody>
</table>

phase composition was found for samples formed after 24 h of autoclaving in the presence of a higher ruthenium concentration (samples R5 and R7). Samples formed after 2 h of autoclaving (R4 and R6) showed only the lines characteristic of α-FeOOH. XRD analysis of the precipitates showed a very strong effect of the small amounts of ruthenium ions, initially added as a Ru(NO)³⁺ complex. The presence of ruthenium created reductive conditions in the precipitation system, and as a result Fe₃O₄ could precipitate as a single Fe-bearing phase.

57Fe Mössbauer Spectroscopy

The results of Mössbauer spectroscopic measurements are summarized in Figures 3 and 4, whereas the calculated Mössbauer parameters are given in Table III. Mössbauer spectra of samples G, G1, R4 and R6 correspond to α-FeOOH (Figure 3). These spectra show a sextet with broadened spectral lines which deviate from the theoretical intensity ratio 3:2:1:1:2:3. The spectrum of sample G1 displays noticeably better shaping due to increased crystallinity at a prolonged autoclaving time. The RT Mössbauer spectrum of α-FeOOH may vary from one paramagnetic doublet up to a well-shaped sextet, which depends on the size and crystallinity of α-FeOOH particles. α-FeOOH particles smaller than ≈15–20 nm show a superparamagnetic type of the Mössbauer spectrum at RT, whereas α-FeOOH particles smaller than 8 nm show a superparamagnetic type of the Möss-

Figure 3. 57Fe Mössbauer spectra of samples G, G1, R4 and R6, recorded at RT.

Figure 4. 57Fe Mössbauer spectra of samples R1, R2, R3 and R5, recorded at RT.
The goethite sextets in the spectra of samples G, G1, R1, R4 and R6 were fitted taking into account the distribution of hyperfine magnetic field (HMF) in the range from 20 to 40 T with a step of 0.25 T. Sample G1 (Figure 3) showed the narrowest distribution of HMF and a ratio of the relative intensities of spectral lines not far from the theoretical one, 3:2:1:1:2:3. Mössbauer spectra of \( \alpha \)-FeOOH samples obtained in the presence of ruthenium ions (samples R4 and R6) showed the broadening of spectral lines and the HMF distribution as well as a decrease in average and most probably hyperfine magnetic field \( B_{hf} \) (Table III). The origin of this reduction in \( B_{hf} \) is the incorporation of ruthenium ions into the \( \alpha \)-FeOOH crystal structure. Adding very small amounts of ruthenium ions, as a Ru(NO)\(_3^+\) complex, to the precipitation system caused a great change in the phase composition of the precipitates formed after longer ageing periods (Figure 4). The calculated Mössbauer parameters and fraction percentages of these phases are given in Table III. Phase analysis of samples R3 to R7 by Mössbauer spectroscopy confirmed the results obtained by XRD. Mössbauer spectra of samples R3, R5 and R7 showed the formation of stoichiometric magnetite (Fe\(_3\)O\(_4\)). In an earlier work\(^{21}\) we have also observed the formation of stoichiometric magnetite by autoclaving for 24 h at 160 °C the suspensions with initial \( r \) between \( 2.91 \times 10^{-2} \) and \( 9.09 \times 10^{-2} \). The Mössbauer parameters calculated for magnetite obtained in the present work corresponded to those reported by Murad and Johnston.\(^{23}\)

**FT-IR spectroscopy**

Figure 5 shows the FT-IR spectra of samples G, G1, R4 and R6 (left side) and R3, R5 and R7 (right side). FT-IR spectra of samples G, G1, R4 and R6 correspond to the \( \alpha \)-FeOOH crystal structure. Sample G shows two IR bands at 896 and

**TABLE III.** \(^{57}\)Fe Mössbauer parameters calculated for samples G, G1 and R1 to R7 and identification

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spectral line</th>
<th>( \delta^{(a),(b)} / \text{mm s}^{-1} )</th>
<th>( E_q^{(b)} / \text{mm s}^{-1} )</th>
<th>( B_{hf}^{(b)} / \text{T} )</th>
<th>( B_{hf}^{(b)} / \text{T} )</th>
<th>( \Gamma / \text{mm s}^{-1} )</th>
<th>Area / %</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>M</td>
<td>0.37</td>
<td>–0.26</td>
<td>35.3</td>
<td>38.2</td>
<td>0.28</td>
<td>100</td>
<td>( \alpha )-FeOOH</td>
</tr>
<tr>
<td>G1</td>
<td>M</td>
<td>0.37</td>
<td>–0.26</td>
<td>36.7</td>
<td>38.7</td>
<td>0.20</td>
<td>100</td>
<td>( \alpha )-FeOOH</td>
</tr>
<tr>
<td>R1</td>
<td>M1</td>
<td>0.37</td>
<td>–0.28</td>
<td>36.1</td>
<td>38.5</td>
<td>0.22</td>
<td>50.8</td>
<td>( \alpha )-FeOOH</td>
</tr>
<tr>
<td></td>
<td>M2</td>
<td>0.37</td>
<td>–0.22</td>
<td>51.7</td>
<td>0.25</td>
<td>49.2</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
<td></td>
</tr>
<tr>
<td>R2</td>
<td>M1</td>
<td>0.36</td>
<td>–0.26</td>
<td>38.7</td>
<td>0.31</td>
<td>43.3</td>
<td>( \alpha )-FeOOH</td>
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</tr>
<tr>
<td></td>
<td>M2</td>
<td>0.37</td>
<td>–0.20</td>
<td>51.7</td>
<td>0.29</td>
<td>10.7</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
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<tr>
<td>R3</td>
<td>M3</td>
<td>0.29</td>
<td>–0.02</td>
<td>49.1</td>
<td>0.25</td>
<td>18.5</td>
<td>Fe(_{III})(tetr.) in Fe(_3)O(_4)</td>
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<tr>
<td></td>
<td>M4</td>
<td>0.67</td>
<td>0.01</td>
<td>46.1</td>
<td>0.30</td>
<td>27.5</td>
<td>Fe(<em>{II}/Fe</em>{III})(oct.) in Fe(_3)O(_4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>M1</td>
<td>0.28</td>
<td>–0.02</td>
<td>49.1</td>
<td>0.27</td>
<td>31.0</td>
<td>( \alpha )-FeOOH</td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>M2</td>
<td>0.66</td>
<td>0.01</td>
<td>46.1</td>
<td>0.40</td>
<td>69.0</td>
<td>( \alpha )-FeOOH</td>
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<tr>
<td>R5</td>
<td>M1</td>
<td>0.28</td>
<td>–0.02</td>
<td>49.1</td>
<td>0.33</td>
<td>34.9</td>
<td>Fe(_{III})(tetr.) in Fe(_3)O(_4)</td>
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</tr>
<tr>
<td></td>
<td>M2</td>
<td>0.66</td>
<td>0.02</td>
<td>46.1</td>
<td>0.39</td>
<td>65.1</td>
<td>Fe(<em>{II}/Fe</em>{III})(oct.) in Fe(_3)O(_4)</td>
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<tr>
<td>R6</td>
<td>M</td>
<td>0.37</td>
<td>–0.26</td>
<td>33.9</td>
<td>37.5</td>
<td>0.27</td>
<td>100</td>
<td>( \alpha )-FeOOH</td>
</tr>
<tr>
<td>R7</td>
<td>M1</td>
<td>0.27</td>
<td>–0.02</td>
<td>49.2</td>
<td>0.39</td>
<td>33.6</td>
<td>( \alpha )-FeOOH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>M2</td>
<td>0.67</td>
<td>0.01</td>
<td>46.1</td>
<td>0.48</td>
<td>66.4</td>
<td>( \alpha )-FeOOH</td>
<td></td>
</tr>
</tbody>
</table>

\(^{(a)}\) Isomer shift (\( \delta \)) is given relative to \( \alpha \)-Fe.

\(^{(b)}\) Errors: \( \delta = \pm 0.01 \text{ mm s}^{-1} \), \( E_q = \pm 0.01 \text{ mm s}^{-1} \), \( B_{hf} = \pm 0.2 \text{ T} \).
798 cm⁻¹ which can be assigned to Fe-O-H bending vibrations in α-FeOOH. These bands are usually used for the identification of α-FeOOH in a qualitative phase analysis of iron oxide mixtures. The IR band at 634 cm⁻¹ with a shoulder at 664 cm⁻¹, very strong and broad IR bands at 409 cm⁻¹ with a shoulder at 496 cm⁻¹, and small intensity IR bands at 455 and 377 cm⁻¹ were present in the spectrum of sample G. Verdonck et al.²⁴ studied the IR spectrum of α-FeOOH using the normal coordinate analysis, and compared the results with the experimental spectra of α-FeOOH and α-FeOOD. The IR bands recorded at 630, 495 and 270 cm⁻¹ were rather insensitive to deuteration, so the authors concluded that these IR bands were due to Fe-O stretching vibrations in α-FeOOH. A similar interpretation of IR bands below 650 cm⁻¹ was given by Cambier,²⁵ who also reported that an intense IR band around 630 cm⁻¹ was influenced by the shape of α-FeOOH particles. Weckler and Lutz²⁶ also investigated the IR spectrum of α-FeOOH.

Main spectral features of samples G and G1 were the same; in the spectra of these two samples, however, there were shifts of IR bands. The most pronounced shifts from sample G to sample G1 were 634→619 cm⁻¹ (a lattice band with the transition moment parallel to the a-axis) and 409 to 425 cm⁻¹ (a lattice band with the transition moment parallel to the c-axis). The shoulder at 664 cm⁻¹ for sample G changed to a band of weak intensity at 667 cm⁻¹ for sample G1 and the weak band at 377 cm⁻¹ for sample G was better pronounced at 383 cm⁻¹ for sample G1. The IR band at 425 cm⁻¹ (sample G1) was also less broadened. These differences can be assigned to a better crystallinity of α-FeOOH particles in sample G1 than in sample G, an increase in particle thickness (the a-axis direction) and a decrease in their shape anisotropy at a longer ageing time.

α-FeOOH particles precipitated in the presence of ruthenium ions (samples R4 and R6) showed lattice vibration bands at 642 and 402 cm⁻¹ for sample R4, and 642 and 401 cm⁻¹ for sample R6. The shifts in the positions of those bands, in comparison with the bands in the spectrum of sample G, can be assigned to the formation of solid solutions α-(Fe,Ru)OOH and to an elongation of particles in the c-axis direction. Moreover, the positions of OH bending bands at 891 and 796 cm⁻¹ for sample R4 and 890 and 795 cm⁻¹ for sample R6 were slightly different from those recorded for sample G (896 and 798 cm⁻¹). These results show that the most influenced IR bands in α-FeOOH doped with ruthenium ions are those related to Fe-O stretching (lattice) vibrations, thus confirming the incorporation of ruthenium ions in the α-FeOOH structure. It can be concluded that a lower degree of crystallinity of α-FeOOH and Ru substitution in α-FeOOH had a similar effect on the corresponding IR spectrum.

FT-IR spectra of samples R3, R5 and R7 showed an IR band centred between 580 and 587 cm⁻¹ and a very broad shoulder (band) at ≈400 cm⁻¹. These spectra are consistent with the spectrum of maghemite quoted in literature.²⁷

**FE-SEM**

Figure 6 shows the FE-SEM micrographs of the particles in samples G and G1 which correspond to α-FeOOH. Acicular and uniform α-FeOOH particles (Figure 6a) were obtained by autoclaving of the starting suspension for 2 h at 160 °C. With a heating time prolonged up to 72 h these particles did not much increase in length (Figure 6b). However, within that time a lateral aggregation of α-FeOOH rods was observed, and as a result the width of α-FeOOH particles increased. Electron microscope inspection showed that the crystal growth of bigger (secondary) α-FeOOH particles was governed by a lateral aggregation of primary α-FeOOH rods.

Figure 7a shows rod-like α-FeOOH particles deposited on much bigger α-Fe₂O₃ particles (sample R1). The HMF value of 51.7 T was measured by Mössbauer spectroscopy for the α-Fe₂O₃ fraction in sample R1. This HMF value is typically obtained for large and well-crystallized α-Fe₂O₃ particles. It can be inferred that these α-Fe₂O₃ particles did not show a tendency to form α-(Fe,Ru)₂O₃ solid solutions. Figure 7b shows a great population of small α-FeOOH rods and a large Fe₂O₃ (or α-Fe₂O₃) particle (sample R2). Figure 7c shows α-(Fe,Ru)OOH particles (sample R4) elongated along the crystallographic c-axis. These particles were grown during the autoclaving of the initial suspension (r = 2.5 × 10⁻⁵) for 2 h at 160 °C. The formation of μm size Fe₂O₃ particles...
with characteristic octahedral shape was observed upon a prolonged heating time (24 h) at 160 °C (Figure 7d; sample R5).

Figure 8a shows α-(Fe,Ru)OOH particles in sample R6. These particles are elongated along the crystallographic c-axis, and the decreased HMF value indicates the incorporation of ruthenium ions into the α-FeOOH crystal structure. The formation of μm range Fe$_3$O$_4$ particles was observed upon a prolonged heating time (24 h) at 160 °C (Figure 8b). Figure 8c shows one plane of a Fe$_3$O$_4$ crystal at high optical magnification, covered with nanosize particles some of which are aggregated. With an aim to obtain more data about these particles we analysed them by EDS. Generally, the population of these small particles increased in the precipitation systems with an increase in the starting Ru(NO)(NO$_3$)$_3$ concentration. Figures 9a,c show the FE-SEM micrograph of sample R3 ($r = 1.0 \times 10^{-3}$) precipitated for 24 h at 160 °C. Two selected areas were analysed by EDS. One (Figure 9a) represents a part of one plane of the Fe$_3$O$_4$ crystal which was not covered with small particles (light spots). EDS analysis of this selected area showed only iron and oxygen. EDS analysis of the other one (Figure 9c) within a cluster of small particles (light spots) showed a significant amount of ruthenium (Figure 9d). FE-SEM of this cluster under high optical magnification showed both ruthenium particles and small Fe$_3$O$_4$ particles. The size of these Fe$_3$O$_4$ particles was ≈100 nm or less. EDS results are consistent with Mössbauer measurements which did not prove the incorporation of ruthenium in ionic state into the Fe$_3$O$_4$ crystal structure.

**Effect of Ruthenium Ions on the Precipitation Mechanism**

The present work has indicated a complex mechanism of the precipitation of iron oxides in the presence of ruthenium. A reference sample of α-FeOOH was obtained using the procedure described in our previous work.$^{28}$ Under the precipitation conditions utilised in that work as well as in this one, very high pH values ≈13.5–13.8 can be obtained using TMAH as a precipitating agent. In the case of TMAH application the initially formed precipitate (ferrihydrite) can be dissolved on strong shaking, as observed by the naked eye. α-FeOOH is formed after some ageing time under homogeneous precipitation conditions. Due to that, by autoclaving of the precipitation system at 160 °C it was possible to obtain
acicular α-FeOOH particles with narrow size distribution. Thus obtained α-FeOOH particles were structurally very stable and did not transform into other iron oxides in the corresponding suspensions.

The addition of a very small amount of ruthenium in the form of a Ru(NO)₃⁺ complex to the starting solution (before adding the TMAH solution) had a drastic effect on the precipitation systems investigated in the present work. At the beginning of the precipitation process ruthenium ions were incorporated into ferrihydrite substituting Fe³⁺ ions, or as a co-gel (ferrihydrite + ruthenium (hydrous)oxide). Substitution of ruthenium for Fe³⁺ ions was possible due to similarities in the ionic radii of Fe³⁺ (0.645 Å) and Ru⁴⁺ (0.62 Å). Crystallization of α-FeOOH as a single phase was observed for shorter times (2h in the present work), whereas the incorporation of ruthenium ions into the α-FeOOH structure was proved by Mössbauer spectroscopy. The incorporation of ruthenium ions delayed the crystallization of α-FeOOH, then favoured the crystallization of α-Fe₂O₃. Factors such as the Fe³⁺ concentration in the solution, the incorporation of ruthenium ions into the α-FeOOH crystal structure, as well as different nucleation rates between α-FeOOH and α-Fe₂O₃ were responsible for the formation of α-(Fe,Ru)OOH and α-Fe₂O₃ phases. Upon a prolonged autoclaving time Fe₃O₄ was formed. Under given experimental conditions Fe₃O₄ can be obtained as a single Fe-bearing phase, as shown in the present work. Mössbauer spectroscopy showed the formation of stoichiometric magnetite, thus suggesting reductive conditions created in the precipitation systems (suspensions). In that part of the overall precipitation mechanism the role of ruthenium is dominant, which can be explained by the catalytic action of ruthenium. Generally, ruthenium dioxide, ruthenium black and ruthenium supported on various carriers are well-known catalysts. The role of ruthenium in our precipitation systems can be associated with the behaviour of TMAH, which decomposes at elevated temperatures while yielding a dominant NH₃, volatile amines and CH₃OH. In the presence of the ruthenium catalyst, NH₃ decomposes to N₂ and H₂, whereas CH₃OH decomposes to CO and H₂. In the present experiments it should be the formation of nascent hydrogen which easily reduces Fe³⁺ to Fe²⁺. In such a way the conditions for the formation of Fe₃O₄ at high pH are created. Mössbauer spectroscopy did not provide evidence of the incorporation of ruthenium ions into the Fe₃O₄ crystal structure.

The effects of ruthenium catalysts were also observed in some other works. For example, the formation of Fe₃O₄/γ-Fe₂O₃ by a reduction of α-Fe₂O₃ was observed during the investigation of the activity of the ruthenium catalyst in a water-gas shift reaction (WGSR). Berry et al. used in situ ⁵⁷Fe Mössbauer spectroscopy to investigate the effects of pre-treatment of titania-supported iron-ruthenium and iron-iridium catalysts in a hydrogen atmosphere. Musić et al. used a ruthenium catalyst in the denitration of simulated highly radioactive liquid waste (HRLW) compositions using the formic acid as a reducing agent. Ruthenium was added as the Ru(NO)(NO₃)₃ salt or as the so-called soluble Ru₂O₂ · xH₂O. The influence of rhodium and palladium on denitration reactions was also investigated. Ruthenium and rhodium were good catalysts for denitration reactions during which they created reductive conditions, so the reduction of Fe³⁺ to Fe²⁺ was observed. Fe²⁺ ions were reoxidised by a careful ad-

Figure 8. FE-SEM micrographs of samples: (a) R6, (b) R7 at lower optical magnification, and (c) R7 at higher optical magnification of one plane of the Fe₃O₄ particle.
dition of the concentrated H₂O₂ solution. α-FeOOH and an amorphous fraction were the principal phases in the precipitates upon Fe²⁺ oxidation by H₂O₂.

In the present work the concentrations of ruthenium in the precipitation systems have been very small, so that the ruthenium phase could not be detected with certainty. For that reason we prepared the precipitation system with an increased ruthenium concentration \((r = 3.333 \times 10^{-1})\). XRD of the precipitate formed upon 24 h of autoclaving at 160 °C showed the presence of α-Fe₂O₃ and 2-line ferrihydrite with ruthenium ions incorporated. The presence of metallic ruthenium was not detected by XRD. On the other hand, Fe₃O₄ and metallic ruthenium were detected in the precipitate obtained upon 72 h of autoclaving at 160 °C. Furthermore, the precipitation system (\(r = 4.76 \times 10^{-2}\)) prepared with NaOH alkali by autoclaving for 24 h did not show the formation of Fe₃O₄. Finally, taking into account these results it can be concluded that the formation of Fe₃O₄ in highly alkaline pH media is a combining effect of the thermal decomposition of TMAH and the catalytic action of ruthenium.

**CONCLUSION**

- Acicular and uniform α-FeOOH particles were precipitated in line with the procedure described by Kre‐

hula *et al.*²⁸ TMAH was used as a precipitating agent. The phase composition of the α-FeOOH precipitate did not change up to 72 h of autoclaving at 160 °C. The crystal growth of α-FeOOH particles was governed by a lateral aggregation of these particles.

  - Adding small amounts of ruthenium in the form of a Ru(NO)(NO₃)₃ complex to the starting FeCl₃ solution had a drastic effect on the above-mentioned precipitation process at 160 °C. A mixture of α-FeOOH and α-Fe₂O₃ was obtained at an initial concentration ratio \(r = 1.0 \times 10^{-4}\) and 72 h of autoclaving. At \(r = 2.5 \times 10^{-4}\) and 24 h of autoclaving a mixture of α-FeOOH, Fe₃O₄ and α-Fe₂O₃ was obtained. Fe₃O₄ as a single Fe-bearing phase was obtained at \(r = 1.0 \times 10^{-3}\), and higher initial concentrations of Ru(NO)(NO₃)₃ after 24 h of autoclaving.

  - Addition of ruthenium favoured the formation of stoichiometric Fe₃O₄. The formation of solid solutions was not proved. Mössbauer spectroscopy did not prove the formation of solid solutions between ruthenium and Fe₃O₄ or α-Fe₂O₃, but did prove the formation of α-(Fe,Ru)OOH solid solutions. The phase composition of samples determined by Mössbauer spectroscopy was in line with XRD measurements.

  - FT-IR measurements showed that the most influenced IR-bands in the spectra of α-FeOOH particles doped...
with ruthenium were those related to Fe-O stretching (lattice) vibrations, thus confirming a conclusion about the incorporation of ruthenium ions into the α-FeOOH crystal structure.

- FE-SEM showed the formation of octahedral Fe₃O₄ particles (crystals) within the μm range size. Ruthenium particles (≈20 nm in size) were deposited on the surface of Fe₃O₄ particles. They were also present in the form of clusters. These clusters contained octahedral Fe₃O₄ particles; their size, however, was in the nanosize range (≈100 nm or less).

The formation of Fe₃O₄ was explained by a combining effect of the products of TMAH decomposition and the catalytic activity of ruthenium under autoclaving conditions. This conclusion was supported by additional experiments. By using NaOH instead of TMAH under the same experimental conditions Fe₃O₄ was not formed. It has not been possible to prove with certainty the formation of metallic ruthenium at small concentrations of added Ru(NO)(NO₃)₃ and a prolonged autoclaving time. However, at the initial concentrations of Ru(NO)(NO₃)₃ much higher than those reported in the present work the formation of metallic ruthenium was confirmed by XRD.

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SAŽETAK

Nastajanje magnetita u jako lužnatom mediju u prisutnosti malih količina rutenija

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Istraživan je utjecaj malih količina rutenija na nastajanje magnetita u jako lužnom mediju primjenom rentgenske difrakcije u prahu, Mössbauerove spektroskopije, FT-IR spektroskopije, visokorezolucijske pretražne elektronske mikroskopije (FE-SEM) i spektroskopije karakterističnog rentgenskog zračenja (EDS). Izdužene čestice α-FeOOH, pripravljene u jako lužnom mediju dodatkom tetrametilamonijeva hidroksida (TMAH), koristi se kao referentni materijal. Prisutnost malih količina Ru(NO)(NO₃)₃ u taložnom sustavu snažno je utjecala na nastajanje željezovih oksida i njihova svojstva. Dodatak Ru(NO)(NO₃)₃ uzrokovao je nastajanje stehiometrijskog Fe₃O₄. S povećanjem početne koncentracije Ru(NO)(NO₃)₃ u taložnom je sustavu smanjeno vrijeme potrebno za nastajanje Fe₃O₄ kao jedine faze u talogu koja sadrži željezo. Rutenijevi su ioni ugrađeni u čvrste otopine α-(Fe,Ru)OOH, međutim, nije bilo naznaka o nastajanju čvrstih otopina s α-Fe₂O₃ i Fe₃O₄. Mössbauerova i FT-IR spektroskopija podržale su tvrdnju o nastajanju čvrstih otopina α-(Fe,Ru)OOH. Tehnika FE-SEM pokazala je nastajanje oktaedarskih čestica Fe₃O₄ veličine nekoliko μm. Na površini čestica Fe₃O₄ deponirane su čestice rutenija (veličine ≈ 20 nm). Ove čestice su također prisutne u obliku nakupina koje sadrže i oktaedarske čestice Fe₃O₄ veličine ≈ 100 nm ili manje. Nastajanje Fe₃O₄ objašnjeno je kombiniranim efektom produkata termičke razgradnje TMAH pri hidrotermičkim uvjetima i katalitičkog djelovanja rutenija, čime se stvaraju jaki reduktijski uvjeti u istraživanom taložnom sustavu.