

## **The impact of water quality parameters on iron release from corroded scales**

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### **Abstract**

The subjects of this study are iron and steel pipes that were distributed within Belgrade drinking water distribution system. In order to investigate mutual effects of corrosion and water quality the corrosion deposits on pipes and key water quality parameters, such as pH, dissolved oxygen (DO) and temperature were analyzed. In that way reasons for better control of pipes corrosion is provided. Depending on the composition of the water next to the pipe surface, corrosion of iron results in the formation of different compounds and solid phases. Fe(II) deposits are formed under reducing conditions, the presence of relatively soluble Fe(II) deposit such as siderite and ferrous oxides is confirmed. In the presence of carbonic species, siderite ( $\text{FeCO}_3$ ) is one of the present ferrous deposits. Green rust was not detected in the iron scale since it is not stable and was further oxidized in contact with air to a more stable phase, like  $\alpha\text{-FeOOH}$  or  $\text{Fe}_3\text{O}_4$ .

pH values of water have significant influence not only on the stability of corrosion deposits but also to valence of iron ions present in the water. According to measurements which correspond to solubility constant of  $\text{Fe}(\text{OH})_2$ , at pH range 6.0-8.0 the representative and typical ions in water are  $\text{Fe}^{2+}$ -ions. Changes in temperature of water and DO affect corrosion rate, iron by-product speciation and concentration, and the type of scale formed, but it is observed that the rate of iron release does not give simple relationship to the rate of iron corrosion. Further studies are needed to get deeper knowledge on the mechanism of iron release from corroded pipes and to get better insight on the influence of water quality to corrosion of iron.

*Keywords:* corrosion, iron, pipe water

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## 1. Introduction

Corrosion plays an important role in modifying water quality in drinking water distribution systems (Sarin et al., 2001). The rate of iron release can not be attributed to the simple relationship with the rate of iron corrosion. In this paper the subjects of the investigation were iron and steel pipes that were exploited within Belgrade drinking water distribution system. The corrosion deposits on corroded iron and steel pipes were analyzed. Water quality parameters which have been investigated were: pH, dissolved oxygen (DO) and temperature. In this way the parameters that have great influence on corrosion were analyzed. The obtained results could provide some directions for better control of corrosion of pipes. In recent years, considerable effort has been expended to understand the mechanisms of iron release from pipes and corrosion scales, the rates at which corrosion occurs and various chemical and hydraulic conditions, as well as the effectiveness of methods to control corrosion and/or iron release [(Sarin et al., 2001) and (Sarin et al., 2004)]. For example, Sarin et al. (2004), found that low dissolved oxygen (DO) levels and stagnant conditions led to increased release rates of ferrous iron Fe(II), while higher DO levels and flowing conditions led to oxidation of soluble/mobile Fe(II) in the corrosion scales and lower release rates. Alkalinity, pH, and phosphate levels were also found to influence iron release rates (Sarin et al., 2004). The focus of these efforts has largely been to reduce water quality problems. Numerous studies have shown that Fe(II) in the presence of iron oxide minerals is a potent reductant (Pecher et al., 2002) and that ferrous iron-bearing iron oxides (such as magnetite and green rusts) are also able to act as reductants (Elsner et al. 2004). Because pipe corrosion products contain both iron oxide minerals and ferrous iron, it is feasible that the corroded pipe surface may degrade via abiotic reduction.

In this research, batch experiments with corrosion products collected from Belgrade water distribution system were conducted to determine the connection between corrosion solids to key quality parameters of water. Experiments were conducted under oxic and anoxic conditions at different pH values and temperatures. The characteristics of the pipe solids were also evaluated.

The obtained results could provide directions and some answers for better control of corrosion of pipes.

## **2. Material and methods**

### **2.1. Chemicals**

pH values were adjusted with 1 M NaOH (97 %, Aldrich) and 1M HCl (36.5 %, Zorka, Sabac) and 2M H<sub>2</sub>SO<sub>4</sub> (96 %, Sigma-Aldrich). Chemicals used for the quantification of iron were FerroZine (97 %, Aldrich). Standard solutions for ICP-MS were prepared with Fluka multielement standard solution 70 006.

Ultra-high purity nitrogen gas, obtained from Messer, was purified with an in-line molecular sieve and oxygen trap, and used for deoxygenation. All aqueous solutions were prepared with ultra-pure water (Milli-Q, Millipore).

### **2.2. Pipe solid sample collection and preparation**

The analyzed samples of pipe solids were collected from Belgrade drinking water distribution system. Two samples were analysed from two characteristic points in the system: Senjak, sample #1 and Njegoseva, sample #2. Pipes were extracted after an accidental damage, due to corrosion, and cut into 50 cm long sections on site. The pipes were transported to the lab within 24 h after the extraction. Solids were removed from the interior pipe surface by scraping with a sterilized spatula. The tubercles that were removed from the pipe surface had a relatively hard exterior surface. Underneath this hard shell layer were softer solids. A composite sample of the hard exterior solids and soft interior solids was collected for every sample. Each sample was prepared by grinding solids. The pulverized samples were used for the characterization of the corrosion solids in batch experiments.

The analysed samples of pipes belong to the group of steel pipes, the most common pipe material used in Belgrade water supply network of all the materials used for the pipes (PUC BWS-Annual report, 2008). The age of the analysed pipes is over 50 years. In general, most of the water pipes in Belgrade water supply network have been replaced on time and the system is functioning with proper maintenance (PUC BWS-Annual report, 2008).

### 2.3. Characterization of iron pipe corrosion products

Each pipe corrosion scale sample was analysed by classical analytical method. The microstructure of the analyzed corrosion scales samples was examined by scanning electron microscopy (SEM) using a Jeol JSM 5800 instrument (operated at 25 kV). To determine the mineralogy of the solid samples, samples were also analyzed by X-ray diffraction (XRD), using a Bruker D8 Advance diffraction system, with Cu  $K\alpha_{1,2}$  radiation in theta/theta reflection geometry ( $\lambda = 1.5418 \text{ \AA}$ ). The diffraction intensity was measured by the scanning technique in the range of  $2\theta = 10\text{--}80^\circ$  by a  $0.05^\circ$  step for 5 s per point. The obtained diffractograms were analyzed with EVA V 9.0 software in accordance with PDF-2 database in order to compare the collected patterns with the reference powder diffraction files to determine the presence of various mineral species. Total iron content of the pipe solids were also quantified. In all cases, the iron was quantified via the Ferrozine method. When possible, both ferrous, Fe(II) and ferric, Fe(III) iron were quantified separately. Samples were analyzed in triplicate, and the average values for quantitative speciation are reported.

### 2.4. Batch experiments

All batch experiments were conducted in the following way. Pipe solids (5.00 g) were placed in Erlenmeyer flask (500 mL) with 300.0 mL of pipe water buffered at proper pH value. Three pH values were adjusted: 6.00, 7.00 and 8.00. pH values were adjusted by NaOH or HCl. Original water had pH 7.50. The prepared samples were placed in chamber with defined temperature. The temperatures were adjusted at three different values: 5, 10 and 20 °C. To investigate DO effects on degradation of iron, separate experiments were conducted in anoxic conditions, when pH 7.50 and at temperature of 20 °C.

### 2.5. Analytical methods

A portable multiparameter (WTW 340i) was used to measure pH, DO and temperature of pipe water. The accuracy of the pH meter was  $\pm 0.01$ . Concentration of iron in water was determined by iron/ferrozine complex using a UV/Visible spectrophotometer (Hach-Lange, 2800). Control and detailed measurements of the iron were performed by ICP-MS (Agilent Technologies 7500), (detection limit 1 ng/L).

### 3. Results

#### 3.1. Mineralogy and the composition of the corrosion scales of pipes

In order to elucidate the mineralogy and composition of corrosion scales three types of investigations were accomplished: classical content analysis, SEM and XRD measurements.

The composition of two chosen samples of corrosion scales are summarized in Table 1.

Some typical results of SEM investigations are presented in Fig.1.

Some representative results of XRD investigations are shown in Fig.2 and Fig. 3.

Table 1 The content of different compounds of analysed corrosion scales

The compound	The content (%)*	
	#1	#2
Silicon dioxide, SiO <sub>2</sub>	<0.01	12.27
Iron-oxide, Fe <sub>2</sub> O <sub>3</sub>	34.38	31.90
Iron-oxide, FeO	33.96	5.67
Aluminum-oxide, Al <sub>2</sub> O <sub>3</sub>	/	/
Calcium-oxide, CaO	<0.01	46.97
Magnesium-oxide, MgO	<0.01	0.015
Other metals content		
Zinc, Zn	0.024	0.023
Nickel, Ni	0.019	<0.001
Copper, Cu	0.115	0.039
Manganese, Mn	0.073	0.032
Cadmium, Cd	0.0002	<0.0001
Lead, Pb	<0.001	<0.001
Chromium, Cr	<0.001	<0.001

\* All measurements are the result of three probes, and the result is the mean value of these three measurement

The results obtained from the classical analysis of the corrosion scales show that these samples have different content of silicon dioxide and iron-oxide, which is probably due to

different performances over time. These results show that the composition differs due to different operational conditions of each analyzed sample.

SEM investigations of the samples were performed (Fig.1) in order to investigate the size, surface morphology and homogeneity of the samples. The #1 and #2 sample contain particles of corroded scales with different shapes and with size in the range of 200  $\mu\text{m}$  - 2 mm (Fig 1a). When going deeper in the analysis of the surface of corrosion scale #1 and #2 the surface is full of rigs and the surface of the analyzed samples is uneven (Fig 1b and Fig 1c). Opposite to the structure of surface of sample #1, sample #2 has surface (Fig 1c) covered with crystalline forms of calcium-carbonate (Fig 1d). These results are consistent with the XRD data and classical analysis where a considerable amount of CaO, as well as siderite,  $\text{FeCO}_3$ , was observed, and the calcification process has reached certain level. The reason for different surface of corrosion scale samples is probably due to operating conditions that this pipe was exposed to during its performance.

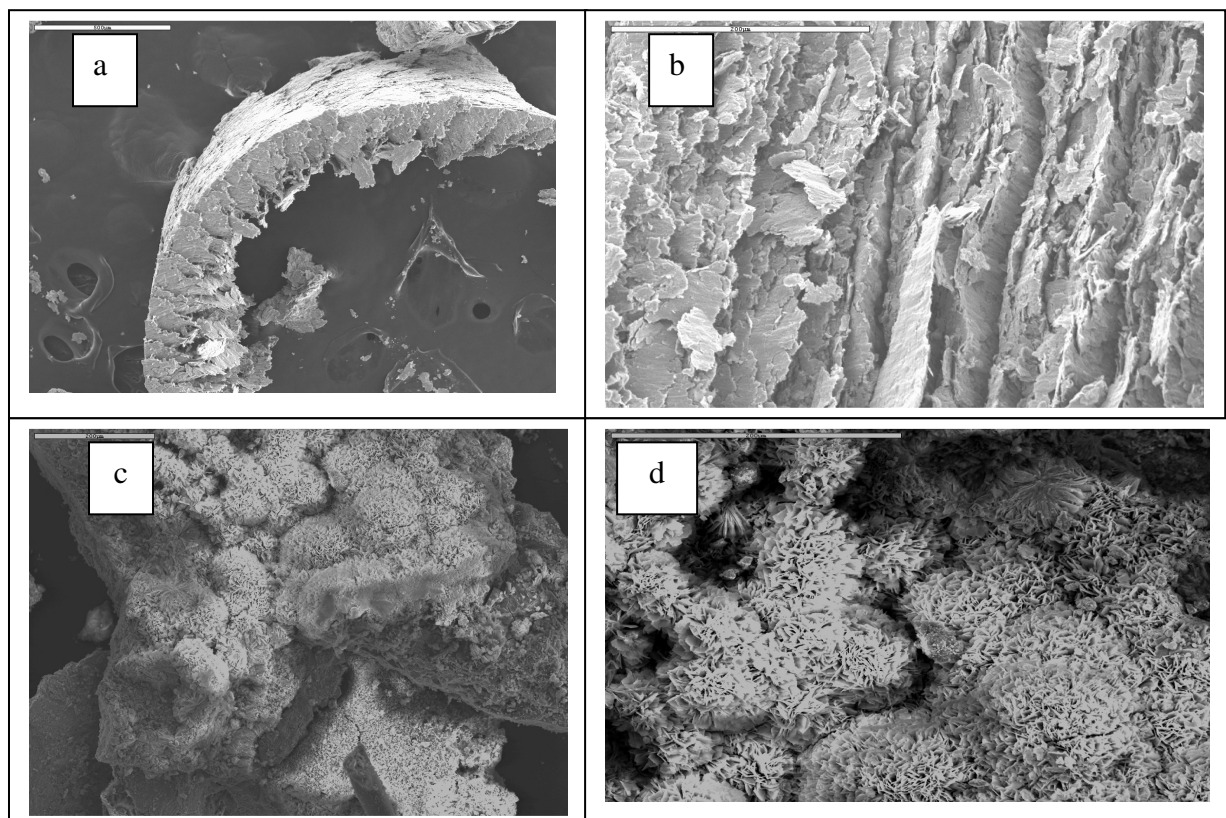
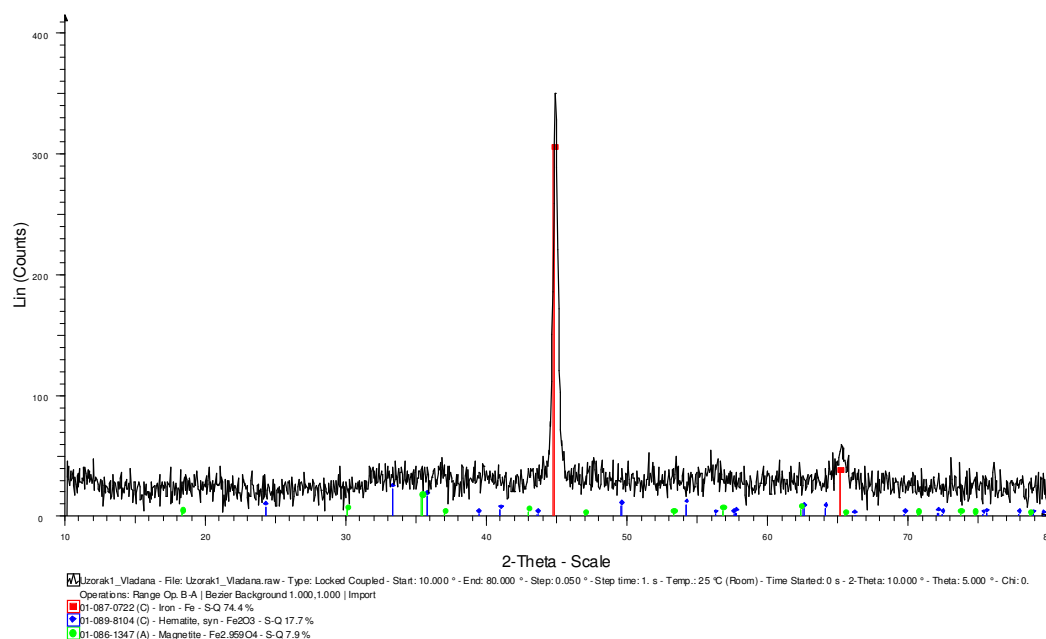


Fig.1 SEM microphotographs of sample #1 (a, b) and sample #2 (c,d)  
(Magnification for microphotograph: a) 500  $\mu\text{m}$  b) 200  $\mu\text{m}$  c) 200  $\mu\text{m}$  d) 200  $\mu\text{m}$ )

The corrosion scale samples were also analyzed by XRD and a representative XRD patterns are shown in Fig.2 (for sample #1) and Fig. 3 (for sample #2).

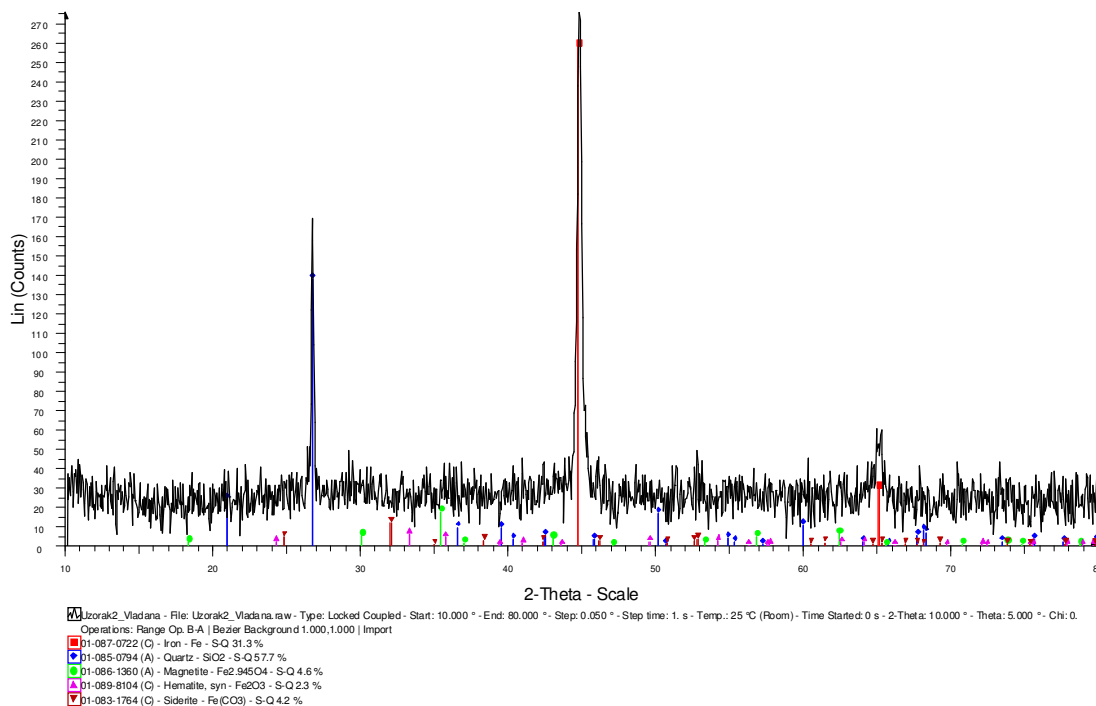
The collected patterns were compared with the reference powder diffraction files to determine the presence of various mineral species. Samples were analyzed in triplicate, and the average values for quantitative speciation are reported.

Elemental iron (Fe, 74.4 %), hematite ( $\text{Fe}_2\text{O}_3$ , 17.7 %) and magnetite ( $\text{Fe}_3\text{O}_4$ , 7.9 %) were identified as the main crystalline components in sample #1 (Fig.2.). The high zero-valent iron content in this sample is attributed to removal of iron metal with the oxide layer while scraping the pipe.



#1

Fig. 2 XRD of samples #1



#2

Fig. 3 XRD of samples #2

The iron oxide minerals detected as the main crystalline components in sample #2 (Fig.3.) were hematite (Fe<sub>2</sub>O<sub>3</sub>, 2.3 %), magnetite (Fe<sub>3</sub>O<sub>4</sub>, 4.6 %) and siderite (FeCO<sub>3</sub>, 4.2 %). Beside listed iron oxide minerals elemental iron (Fe, 31.3 %) and silicon-dioxide (SiO<sub>2</sub>, 57.7 %) were also found. Siderite was likely present in minor amounts since it is not stable when exposed to air. These results were similar to the results reported by other researchers ([Sarin et al., 2001], [Sarin et al., 2004] and [Lee et al.,2008]). Green rust was not detected in the iron scale since it is not stable and can be further oxidized in contact with air to a more stable phase, like  $\alpha$ -FeOOH or Fe<sub>3</sub>O<sub>4</sub>.

### 3.2 pH measurements

In order to observe the influence of pH two sets of experiments were performed in batch system. First set was designed in order to follow the rate of iron release (from sample #1) into water. It was accomplished when pH was adjusted to correspond to pH values in real water supply systems, at pH 6.0-8.0. In this pH range total concentration of iron presents amount of Fe<sup>2+</sup>-ions. The obtained results of iron release from corrosion scales are presented in Fig. 4.



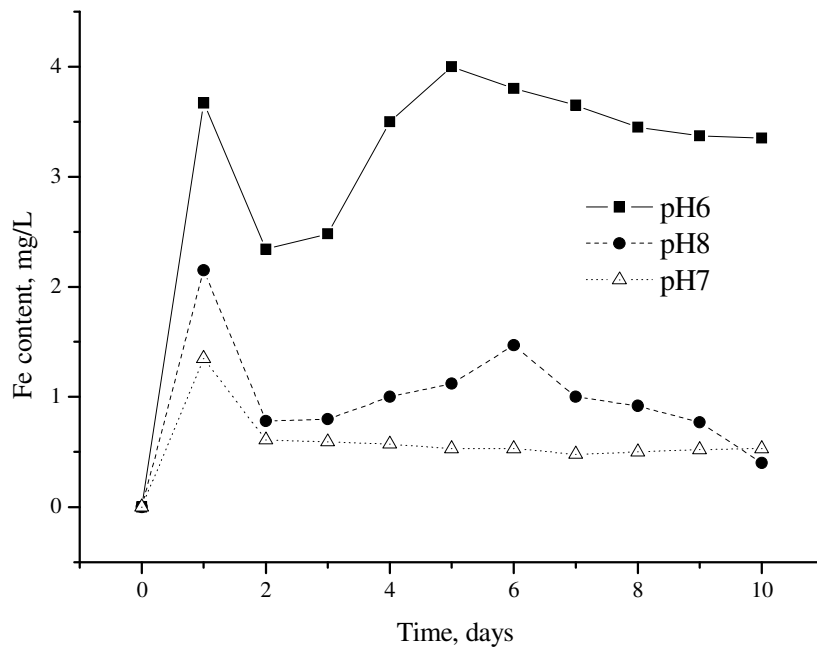


Fig. 4 The rate of iron release from corrosion scale to distilled water  
 $m(\text{corrosion scale})=5.0 \text{ g}$ ;  $V(\text{water})=300 \text{ mL}$ ;  $t=20^\circ\text{C}$ ;  $\tau=8 \text{ days}$

It can be concluded that iron concentration in water stabilizes within 10 days. At the beginning a relatively huge concentration is observed (the concentration is even higher than the solubility of  $\text{Fe}(\text{OH})_2$  which can be explained with high driving force (due to zero concentration in distilled water) which leads to the solubility of both iron-oxides. After this process the balance between ions and precipitate of iron-hydroxide(s) is being re-established. Maximal iron concentration measured in this experimental set-up was  $4.0 \text{ mg/L}$  ( $7 \cdot 10^{-5} \text{ mol/L}$ ). Minimal concentration measured was  $0.4 \text{ mg/L}$  ( $7 \cdot 10^{-6} \text{ mol/L}$ ) which corresponds with constant of solubility,  $K$ , and solubility,  $S$ , of characteristic compounds, for example: for  $\text{Fe}(\text{OH})_2$ ,  $K=7.9 \cdot 10^{-15}$ ,  $S=1.25 \cdot 10^{-5} \text{ mol/L}$  and for  $\text{Fe}(\text{OH})_3$ ,  $K=6.3 \cdot 10^{-38}$ ,  $S=3.54 \cdot 10^{-10} \text{ mol/L}$  (Schwertmann et al., 1991).

The result of more detailed investigations when pH is analysed are presented in Fig. 5. At the same figure the typical distribution of iron ions and molecules depending of pH values are enclosed.

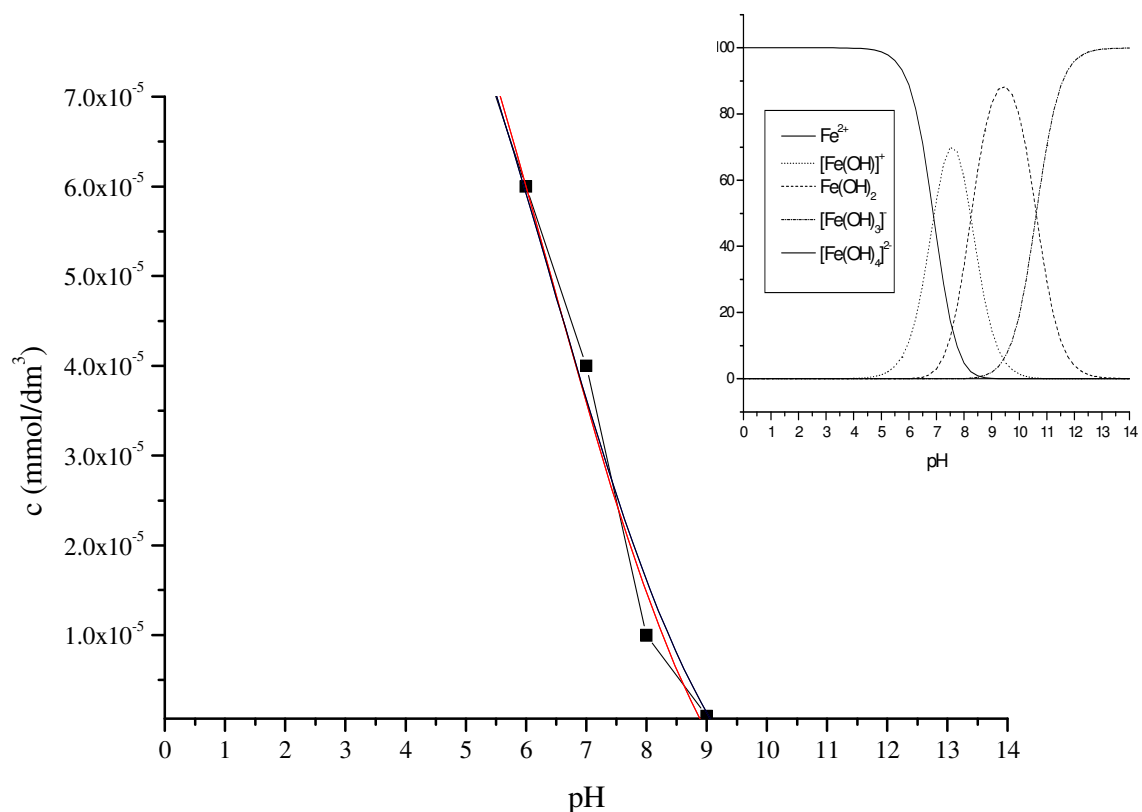


Fig. 5. Concentration of iron ( $\text{Fe}^{2+}$ ) in distilled water vs. pH value of water

$m(\text{corrosion scale})=5.0 \text{ g}$ ;  $V(\text{water})=300 \text{ mL}$ ;  $t=20^\circ\text{C}$ ;  $\tau=8 \text{ days}$

Iron, Fe(II) occurs in different ionic and molecular forms such as  $\text{Fe}^{2+}$ ,  $[\text{Fe}(\text{OH})]^+$ ,  $\text{Fe}(\text{OH})_2$ ,  $[\text{Fe}(\text{OH})_3]^-$ ,  $[\text{Fe}(\text{OH})_4]^{2-}$ , mono, di and tri-valent ions (the distribution of iron species is shown in the corner of the Fig.5). Total concentration of iron in balance could be ascribed to the  $\text{Fe}^{2+}$  ion concentration (Schwertmann et al.,1991).

The increase of iron concentration could be ascribed to disbalance, particularly at the beginning of process when the highest concentration of iron ( $\text{Fe}^{2+}$ ) is observed. After a few days the concentration from  $7 \cdot 10^{-5} \text{ mol/L}$  decreases to  $7 \cdot 10^{-6} \text{ mol/L}$  (10 times).

### 3.3. Temperature measurements

Temperature, a potentially important factor in iron corrosion, is rarely taken into account when iron corrosion is assessed. In order to observe the influence of temperature on iron release three different temperatures were investigated in our research. Obtained results, for chosen sample #1, are shown in Fig.6.

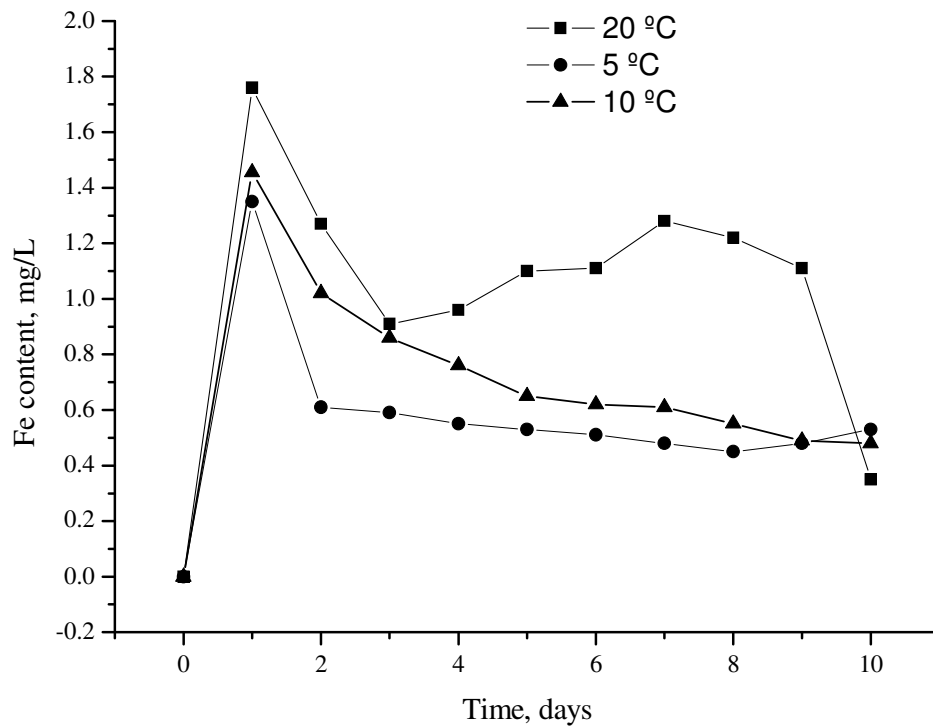


Fig.6. The variation of iron concentration within time at different temperatures

$m(\text{corrosion scale})=5.0 \text{ g}$ ;  $V(\text{water})=300 \text{ mL}$ ;  $\tau=8 \text{ days}$

There are two possibilities that should be considered when investigating the influence of temperature on iron corrosion (Volk et al., 2000). The first is that corrosion may be significantly different at one constant temperature compared to another for a given water quality. For example, a pipe at 20 °C may experience more corrosion problems than a pipe at 5 °C. The second possibility is that temperature variations might affect iron corrosion. That is, a pipe in which the temperature is varied between two temperatures (either increasing, decreasing, or cyclic) over a short period of time might corrode differently than a pipe held at

constant temperature. Pipes in a distribution system are almost always buried, and the temperature of the surrounding soil remains relatively constant. However, the water temperature within a pipe can change throughout the year due to seasonal variations of the water source. Thus, a pipe may exhibit different corrosion behavior in the winter versus the summer.

In our research, the release of iron decreases for samples held at 5 °C compared to samples held at 10 °C or 20 °C. It implies that lower iron concentrations and corrosion rates are present during lower temperatures. Obtained results are in accordance with some previous researchers (Volk et al., 2000).

Total concentration of iron in balance could be, as mentioned before, ascribed to the  $\text{Fe}^{2+}$  ion concentration (Schwertmann et al., 1991). The increase of iron concentration at the beginning of the measurements could be ascribed to disbalance of iron content on the surface of scales and in the water, when the highest concentration of iron ( $\text{Fe}^{2+}$ ) is observed. After a few days the concentration of iron decreases significantly, until it reaches the constant value (after approximately 8 days). It seems that temperature has the highest effect at the beginning of the process. After a while the whole process of iron release reaches relatively constant and balanced behavior.

What can also be taken into account is the relation with oxygen solubility and temperature. The oxygen solubility decreases at higher temperature. At a pressure of 1 atmosphere, DO saturation is 8.26 mg/L at 25 °C versus 12.77 mg/L at 5 °C. This difference could have three effects on iron corrosion. First, oxygen is the key electron acceptor for the corrosion of iron metal. At higher temperatures, there is less oxygen so the extent and rate of corrosion are more likely to be limited. Secondly, oxygen plays an important role in oxidizing ferrous compounds. Finally, depletion of oxygen may allow the Kuch reaction to occur, whereby existing ferric iron scale acts as the electron acceptor for the oxidation of iron metal to ferrous metal:



This reaction is exothermic, so it might proceed more slowly at higher temperature (Kuch, 1988). Thus, changes in DO solubility could affect corrosion rate, iron by-product speciation and concentration, and the type of scale formed.

### 3.4 Dissolved oxygen (DO) measurements

In Fig. 7 the results of DO measurements are shown.

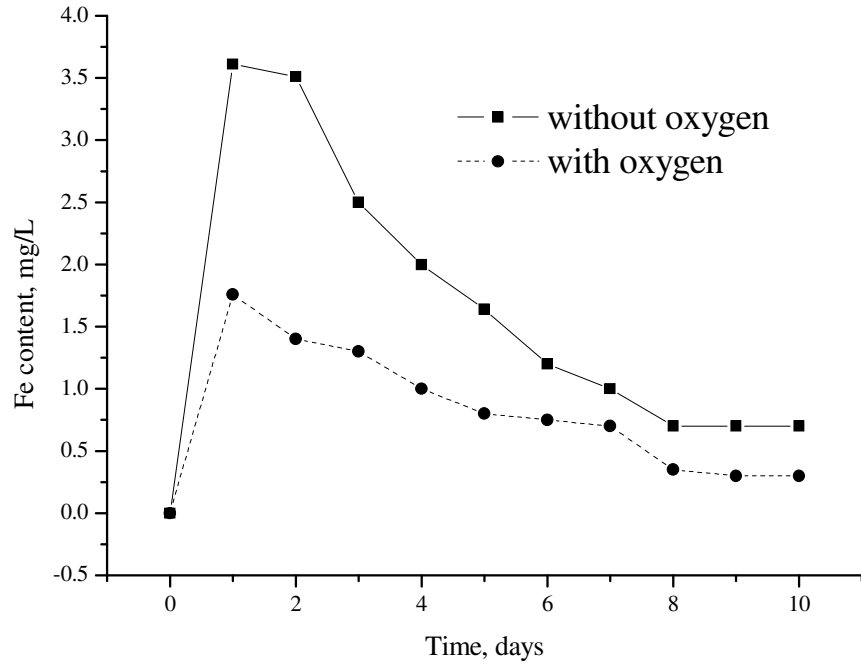


Fig.7. The variation of iron concentration within time with and without oxygen  
 $m(\text{corrosion scale})=5.0 \text{ g}$ ;  $V(\text{water})=300 \text{ mL}$ ;  $t=20 \text{ }^{\circ}\text{C}$ ;  $\tau=8 \text{ days}$ .

It can be conclude that iron concentration, with or without oxygen, in our experimental set-up stabilizes within 10 days. In some other investigations it was discovered that low dissolved oxygen (DO) levels led to increased release rates of ferrous iron Fe(II), while higher DO levels led to oxidation of soluble/mobile Fe(II) in the corrosion scales and lower release rates (Sarin et al., 2001). It was confirmed with our experimental results. After a while (approximately 8 days) the whole process of iron release reaches relatively constant and balanced behavior, for both oxic and anoxic conditions. It seems as all the forms of iron have reached their most wanted form or phase.

#### 4. Conclusion

In this work key-corrosion influencing water parameters (pH, dissolved oxygen and temperature) and corrosion deposits from iron and steel pipes of Belgrade drinking water distribution system were analyzed. It was concluded that depending on the composition of the water next to the pipe surface, corrosion of iron results in the formation of different compounds and solid phases. Corroded iron pipe immersed in the distilled water release iron in the water. Under real conditions, pH 6.0-8.0 at room temperature and DO content of 5.26 mg/L (at 22 °C) the content of  $\text{Fe}^{2+}$  ions is prevailing. The iron concentration in water stabilized within 10 days. Maximal iron concentration measured in this experimental set-up was 4.0 mg/L ( $7 \cdot 10^{-5}$  mol/L). Minimal concentration measured was 0.4 mg/L ( $7 \cdot 10^{-6}$  mol/L).

The release of iron depends on temperature of water. The concentration of iron decreased for samples held at 5 °C compared to samples held at 10 °C or 20 °C. It implies that lower iron concentrations and corrosion rates are present during the colder weather conditions. It seems that temperature has the highest effect at the beginning of the process. After a while the whole process of iron release reaches relatively constant and balanced behavior. What was also analyzed was the effect of oxygen. It was discovered that low dissolved oxygen (DO) levels led to increased release rates of ferrous iron Fe(II), while higher DO levels led to oxidation of soluble/mobile Fe(II) in the corrosion scales and lower release rates.

As a general conclusion, it can be once more emphasized that corrosion plays an important role in modifying water quality in drinking water distribution systems. The rate of iron release often does not give simple relationship to the rate of iron corrosion.

Further studies of corrosion are needed for many reasons, to get deeper knowledge on the mechanism of iron release from corroded pipes and to get better insight on the influence of water quality to corrosion of iron.

#### 5. Literature

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