Bacterial contribution to the deposits formation in steel water pipeline: X-ray diffraction study

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Please cite as: CHEMIK 2015, **69**, 9, 586–591

Introduction

Modern water treatment plants efficiently produce water of high quality and safe for consumers regardless of its origin and quality. The produced water as all natural waters is not sterile. Various microorganisms can survive treatment of potable water and enter drinking water distribution system (LeChevallier et al. 1987; Szewzyk et al. 2000). Microorganisms which colonize interior of drinking water distribution pipes might contribute to corrosion – microbiologically influenced corrosion (MIC).

X-ray diffraction (XRD) as a non-destructive analytical technique is used for identification of different crystalline phases (Tang et al. 2006; Hryniszyn and Cwalina 2014). The XRD technique was applied to determine biofilm impact on the composition of crystalline phases forming corrosion scales under simulated conditions typical of drinking water distribution systems (DWDS) (Teng et al. 2008). XRD was also used to study the effects of formation and transformation of corrosion products in DWDS through microbial activity and to compare the composition of corrosion products which were formed on pipe fragments, which were collected from places supplied with water from different sources (Sun et al. 2014). XRD can be used to study the impact of sulphates present in water on transformation of corrosion products and on microorganisms which colonize water pipelines. Additionally, XRD facilitates determination of relationship between the occurrence of specific corrosion products and activity of specific bacterial groups (Yang et al. 2014). It is also useful to assess the corrosion and MIC occurrence in drinking water distribution systems where disinfectants are used and the role of microorganisms in the corrosion process (inhibition or acceleration) (Wang et al. 2012).

The overview of literature about the application of XRD in studies of MIC products (Hryniszyn and Cwalina, 2014) has proved that the crystalline phases which are present inside the drinking water distribution system can indicate which group of microorganisms contributes to their formation. They facilitate also assessment of their role in corrosion. Thus, efforts have been made to analyse naturally dehydrated deposits from corroded steel pipe (a fragment sampled from drinking water distribution system) through XRD. The aim of this study was to determine possible participation of specific microbial groups in formation of deposits and to indicate their probable role in corrosion.

Material and Methods

Naturally dehydrated deposits were collected from different fragments of corroded steel pipe from drinking water distribution system (Fig. 1). Samples of the deposists were homogenised in a grinder. The XRD analysis of the powdered samples was carried out using XRD 7 X-ray diffractometer (Seifert-FPM) with Co K_α radiation (k=1. 79021Å) at a scanning range of $2\theta=10° – 100°$ (θ – angle of incidence/reflection which is defined as the angle between radiation beam and crystal plane). The Seifert software and ICCD catalogue data (2007) were used for the crystalline phase identification. Quantitative phase analysis of samples was performed by using Rietveld Method through SIRQUANT ™ software.

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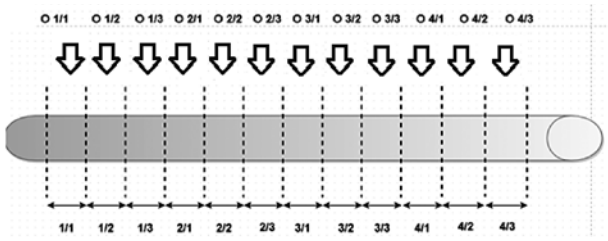

Fig. 1. Scheme of samples collection from the inner walls of corroded steel pipe; O 1/1 – O 4/3 - samples of deposits removed from respective pipe fragments

Results and discussion

The qualitative analysis of the O1/1, O1/2 and O1/3 samples showed the presence of goethite (FeOOH), magnetite (Fe_3O_4), hematite (Fe_2O_3), siderite ($FeCO_3$) and mackinawite (FeS). The mackinawite was absent in the other analysed samples. Iron oxyhydroxides and iron hydroxides ($Fe(OH)_x$) other than goethite were not detected in any of the samples.

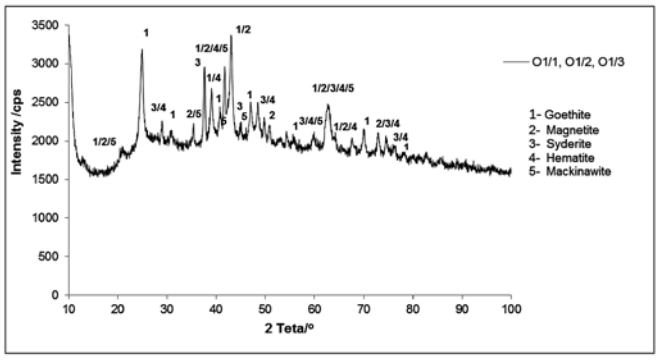

Fig. 2. Representative XRD pattern of naturally dehydrated deposits from corroded steel pipe – O1/1 to O1/3 samples

The presence of mackinawite (FeS) is a consequence of hydrogen sulfide production by sulphate reducing bacteria (SRB). This mineral is considered to be the first solid phase to be precipitated during mineralization performed by SRB (El Mendili et al. 2013). Mackinawite is not stable and may dissolve depending on the solution saturation level. For pH 4-7 (specific for environment which is beneficial for the growth and activity of SRB) the solution is supersaturated with respect to iron sulfide so the mackinawite does not dissolve (AlAbbas et al. 2013).

In the analysed samples pyrrhotite was not detected (FeS; magnetic pyrite). It might be associated with small amount of produced hydrogen sulphide and concentration of sulphides because when the concentration of sulphides is high mackinawite transforms to pyrrhotite (El Mendil et al., 2013).

Apart from mackinawite which is corrosion product formed by activity of SRB in anaerobic conditions (prevailing in layer of biofilm which directly adheres to metal surface), ferric oxides – magnetite, hematite and ferric oxyhydroxide – goethite (particularly high concentration in samples) were present (Tab. 1). The presence of these crystalline phases might be the effect of oxidation of biogenic iron sulphides (previously formed by SRB in anaerobic conditions) in aerobic conditions (prevailing in outer layer of biofilm which is exposed to flowing water) (Jack 2002). This oxidation might be abiotic and/or biotic process where iron oxidizing bacteria (IOB) are involved. IOB derive energy necessary to growth and activity from the oxidation of Fe(II) to Fe(III). Since the amount of energy extracted from this reaction is quite small for iron bacteria, large quantities of Fe(II) have to be oxidized. It was proved before (Hamzah et al. 2013), that in the presence of IOB the corrosion products include crystalline phases, such as ferric oxides and ferric hydroxides. Detection of goethite, magnetite and hematite in analysed samples (Fig. 2, Tab. 1) does not allow to determine unambiguously whether IOB have participated in their formation or whether they were oxidized abiotically. The amount of detected ferric oxides and ferric hydroxides (especially very high concentration of goethite in analysed deposits) suggests that oxidized forms of ferric iron might have been formed by IOB.

Table 1

The mean content of crystalline phases in corrosion products which were removed from steel pipe; the content of crystalline phases is expressed as mass percent

Sample	Mean content of crystalline phase, % (w/w)				
	Goethite (FeOOH)	Magnetite (Fe_3O_4)	Hematite (Fe_2O_3)	Siderite ($FeCO_3$)	Mackinawite (FeS)
O 1/1 – O 1/3	62.0 ± 0.2	14.2 ± 0.4	4.2 ± 0.6	18.6 ± 0.4	1.0 ± 0.4
O 2/1 – O 2/3	70.4 ± 0.8	18.9 ± 0.4	4.7 ± 0.8	8.8 ± 0.6	-
O 3/1 – O 3/3	57.4 ± 0.5	35.9 ± 0.4	1.7 ± 0.4	5.0 ± 0.4	-
O 4/1 – O 4/3	68.0 ± 0.5	13.2 ± 0.3	0.7 ± 0.3	18.1 ± 0.3	-

- not detected

Siderite ($FeCO_3$) was present in all the analysed samples. It might be produced during reaction of Fe (II) which was not bound to sulphides with carbonates and bicarbonates present in water.

The presence of mackinawite and siderite in corrosion deposits in the analysed sample might indicate corrosion caused by the activity of SRB and this process occurred according to so-called Electrical Microbially Influenced Corrosion (EMIC) (Enning et al., 2012; Venzlaff et al., 2013). EMIC assumes that some SRB use electrons from oxidation of metallic iron ($4Fe^0 \rightarrow 4Fe^{2+} + 8e^-$) which flow through sulfides (which are semiconductive) to cells of SRB. The EMIC mechanism might be assigned to corrosion of analysed drinking water distribution system pipe because a reaction which determines rate of all processes associated with metabolic activity of SRB is dissimilatory sulphate reduction ($8e^- + SO_4^{2-} + 9H^+ \rightarrow HS^- + 4H_2O$). In the case of small amount of protons (which occurs in drinking water) SRB reduce sulphates using bicarbonate present in water (reaction 1), which leads to formation of mackinawite and siderite (Enning et al., 2012):

$$4Fe^0 + SO_4^{2-} + 3HCO_3^- + H_2O \rightarrow FeS + 3FeCO_3 + 5OH^- \quad (1)$$

In each analysed sample the calcite was not detected, which might indicate that microorganisms were involved in formation of deposits present inside analysed pipe. Total hardness of water provided to consumers in Gliwice is high (326 mg/L $CaCO_3$) therefore limescale should be precipitated inside the pipe. In addition, hydroxyl ions which are produced during cathodic reduction of oxygen should shift the equilibrium of reaction (2) towards the carbonates production (Teng et al., 2008):

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \quad (2)$$

Carbonates should react with calcium cations present in water which should result in production of calcite ($CaCO_3$) according to the reaction (3) (Teng et al. 2008):

$$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3 \quad (3)$$

Considering these relations, in all the analysed samples calcite formed during reactions (2) and (3) should have been present in all the analysed samples but it was not detected. The reason of this might have been the presence of bacterial biofilm on the inner surface of the pipe. In these conditions calcium ions may have been absorbed by extracellular polymeric substances (EPS) which are synthesized by bacteria. Components of EPS include carboxylic and hydroxyl groups, which might bind strongly cations which might result in the lack of calcite precipitation (Zippel and Neu, 2011). This effect may indicate indirectly that bacteria participate in corrosion of the analysed pipe.

Summary

The determination of which crystalline phases may be formed as products of microbiologically influenced corrosion and are specific for corrosion processes running through different mechanisms was performed based on selected publications concerning MIC.

Consequently, the studies of deposits from corroded steel pipe which was a fragment of drinking water distribution system performed by X-Ray Diffraction(XRD) showed the presence of mackinawite (FeS), siderite ($FeCO_3$), goethite (FeOOH), magnetite (Fe_3O_4) and hematite (Fe_2O_3). The obtained results suggest that sulphate reducing bacteria and iron oxidizing bacteria might contribute to the corrosion of the analysed pipe.

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