

## Clogging of water supply wells in alluvial aquifers by mineral incrustations, central Serbia

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**Abstract.** The formation of incrustations on public water supply well screens reduces their performance considerably. The incrustations increase hydraulic losses, reduce the capacity of the well and screen, affect the quality of the pumped water and increase maintenance costs. In alluvial environments, the most common deposits are iron and manganese hydroxides. However, the rates of formation, compositions and levels of crystallization vary, depending on the geochemical characteristics of the alluvial environment, the microbiological characteristics of the groundwater and the abstraction method. Samples of 15 incrustations were collected from wells that tap shallow alluvial aquifers and were found to be dominated by iron. XRD analyses detected low-crystalline ferrihydrite and manganese hydroxide in the samples collected from the water supply source at Trnovče (Velika Morava alluvial). The incrustations from the Belgrade Groundwater Source revealed the presence of ferrihydrite and a substantial amount of goethite  $\alpha$ -FeOOH. Apart from goethite, greigite ( $\text{Fe}_3\text{S}_4$ ) was detected in three samples, while one sample additionally contained bernalite  $\text{Fe}(\text{OH})_3$  and monoclinic sulfur  $\text{S}_8$ . Among carbonates, only siderite was detected. Iron oxidizing bacteria generally catalyze deposition processes in wells, while sulfate reducing bacteria (SRB) play a role in the biogenic formation of greigite. Determining the nature of the deposited material allows better selection of rehabilitation chemicals and procedure.

**Key words:** alluvial aquifers, water supply wells, mineral incrustations, bacteria, central Serbia.

**Апстракт.** Формирање инкрустација на филтерским конструкцијама бунара смањује њихове перформансе. Створени талози повећавају хидрауличке губитке, смањују капацитет бунара, погоршавају квалитет експлоатисане воде и повећавају трошкове одржавања водозавхвата. У бунарима који захватају подземне воде алувијалних издани најчешће се јављају талози гвожђа и мангана. Ипак, брзина формирања, састав и степен кристалинитета талоба, зависе од геохемијских карактеристика средине, микробиолошких карактеристика и методе захватања воде. За потребе истраживања анализирано је 15 узорка инкрустација узетих из бунара који каптирају плитке алувијалне издани. Ренгенска дифракција показала је доминантно учешће ферихидрита и хидроксида мангана ниског степена кристалинитета у узорцима талоба са изворишта Трновче (алувијон Велике Мораве). Инкрустације из бунара са хоризонталним дренажним Београдског изворишта подземних вода осим ферихидрита садрже значајне количине гетита  $\alpha$ -FeOOH. У три узорка осим гетита, доказано је присуство грејгита ( $\text{Fe}_3\text{S}_4$ ), док је један узорак садржао поред ових минерала берналит ( $\text{Fe}(\text{OH})_3$ ) и моноклинични сумпор  $\text{S}_8$ . Од карбонатних минерала детектован је сидерит. Гвожђе оксидишуће бактерије катализују процесе формирања талоба у бунарима, док сулфато-редукујуће бактерије (СРБ) имају улогу у биогеном формирању грејгита. Одређивање минералског састава бунарских талоба и начина њиховог формирања кључно је за бољи одабир поступака и средстава за физичко-хемијске регенерације бунара.

**Кључне речи:** алувијалне издани, бунари, инкрустације, бактерије, централна Србија.

### Introduction

Alluvial environments are collectors of groundwater, which is often used for the public water supply. In Ser-

bia, around 70% of the water supply comes from groundwater of which over 50 % comes from alluvial aquifers (DIMKIĆ *et al.* 2007a). However, groundwater abstraction is often hindered by well clogging. It is well-

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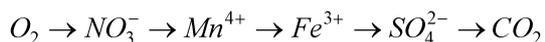
known that the formation of well incrustations leads to numerous adverse consequences, such as declining well capacity over time, reduction in conveyance capacity of the well screens and growing hydraulic losses.

The aim of this paper is to indicate the different mineralogical incrustations formed on screen slots of shallow wells taps different redox environments. The given results could improve well rehabilitation techniques and help in decision making for using appropriate chemicals depending on incrustation type.

Because of the adverse impact on groundwater abstraction, incrustation has been studied with regard to the iron oxidation rate and the formation of oxy(hydroxides) on screen slots by APPLIN & ZHAO 1989; WALTER 1997, HOUBEN 2006, HOUBEN & TRESKATIS 2007, MAJKIĆ 2013, while van BEEK 2011 examined declining well capacity as a result of mechanical clogging. Incrustations of screen slots are most often formed when the screens are positioned such that they tap different vertical geochemical zones (HOUBEN 2006, MAJKIĆ-DURSUN *et al.* 2012).

Most aquifers feature hydrochemical zonality. In alluvial aquifers, for instance, the amount of dissolved oxygen tends to decrease along the flow from the river to the aquifer, but also in the vertical direction, from the ground surface to the depth of groundwater. Being a strong oxidant, oxygen is generally used for oxidizing organic substances, but it is also expended in mineral weathering. The deeper and more distant the well is from the river, the tapped groundwater becomes an increasingly reducing. In neutral media (pH =7), redox zones can be identified according to the following descending sequence (JURGENS *et al.* 2009):

As the redox potential decreases, the following re-



duction reactions will take place: transformation of nitrate into nitrogen, reduction of manganese(IV), reduction of Fe(III), transformation of sulfate into hydrogen sulfide and, at a very low redox potential, methanogenesis (MCMAHON & CHAPPELLE 2008, JURGENS *et al.* 2009).

Iron, as the fourth major constituent of the Earth's crust, plays an enormous role in biogeochemical reactions (STRAUB *et al.* 2001, RODEN *et al.* 2004, FORTIN & LONGLEY 2005, DIMKIĆ *et al.* 2011). Under reduction conditions, iron travels underground as dissolved Fe(II). In the presence of oxygen, in media exhibiting close-to-neutral pH value, iron rapidly oxidizes into insoluble Fe(III), producing iron oxy(hydroxides) and oxides (DAVIDSON & SEED 1983, STUMM & MORGAN 1996, HOUBEN 2003, MAJKIĆ 2013). The transformation of soluble Fe(II) into insoluble Fe-oxy(hydroxide) requires mixing of oxygen-containing water with reducing water carrying dissolved iron ions (van BEEK *et al.* 2010). Mixing of groundwater from different geochemical zones can also be a result of permanent

drawdown in the near-well region, due to over-exploitation (APPLIN & ZHAO 1989, LARROQUE & FRANCE-SCHI 2011, MAJKIĆ 2013). Increasing pH levels and the release of CO<sub>2</sub> also affect the rate of iron oxidation (DAVIDSON & SEED 1983).

Oxidation of Mn(II) requires a higher oxidation potential (0.6–1.2 V) than the oxidation of Fe(II) (0.0–0.5 V) (HOUBEN & TRESKATIS 2007). The deposition of manganese is much slower than that of iron; the process is accelerated at high pH values (pH > 8) (MARTIN 2005). Sulfates can be reduced in the groundwater of shallow alluvial sediments, which CHAPPELLE *et al.* (2009) associate with a possibly high reaction rate between Fe(II) and H<sub>2</sub>S, producing insoluble iron sulfides (FeS).

The role of bacteria in the formation of incrustations can be very important in terms of catalyzing reaction rates and forming biofilm, as well as from the perspective of the biogenic origins of minerals (SMITH & TUOVINEN 1985, CULLIMORE 1999, LOVLEY 2000, EHRILCH 2002, FRANKEL & BAZYLINSKI 2003, EMERSON & WEISS 2004).

In order to study well clogging, two different alluvial sources were selected in the present research. Long-term groundwater chemistry monitoring had been undertaken at these water supply sources and the results of microbiological analyses revealed incrustations on well screens. The Water Supply Source Trnovče (Fig 1.) was chosen as an example of extremely rapid clogging and formation of considerable incrustations on well screens and well pump discharge pipes (MAJKIĆ-DURSUN *et al.* 2012, MAJKIĆ 2013). The Belgrade Groundwater Source (Fig 1.) was selected because of its importance for the public water supply of Serbia's capital. The wells at this source tap the alluvium of the Sava River, while those at Trnovče tap the alluvium of the Velika Morava River.

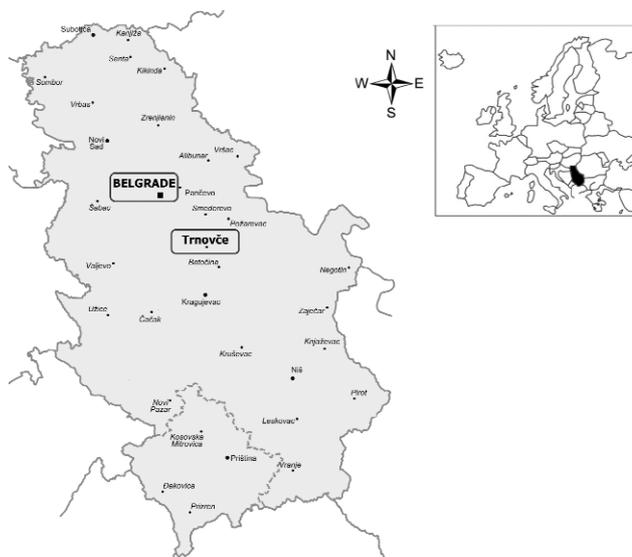


Fig. 1. Sampling sites: water supply sources Trnovče and Belgrade.

## Study Areas

At the location of Trnovče Water Supply Source the aquifer is comprised of alluvial sediments, whose total thickness is about 15 m. The part of the aquifer from which groundwater is extracted is predominantly represented by sandy gravels (Fig. 2.). The average thickness of these sandy-gravels in the Trnovče area is

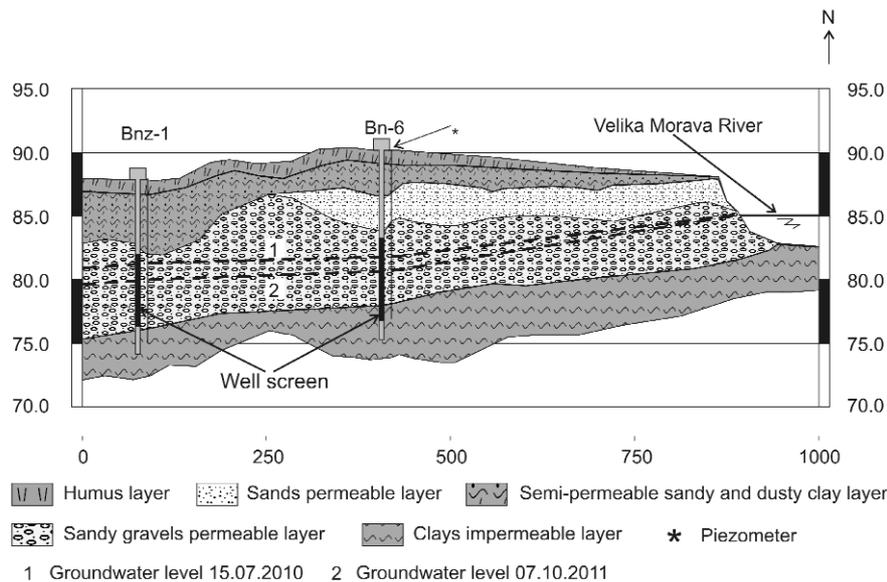


Fig. 2. Simplified hydrogeological cross section from tube well Bnz-1 to Bn-6

Table 1. General data for selected tube wells at the Trnovče groundwater source. BT-16 was drilled in 2007. n.a., not available.

Tube well	Depth (m)	Screen position (m a.s.l)	Pump position (m a.s.l)	Distance from the river (m)	$\frac{Q_{av.2002/}}{Q_{av.2012}}$ Q (L/s)	$Eh_{aver.}$ (mV)
BT-16	15.3	83.12–78.62	77.1	645	-/n.a.	89
Bn-9G	16.0	80.88–76.62	76.0	520	11.2/6.5	229
Bn-8a	15.0	82.50–76.50	78.5	1080	9.2/5.3	n.a
Bn-6	14.5	83.00–77.00	76.5	470	9.9/5.0	175
Bn-5	15.1	82.55–75.15	76.9	350	9.0/3.0	234
Bnz-1	13.6	82.16–76.16	76.2	780	20.0/5.1	162

about 10 m, but the thickness of saturated part of aquifer is usually smaller (MAJKIĆ-DURSUN *et al.* 2012). The sandy-gravel sequence is covered by fine-grain sediments, generally sandy and dusty clays, dusty sands and sandy clays whose thickness ranges from 5 to 6 m (Fig. 2.). Aquifer floor is made from Neogene clays. The thickness of water saturated part of the aquifer varies during the year, but generally groundwater pumping levels are felt into zone of well screens (MAJKIĆ-DURSUN *et al.* 2012, MAJKIĆ, 2013) (Table 1).

Six tube wells (BT-16, Bn-9G, Bn-8a, Bn-6, Bn-5 and Bnz-1) were selected at Trnovče groundwater source for well deposits analysis.

General data for each selected tube well from Trnovče groundwater source are given in Table 1.

The Belgrade Groundwater Source is comprised of 99 radial wells and about 50 tube wells, located along the Sava's bank upstream from its confluence with the

Danube. The Sava River alluvial was developed through several sedimentation cycles and sequences: sandy gravel, sands of various grain sizes, and silty and clayey sediments. The thickness of the Quaternary strata is up to 25 m. DIMKIĆ & PUŠIĆ (2014) distinguish, two cross-sectional zones, with regard to the grain sizes of the sediments. According to those authors, Lower zone is consisting of coarse-grain sediments (Fig 3) in which radial well laterals are installed (Table 2). Grain sizes of Lower zone rang from medium-grain sand to fine-grain gravel. These sediments occasionally feature clay, sandy clay and silt interbeds and

lenses: while the Upper zone is consisting of fine-grain sediments, with poorer filtration properties (Fig. 3).

General data for selected radial wells from Belgrade groundwater source are given in Table 2.

The radial wells are situated adjacent to the river, and some well laterals are below the riverbed, most of the groundwater that flows to the wells is partly from the wider zone of the alluvial aquifer, and partly from the deeper aquifer. The main redox characteristic of this source is a relatively low Eh, generally below 150 mV (Table 2).

Table 2. General data for selected radial wells from Belgrade groundwater source (\*radial well RB-7 set laterals in two positions).

Radial well	Well depth (m)	Lateral position (m a.s.l.)	Total lateral number/ Number of active laterals	Pumping water level (in 2014) (m a.s.l.)	$Q_{\text{initial}}/Q_{\text{well2014}}$ (L/s)	$Eh_{\text{aver.}}$ (mV)
RB-42	25.7	50.5	8/3	55.59	110.0/12.5	85
RB-46	23.6	52.4	8/5	58.03	116.0/16.8	75
RB-48	32.0	45.5	8/6	53.87	135.0/23.0	80
RB-3m	23.2	53.0	8/4	59.16	185.0/44.0	100
RB-3	27.6	48.5	11/1	53.21	225.0/ 5.2	120
RB-4	25.3	50.4	8/8	58.05	318.0/105.0	160
RB-7*	24.5	(I) 50.5 (II) 51.3	10/6	55.20	196.0/18.0	100
RB-69	18.6	58.2	8/3	63.18	100.0/6.3	100
RB-83	24.0	53.0	8/7	56.25	100.0/41.0	110

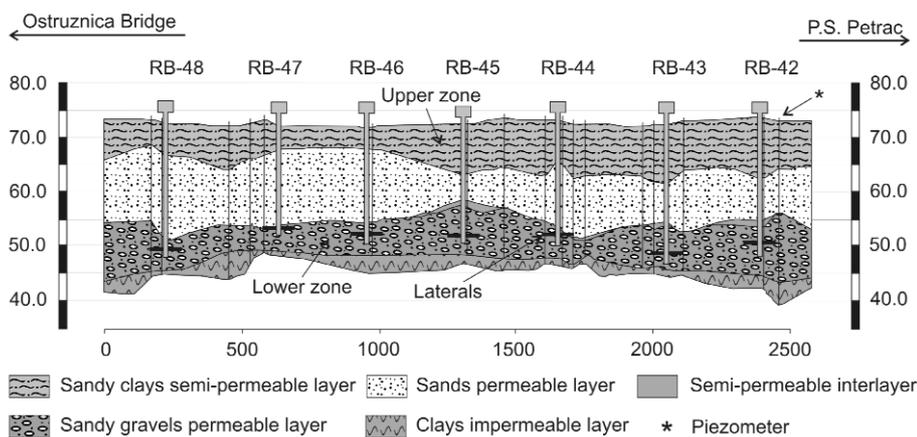


Fig. 3. Simplified hydrogeological cross-section from radial well RB-48 to RB-42 (Belgrade groundwater source - the Sava River right waterside; sector Surčin).

## Materials and methods

Samples of 15 incrustations, collected from wells that tap shallow alluvial aquifers, were analyzed for the purposes of this research, following special-purpose groundwater chemistry monitoring from 2006 to 2013 at Belgrade and 2008–2013 at Trnovče groundwater source. The results of groundwater chemical monitoring were used to define the predominant redox processes, applying the chemical criteria proposed by McMAHON & CHAPPELLE (2008), JURGENS *et al.* (2009) and chemical and microbiological criteria proposed by MAJKIĆ (2013). The redox categories and prevailing redox processes were identified using the input data and the threshold values established in the *Workbook for identifying redox processes* (JURGENS *et al.* 2009). The criterion for the selection of wells whose incrusta-

tions were to be tested was the existence of different oxidation-reduction categories based on the outcomes of groundwater chemical analyses. According to JURGENS *et al.* (2009) and MAJKIĆ (2013), groundwater samples are often mixture of multiple layers of an aquifer, and that mixing in well bore can produce chemistry results that suggest multiple redox condition. Commercial Biological Activity Reaction tests (BART) were used for microbiological analyses of groundwater. During investigation four different BART tests were applied: IRB BART

(for Iron-related bacteria), SRB BART (for Sulfate-reducing bacteria), HAB BART (for Heterotrophic aerobic bacteria) and SLIME BART (for Slime forming bacteria). Six wells were selected at Trnovče groundwater source (BT-16, Bn-9G, Bn-8a, Bn-6, Bn-5 and Bnz-1), where the redox category was determined to be mixed oxic-anoxic (mixture of oxygen and iron-reducing groundwater  $O_2$ -Fe(III)). At Belgrade groundwater source, the selected wells included six radial wells (RB-7, RB-42, RB-4, RB-83, RB-69, RB-3), whose redox category was anoxic (iron-reducing groundwater), and three wells that fell into the mixed anoxic category (wells RB -3m, RB-46 and RB-48), defined as iron and sulfate-reducing groundwater (Fe(III)- $SO_4$ ).

Prior to sampling, the wells were visually inspected with an underwater (GeoVISION Deluxe) camera.

Incrustations from the radial well laterals at Belgrade were sampled by specially-trained divers, who removed the incrustations from the inside of the laterals. At Trnovče, incrustations were sampled from tube wells during the course of mechanical regeneration, prior to applying chemicals.

The samples were placed in sterile jars and refrigerated to prevent oxidation. The samples were dried at a temperature of 60°C (CORRNEL & SCWERTMANN 1996), or 37°C if the samples contained manganese. For analytical purposes, the samples were ground into powder in an agate mortar.

X-ray powder diffraction (XRPD) analyses of the samples were conducted using a Philips PW-1710 automated diffractometer (equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter), including a Cu-tube operated at 40 kV and 30 mA. Data were collected in the 2 $\theta$ -range between 4–80°, with a counting time of 0.25 s per step and a step size of 0.02° 2 $\theta$ . A fixed 2° divergence and 0.2 mm receiving slits were used.

The morphological characteristics were determined and the semi-quantitative chemical analyses of the incrustations performed applying the SEM-EDS technique (SEM model: JEOL JSM – 6610LV). The same instrument was used to photograph the bacteria. The powdered samples were sputter coated with 24-carat gold. The limit of detection for the semi-quantitative analyses was 0.1wt. %. The main shortfall of this method was the high spectrum baseline, which rendered the determination of micro-components in the sample rather difficult.

## Results

The outcomes of the present study of the geochemical compositions of the incrustations (Table 3) showed that ferrihydrite, low-crystallinity iron-oxy(hydroxide) and, to a lesser extent, manganese hydroxides were precipitated in the mixed oxic-anoxic redox environment where the redox process was defined as O<sub>2</sub>-Fe(III) reduction. Ferrihydrite (Fe<sub>5</sub>HO<sub>8</sub>·4H<sub>2</sub>O) is often referred to in the literature as “amorphous iron hydroxide”, although the crystallographic order of this mineral is low (CORNNEL & SCHWERTMANN 2003). Ferrihydrite is generally the most common mineral phase of recent iron incrustations (MAJKIĆ 2013). The proportion of the ferrihydrite mass in the analyzed incrustations was between 625.9 to 762.2 g/kg, while that of Mn(OH)<sub>2</sub> was 2.67 g/kg to 212.8 g/kg. No Mn(OH)<sub>2</sub> deposits were found in the samples collected from anoxic environments (Fig. 4).

Low-crystallinity iron oxy(hydroxides) are considered the dominant sorbents of dissolved metals in groundwater, given their large specific surface and surface capacity due to the existence of a large number of OH<sup>-</sup> groups, such that low-crystallinity Fe-oxy(hy-

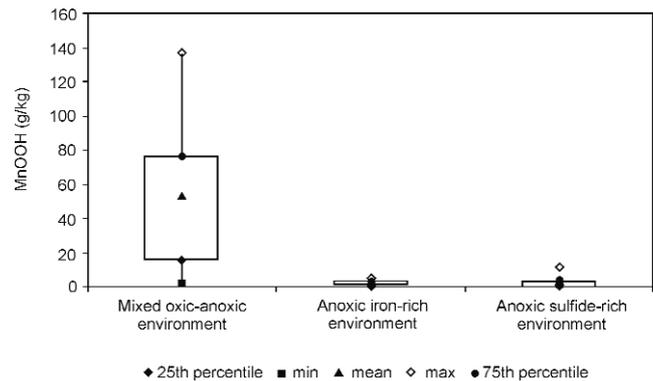


Fig. 4. Box-plot of low-crystallinity Mn(OH)<sub>2</sub> proportions of incrustations in different geochemical environments.

droxides) are chemically more reactive than crystallized Fe-oxides (TADESSE 1997). The results from this investigation also showed that phosphates adsorb very well on ferrihydrite, while the proportion by weight decreased in incrustations where goethite was detected in conjunction with iron sulfides (Table 3).

A scanning microscope detected two species of iron-related bacteria: *Gallionella ferruginea* and *Lepthothrix* sp. in samples (Figs. 5 and 6). In all the samples collected from wells in mixed oxic-anoxic environment, the bacteria were coated with a thick layer of Fe-oxy(hydroxide) (Fig 5). According to RODEN *et al.* (2004), Fe(II) oxidizing bacteria dwell in microaerobic environments, with lower oxygen concentrations. FORTIN & LANGLEY (2005) explained that the metabolic activity of acidophilous and neutrophilous iron bacteria under oxic conditions causes the oxidation of Fe(II) into Fe(III) and the creation of biogenic iron oxides as extracellular deposits on the walls of bacterial cells. This layer has multiple roles (FRENKEL & BAZYLINSKI 2003). HANERT (1992) concluded that the

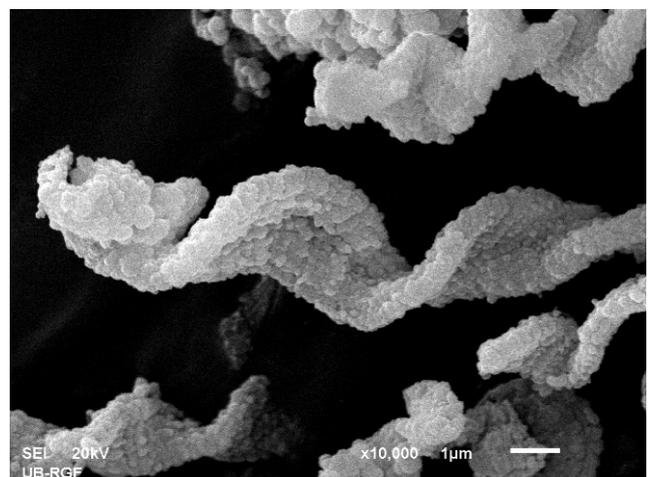


Fig. 5. Scanning electron image of IRB *Gallionella ferruginea* with biogenic mineral coatings on their cells in incrustations of a water well in a mixed oxic-anoxic environment.

Table 3. Selected geochemical parameters of water well incrustations (analyses performed using EDS). \*Oxygen determined by stoichiometry. LLD, low limit detection.

Sample	Water supply source	SiO <sub>2</sub> (wt%)	Al <sub>2</sub> O <sub>3</sub> (wt%)	Fe <sub>2</sub> O <sub>3</sub> (wt%)	MnO (wt%)	CaO (wt%)	P <sub>2</sub> O <sub>5</sub> (wt%)	S (mg/kg)	As (mg/kg)	Ba (mg/kg)	Sn (mg/kg)	Sb (mg/kg)
BT-16	Trnovče	8.6	0.2	69.3	0.3	7.2	12.3	56.7	73.3	383.3	166.7	120.0
Bn-9G		6.9	0.3	72.8	7.7	5.7	4.4	73.3	336.7	483.3	146.7	320.0
Bn-8a		5.6	0.3	72.8	5.4	6.3	7.9	46.7	288.0	366.7	293.3	220.0
Bn-6		9.0	0.4	76.2	1.5	4.9	7.2	<LLD	573.0	306.7	<LLD	83.3
Bn-5		5.3	0.4	62.6	21.3	4.3	4.3	<LLD	507.0	586.7	156.7	<LLD
Bnz-1		6.5	0.4	65.1	13.6	4.3	6.6	<LLD	<LLD	186.7	146.7	336.7
RB-48	Belgrade	5.7	1.0	75.9	0.0	1.3	0.4	15313.3	80.0	<LLD	<LLD	73.3
RB-46		29.1	3.6	53.5	0.0	1.4	0.1	9656.7	61.8	<LLD	<LLD	<LLD
RB-3m		3.8	0.6	79.1	0.0	2.2	2.7	10853.3	<LLD	80.0	<LLD	73.3
RB-42		54.8	6.4	18.1	1.8	12.2	0.0	963.3	<LLD	113.3	393.3	186.7
RB-7		7.3	0.4	77.4	0.2	5.7	7.8	53.3	166.7	<LLD	<LLD	<LLD
RB-4		10.9	0.2	79.3	0.1	3.8	4.3	<LLD	256.7	306.7	<LLD	86.7
RB-83		4.1	0.3	67.2	0.2	9.3	16.3	<LLD	345.0	300.0	<LLD	405.0
RB-69		17.6	4.4	51.9	0.4	10.8	10.4	350.0	104.0	375.0	110.0	235.0
RB-3		43.5	5.1	33.9	0.7	8.7	4.5	<LLD	<LLD	<LLD	<LLD	<LLD

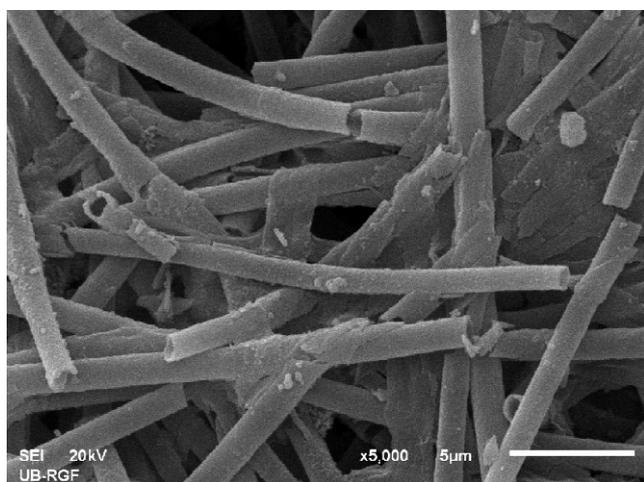


Fig. 6. Scanning electron image of IRB *Leptothrix* sp. without biogenic mineral coatings on their cells in incrustations of a water well in an anoxic environment (well RB-69, Belgrade).

coats become the cores for future mineralization (i.e. they continue to accumulate Fe- oxy(hydroxides)).

In anoxic environments, the formation of incrustations on well screens is slower than in mixed oxic-anoxic environment. The results of XRD analyses of incrustations sampled from anoxic iron-rich environments showed the presence of better crystallized forms like goethite  $\alpha$ -FeOOH. The re-crystallization of low-crystalline ferrihydrite into thermodynamical-

ly stable goethite depends on several factors: increasing pH (SCHWERTMANN & MURAD 1983), temperature (DAS *et al.* 2011), the presence of inhibitors like phosphates (GALVEZ *et al.* 1999, WANG *et al.* 2013), silicates (CORNELL & SCWERTMANN 2003), and organic substances (CORNELL & SCWERTMANN 1979), as well as on the concentrations of adsorbed bivalent metals (MARTINEZ and MCBRIGE 1998). Previously adsorbed anions and cations might be released during the re-crystallization process. The occurrence of siderite  $\text{Fe}(\text{CO})_3$  was noted in incrustations sampled from wells that tap anoxic groundwater at Belgrade groundwater source. The presence of siderite can also be associated with the bioreduction of ferrihydrite (MORTIMER & COLEMAN 1997, FREDRICKSON *et al.* 1998) (Fig. 7). The simultaneous presence of Fe oxides, carbonates and sulfides could be indicative of a change in redox conditions during incrustation, or of the presence of different micro-environments in well laterals.

Anoxic S-rich environments are characterized by parallel Fe(III)- $\text{SO}_4$  reduction processes. Such conditions were noted in three of the studied wells at Belgrade groundwater source. The proportions of sulfur in the incrustations on radial well laterals were from 9.66 to 15.3 wt %. In the incrustation sample from well RB-48, XRD diffraction revealed the presence of greigite  $\text{Fe}_3\text{S}_4$ , bernalite  $\text{Fe}(\text{OH})_3$ , sulfur  $\text{S}_8$  and goethite  $\alpha$ -FeOOH. The scanning electron microscopy of the incrustation sample is shown in Fig. 8, while Fig. 9 shows the results of XRD analysis. The

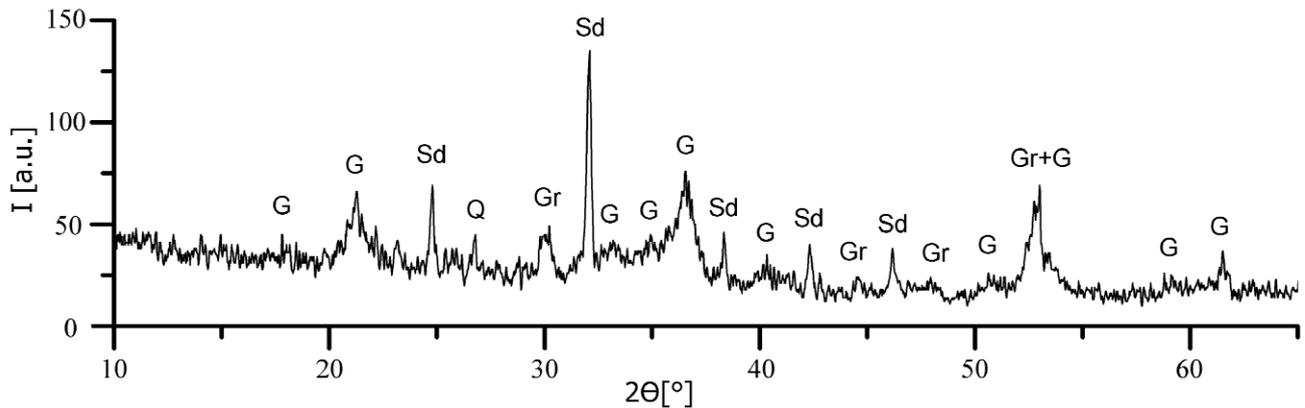


Fig. 7. XRD pattern of incrustation from well RB-3m (Belgrade groundwater source). Legend: **Sd**, siderite ( $\text{Fe}(\text{CO})_3$ ); **Q**, quartz ( $\text{SiO}_2$ ); **G**, goethite ( $\alpha\text{-FeOOH}$ ); **Gr**, greigite ( $\text{Fe}_3\text{S}_4$ ).

occurrence of elemental sulfur in the incrustation sampled from well RB-48 is attributable to sulfide oxidation by means of ferrihydrite and goethite, where elemental sulfur is the end product of oxidation (POULTON *et al.* 2004). Elemental sulfur can also be reduced to sulfide by most sulfate-reducing bacteria (MADIGAN *et al.* 2009). Greigite is a tiospinel of iron, a sulfur analog of magnetite, whose general formula is  $\text{Fe}_3\text{S}_4$ . This metastable mineral can occur biogenically, through the activity of *Desulfovibrio desulfuricans* in the presence of iron salts (RICKARD & LUTHER 2007), or magnetotactic bacteria, including anaerobic sulfate-reducing bacteria, which can synthesize greigite (MANN *et al.* 1990, POSTFAI *et al.* 1998). In Germany, HOUBEN & TRESKATIS (2007) attributed the formation of greigite and the occurrence of sulfur in well incrustations to bacterial activity. The microbiological analyses of the groundwater samples collected from the above-mentioned well revealed the presence of sulfate-reducing bacteria (SRB), but their species could not be identified by the BART method applied.

Bernalite  $\text{Fe}(\text{OH})_3$ , detected in a sample collected from well RB-48 (Fig. 8), occurred as a pseudo-octahedral to pseudo-cubic crystal. FERNANO and SURANGANEE (2009) associate the occurrence of bernalite with acidic sulfate soils that contain iron sulfides. It is rare and its presence in well incrustations should be studied in detail with regard to site-specific micro-environmental conditions.

Quartz  $\text{SiO}_2$  and clay minerals were found in the analyzed samples, as products of the natural environment. Their proportion was higher at Belgrade (3.8–54.8 wt%) than at Trnovče (5.6–9 wt%) as a result of corrosion processes on old laterals.

## Discussion

The decline in water well capacity at the Belgrade Groundwater Source was initially caused by draw-

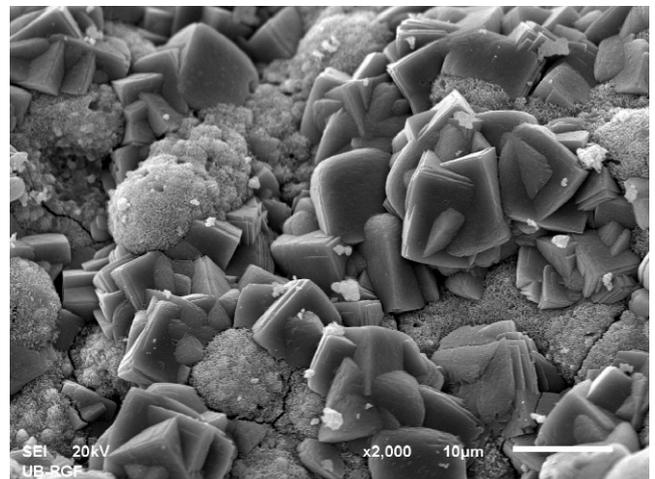


Fig. 8. Scanning electron image of incrustation from well RB-48 (Belgrade groundwater source). Image of bernalite ( $\text{Fe}(\text{OH})_3$ ) associate with greigite ( $\text{Fe}_3\text{S}_4$ ).

down, then by riverbed colmation and finally by well ageing and ruination (DIMKIĆ *et al.* 2007b). During the initial period of service (1956 to 1965), the wells relied on dynamic groundwater reserves to a large extent. This period was characterized by high groundwater levels but there were initial signs of decline. In the second period (1965 to 1986), colmation of the Sava riverbed and well aging due to clogging of radial well laterals resulted in a declining capacity of the source. At that time, the decreasing well capacity was offset by the construction of new wells and physical (and to a lesser extent chemical) regeneration of laterals. Very low groundwater levels were typical of that period. Static groundwater reserves were increasingly being used. The third period (1985 to 2012) was characterized by very low spending for maintenance and development of the source. This was a result of the crisis in Serbia in the 1990s and a lack of funding. As the wells aged and failed, the capacity of the entire source decreased

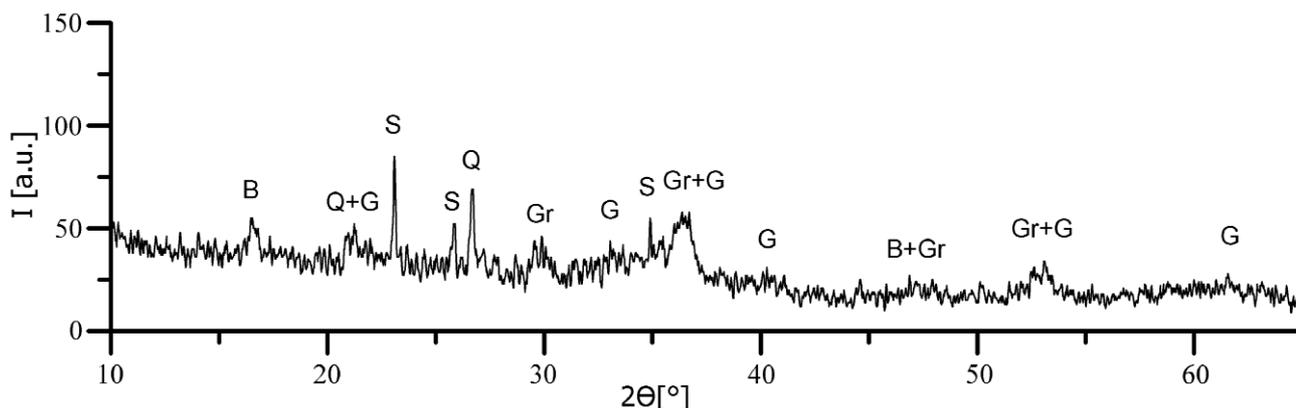


Fig. 9. XRD pattern of incrustation from well RB-48 (Belgrade groundwater source). Legend: **G**, goethite ( $\alpha$ -FeOOH); **B**, bernalite ( $\text{Fe}(\text{OH})_3$ ); **Q**, quartz ( $\text{SiO}_2$ ); **S**, sulfur ( $\text{S}_8$ ); **Gr**, greigite ( $\text{Fe}_3\text{S}_4$ ).

(DIMKIĆ *et al.* 2007b). In the Table 2, are shown data for decreasing capacity of selected radial wells. At Belgrade, physical regeneration has been the method of choice for years, using WOMA pumps with directional nozzles at a pressure of 30–60 bars.

Until the year 1998, the water supply source at Trnovče operated five wells, whose total capacity was 60 l/s. Today, there are 20 tube wells, whose average yield is about 5 l/s per well (Table 1). Available data on well capacity variation at Trnovče over the past ten years indicate that well yield is gradually declining (Table 1) and that post-regeneration capacity is far below the initial capacity (MAJKIĆ-DURSUN *et al.* 2012). Camera inspection was undertaken before and after regeneration in 2011 at Trnovče, to monitor the effectiveness of regeneration (MAJKIĆ 2013). The footage and the post-regeneration groundwater level and discharge monitoring data revealed only short-term effects (several months).

Mineral and chemical analyses showed that iron incrustations of different crystallinity levels were dominant at both water supply sources. Their total proportion by weight ranged from 18.1 to 79.3%. The average was 63.7. The state of disequilibrium was caused by mixing of reduced iron-containing groundwater with oxygenated groundwater (mixed oxic-anoxic groundwater category), while the well was in service. In such environments, incrustations comprised of ferrihydrite ( $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ ) and low-crystallinity  $\text{Mn}(\text{OH})_2$  are common and were typical of the source at Trnovče, while anoxic environments revealed goethite ( $\alpha$ -FeOOH), siderite  $\text{Fe}(\text{CO})_3$ , greigite ( $\text{Fe}_3\text{S}_4$ ), bernalite  $\text{Fe}(\text{OH})_3$  and quartz ( $\text{SiO}_2$ ). Iron sulfide minerals were detected in samples collected from anoxic S-rich geochemical settings.

The crystallinity level was higher in samples collected from wells where the time interval between two regenerations was longer than two years.

Minerals like quartz and clay occurred as products of the media passively incorporated into the well

deposits. Their amounts were the greatest in the wells affected by both clogging and corrosion processes (wells RB-42 and RB-46). Studies have shown that bacteria play an important role in the formation of incrustations, especially *Gallionella ferruginea* and *Leptothrix* sp.

The regenerations carried out at Trnovče were effective only in the short term. The application of hydrochloric acid and citric acid as inhibitor were not sufficient to sanitize the near-well region, resulting in a reduced life of the well. At Belgrade, mechanical regeneration of radial wells tended to sanitize only a part of the lateral, leading to a reduction in the conveyance capacity of the lateral and eventual sealing. High-crystallinity incrustations are rather difficult to remove, so the study of the rate of re-crystallization of ferrihydrite to goethite is of major importance in assessing the proper time interval to the next regeneration.

Apart from scientific significance, the occurrence and re-crystallization of mineral deposits is also important in economic terms. The reduction in solubility and hardening of incrustations determine the method and cost of regeneration. Mineral and chemical analyses of the composition of the incrustation are also important for proper selection of chemical agents that will enhance the effectiveness of regeneration. Given the cost of regeneration, prior analyzing of the incrustations will enable considerable savings and extend the time interval between two regenerations.

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## Резиме

### Колмирање бунара за јавно водоснабдевање у алувијалним аквиферима централне Србије минералним инкрустацијама

Опадање капацитета бунара у времену настаје као последица процеса корозије и колмирања. Процесе корозије могуће је спречити уградњом одговарајућих филтерских конструкција отпорних на корозију, док процеси колмирања могу настати без обзира на врсту уграђеног материјала. Колмирање бунара доводи до опадања капацитета бунара, повећања паразитских губитака, пораста економских средства неопходних за трошкове одржавања и на крају напуштања водозавхвата. Формирање талоба може бити механичко, хемијско и биохемијско. У циљу сагледавања врста талоба формираних у бунарима за јавно водоснабдевање који каптирају алувијалне издани, одабрано је 15 узорак за детаљне анализе. Одабир узорака вршен је тако да се задовоље критеријуми различитих оксидо-редукционих средина (мешано оксично-аноксична средина – извориште Трновче, 6 узорака), аноксична средина у којој преовлађује процес редукције Fe(III) (Београдско извориште подземних вода – 6 узорака) и мешана аноксична средина са преовлађујућим процесом паралелне редукције Fe(III)-SO<sub>4</sub> у подземној води (Београдско извориште подземних вода – 3 узорка). Хемијске и микробиолошке анализе подземних вода извршене су у лабораторији Института „Јарослав Черни“, док су семи-квантитативне анализе хемијског састава талоба и ренгенска дифракција извршене на Рударско-геолошком факултету.

Као доминантне наслаге у бунарима, који каптирају алувијалне издани Велике Мораве и Саве, јављају се (окси)хидроксици гвожђа. Просечан удео ових талоба креће се од 18.1 до 79.3 тежинских процента, са средњом вредношћу од 63.7 теж. процента. Узорци са изворишта Трновче показују да се услед мешања кисеоника са подземним водама богатим двовалентним гвожђем брзо формирају наслаге ферихидрита (625.9 до 762.2 g/kg). У мањем уделу у талозима се јавља манган-хидроксид ниског степена кристалинитета (2.67 g/kg до 212.8 g/kg). Обзиром да је за формирање талоба мангана неопходан већи редокс потенцијал манганове инкрустације нису детектоване у аноксичним срединама. Само у једном узорку (Вп-8а) било је довољно времена између две регенерације бунара за формирање гетита ( $\alpha\text{-FeOOH}$ ). Гвожђе-оксидишуће бактерије у условима брзе хемијске оксидације гвожђа талобе око себе слој ферихидрита чиме се прилагођавају условима мешовите оксично-аноксичне средине. *Gallionella ferruginea* и *Leptothrix* sp. катализују процесе оксидо-редукције гвожђа и

