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The effect of iron oxidation in the groundwater of the alluvial aquifer of the Velika Morava River, Serbia, on the clogging of water supply wells

BRANKICA MAJKIĆ-DURSUN*, ANDELKA PETKOVIĆ and MILAN DIMKIĆ

*Jaroslav Černi Institute for the Development of Water Resources, Jaroslava Černog 80,
Belgrade, Serbia*

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Abstract: The oxidation of iron(II) dissolved in groundwater and subsequent precipitation of the oxidation products on the screens and discharge pipes of water wells that tap shallow alluvial aquifers leads to the formation of well encrustations. The main goal of the presented research was to determine the reasons for the rapid clogging of water supply wells. In the particular case of the alluvial aquifer of the Velika Morava River, Serbia, the encrustations include mostly iron-(hydr)oxides (62.6 to 76.2 wt. %). Groundwater over-exploitation leads to the mixing of different geochemical zones and the formation of a redox front. During the two-year survey, the concentrations of the dissolved oxygen in the groundwater varied over a wide range from 0.1 to 7.1 mg L⁻¹ as the result of unsuitable exploitation regime. The on site measured groundwater temperature, concentrations of dissolved oxygen and pH values, and the laboratory analysis of dissolved iron concentrations showed that iron precipitation was favorable under groundwater over-exploitation conditions.

Keywords: iron encrustations; groundwater over-exploitations; Trnovče; redox front formation.

INTRODUCTION

The rapid formation of encrustations inside the wells of the water supply source Trnovče in Serbia necessitated detailed research of the clogging process. Decreasing groundwater levels and well discharges indicated over-exploitation conditions at this groundwater source. Over-exploitation could be defined as the situation in which the average rate of aquifer abstraction is greater than, or close to, the average recharge rate. Over-exploitation implies intensive use of groundwater, resulting in declining groundwater levels in the wells and over an extended area of the source, changes in the hydraulic gradients and aquifer recharge regime, reduced discharges of natural springs and variations in the oxic

*Corresponding author. E-mail: brankica.majkic@jcerni.co.rs
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state and groundwater quality, which usually deteriorates due to groundwater inflow from the upland. Case studies of rapid well clogging under over-exploitation conditions were presented in the USA,¹ Germany² and France.³ An unsuitable pumping scheme produces a general decline in the groundwater levels and disturbs the geochemical conditions of the initial system.³ Under such conditions, anoxic groundwater become oxidized, while the groundwater composition and microbial ecology are changed.^{3,4}

Based on the chemical analyses of the groundwater samples, a study of data derived from microbiological analyses and assessments of the data on the static and dynamic groundwater levels inside the wells, the Trnovče source was characterized as an alluvial setting where oxic and anoxic ground waters blend.^{5,6} High concentrations of dissolved oxygen in the upper, water unsaturated part, of the aquifer and the inflow of anoxic groundwater featuring elevated iron concentrations from deeper, saturated parts of the aquifer have created a redox front within the well screens (Fig. 1), leading to a thorough precipitation of iron-(hydr)oxides.⁶ The conditions that lead to the formation of ferric deposits in water wells were analyzed in this study. Hydrochemical data were collected during a two-year survey (2010–2011), while the discharge data were analyzed for the last ten years.

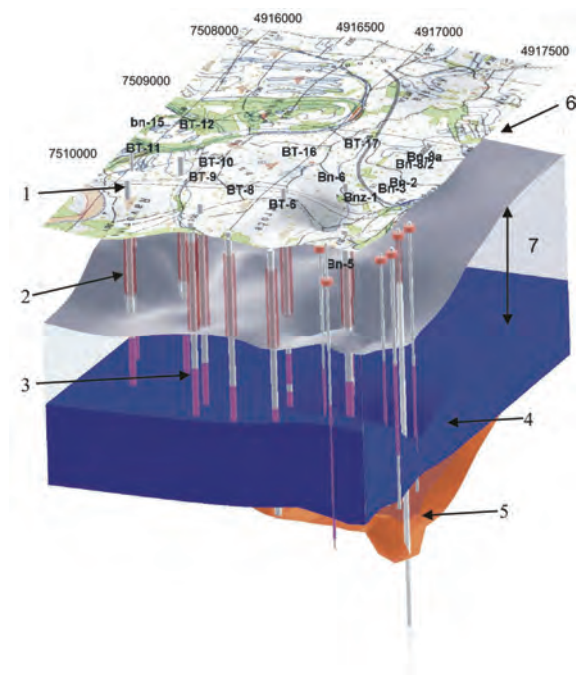


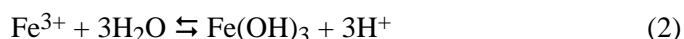
Fig. 1. 3D representation of groundwater levels in the wells and piezometers at the water supply source of Trnovče on 1 September 2011,⁵ modified. Legend: 1 – Zero elevation of the well, 2 – well construction, 3 – well screens above the saturation zone, 4 – water saturated part of the aquifer, the thickness of which varies during the year, 5 – aquifer floor consisting of Neogene clays, 6 – semi-pervious overlying stratum, 3–6 m thick, 7 – zone of blending of oxic and anoxic ground waters.

Applin and Zhao¹ were the first to describe chemical clogging of production wells with iron compounds. The chemical oxidation of ferrous to ferric ions by oxygen and subsequent precipitation is a complex process. The oxidation of dissolved Fe(II) from the groundwater to Fe(III) tends to be gradual.^{7,8} The overall process involves a variety of partially oxidized low-crystalline Fe(II)–Fe(III) intermediate species in aqueous solution. These Fe-intermediates could recrystallize into a variety of stable iron (hydr)oxide end-products (such as goethite) during time.⁹

The iron oxidation in the presence of dissolved oxygen is expressed as:



The produced Fe^{3+} is immediately hydrolyzed:



The overall reaction that describes formation of insoluble iron encrustations^{2,3,8} is given as:



As a result, encrustations appear on the well screen, in the near-well region and, in extreme cases, in the discharge pipes, pumps and equipment installed inside the well (Fig. 2).



Fig. 2. Encrustations in a discharge pipe of Well Bn-6 at the water supply source of Trnovče (picture taken on 1 Sep, 2011).

The rate law of Fe(II) oxidation for mildly acid to neutral waters (pH value 6 to 8) was found to be first-order with respect to the concentrations of both Fe(II) and O_2 and second-order with respect to the OH^- :⁷⁻¹²

$$-d[\text{Fe}]/dt = k[\text{Fe}^{2+}]p(\text{O}_2)[\text{OH}^-]^2 \quad (4)$$

The reaction is rather fast. At pH less than 4, iron as Fe(II) dominates and the oxidation rate is dependent on the pH value.⁹ In addition, studies showed that ferrous oxidation is not dependent on pH if the value exceeds 8.^{9,10}

Many researchers^{7,8} showed that the formed iron-(hydr)oxides have a catalytic effect on the oxidation of dissolved iron. Tamura *et al.*⁷ established an

expanded rate law that includes both Eq. (4) and a heterogeneous reaction at the solid iron-(hydr)oxides surface:

$$r = k_1[\text{Fe}^{2+}][\text{O}_2(\text{aq.})][\text{H}^+]^{-2} + k_2[\text{Fe(III)}][\text{Fe}^{2+}][\text{O}_2][\text{H}^+]^{-2} \quad (5)$$

In Eq. (5), k_1 is the rate constant for iron oxidation and k_2 represents the product of the equilibrium constant, K_{ads} , for the adsorption of ferrous iron onto ferric oxide and the rate constant, k_s , of the oxidation at the surface of the already formed precipitates.^{2,3} Earlier research mentioned that this auto-catalytic effect gains measurable influence only if the initial concentration of Fe(II) is above 3 mg L⁻¹.⁷ Houben presented that only newly formed precipitates that coat older precipitates could act as catalyst and states that the catalysis is more a function of the amount of available surface sites than of the total concentration of ferric iron.⁸ For understanding the process of well clogging, it is also important to consider that low-crystallinity iron-(hydr)oxides, such as ferrihydrite, are more reactive than thermodynamically more stable iron oxides, such as goethite.

The abiotic oxidation presented by the rate law (5) is insufficient to explain the rapid well clogging, which is often observed. In iron-deposits, large numbers of different bacteria are often found that are able to use iron for their metabolic activity. In the presence of low amounts of dissolved oxygen (0.1–1.0 mg L⁻¹), dissolved iron can cause substantial bacteria growth, particularly iron-oxidizing bacteria such as the stalked *Gallionella* and sheathed *Leptothrix*.^{6,13–15} It is believed that these bacteria accelerate iron oxidation.^{13,16}

EXPERIMENTAL

The *in situ* groundwater tests included the determination of the physicochemical parameters: redox potential, E_{H} , groundwater temperature, concentration of dissolved oxygen, mg L⁻¹, the conductance, $\mu\text{S cm}^{-1}$, and pH value of the groundwater. The measurements were conducted using a multi-parameter probe (SEBA multiparameter Dipper KLL-Q, SEBA Hydrometrie, Germany), with the following electrodes: OPP-polymer for the redox potential and SEBA Oxysens II for oxygen. The multi-parameter probe was equipped with an automated groundwater level sensor that enabled sampling from the same depth in each campaign, and allowed data to be collected from various water column depths, in case of depth profile analyses.

The total iron concentration was determined from an acidic solution¹⁷ using ICP-OES (ICP Spectro Genesis EOP II, Spectro Analytical Instruments, Germany). Fe(II) was analyzed in samples filtered on site (0.45 μm) and preserved with HCl.¹⁷ Well discharge data were collected from individual flow meters, to monitor capacity decline over time. Groundwater levels were measured with a level-meter (SEBA level-meter KLL-T, SEBA Hydrometrie, Germany).

The aggressiveness of iron-related bacteria (IRB) was analyzed using the commercial BART test (IRB BARTs, Draycon Bioconcept Inc.). The IRB aggressiveness in water samples was used to estimate the activity level of the bacteria rather than the number of cells (population commonly presented as colony forming units per ml). The IRB aggressiveness was obtained from the relationship between the time lag (expressed in days) and the first

reaction in the IRB-BART™ tests. The bacteria that may be detected by this test include iron oxidizing and reducing bacteria, the sheathed iron bacteria, *Gallionella*, *Pseudomonas* and enteric bacteria.

Chemical analysis on the encrustations were performed using an INCA energy-dispersion X-ray analysis (EDS) instrument, model JEOL JSM-6610LV, USA. The samples were placed in sterile jars and immediately refrigerated to prevent oxidation after sampling. The samples were dried at a temperature of 60 or 37 °C, if the samples contained manganese.^{2,6} For analytical purposes, the samples were ground into powder in an agate mortar. The powdered samples were sputter-coated with 24-carat gold. The detection limits of the applied EDS measurements were 0.2 wt. %.

X-Ray powder diffraction (XRPD) analysis of the sample from well Bn-5 was conducted using a Philips PW-1710 automated diffractometer (equipped with a diffracted beam curved graphite monochromator and an Xe-filled proportional counter), including a Cu-tube operated at 40 kV and 30 mA.

RESULTS AND DISCUSSION

The rate of precipitation of low-crystallinity iron-(hydr)oxides under natural conditions also depends on the groundwater retention time in the well, well pump operation and the groundwater abstraction regime. Apart from the above, the rate of formation of well deposits is affected to a considerable extent by previous well regenerations and the state of “cleanliness” of the near-well region and the well screen. If regeneration was only a short-term, with poor removal of deposited iron-(hydr)oxides, precipitation will be more intensive. The *in situ* measured parameters are given in Table I.

TABLE I. Hydrochemical parameters from the Trnovče water supply source

Well	Sampling date	<i>t</i> °C	pH	[O _{2(aq.)}] mg L ⁻¹	[Fe ²⁺] mg L ⁻¹	EC μS cm ⁻¹	<i>E_H</i> mV
Bnz-1	3/2/2010	13.2	7.1	0.3	1.53	857	163
Bnz-1	24/5/2010	13.1	7.2	1	1.16	814	181
Bnz-1	9/11/2010	13.0	7.1	0.5	1.45	838	156
Bnz-1	13/5/2011	13.2	7.1	0.6	1.13	862	155
Bnz-1	1/9/2011	13.4	7.1	0.4	2.32	863	110
Bn-5	3/2/2010	11.9	7.1	0.8	0.30	532	262
Bn-5	24/5/2010	11.8	7.2	0.1	0.25	620	246
Bn-5	13/5/2011	11.9	7.1	1.2	0.21	619	212
Bn-5	1/9/2011	14.6	7.2	7.1	0.32	672	249
Bn-6	3/2/2010	12.6	7.1	2.3	1.53	623	236
Bn-6	24/5/2010	12.4	7.1	0.8	1.20	635	233
Bn-6	9/11/2010	12.5	7.1	0.5	3.40	644	138
Bn-6	13/5/2011	12.8	7.0	0.8	1.44	645	148
Bn-6	7/11/2011	12.7	7.2	0.1	2.12	541	78
Bn-9G	1/9/2011	12.3	7.1	1.1	0.49	695	280
Bn-9G	7/11/2011	11.9	6.9	7.9	0.82	688	188

The main question is whether the parameter values given in Table I are favorable for the considerable well clogging shown in Fig. 2.

The groundwater at the Trnovče water supply source has pH values between 6.9 and 7.2 (Table I). For roughly neutral groundwater, as in the presented case study, iron oxidation is strongly pH dependent. It also means that small variation in pH values could change the amount of mass converted from ferrous to ferric iron during time. These conditions favor the rapid formation of iron-(hydr)oxide.

On the other hand, the oxidation rate shows a linear dependence on O_2 , Eq. (5).^{7,10,18} During the two-year survey, the concentrations of dissolved oxygen in the groundwater varied over a wide range (Table I). Generally, as river waters flow into the aquifer, removal of O_2 may occur through oxidation of organic matter or adjacent sediments. There are several reasons for the large variations in O_2 content: the setting of submersible pumps into the screen slot, the declining of static and dynamic groundwater levels into the casing interval, an unsuitable pump work scheme and aquifer recharge mode. Research performed in France³ showed that the well de-watering process induced important perturbations of the physical and chemical equilibria in the water within the aquifer around the well, which led to deposition of scale materials. An introduction of the piezometric heads into the screen slots (Fig. 1) leads to exposure of the groundwater to atmospheric conditions, resulting in an oxygen uptake (high values presented in Table I). The formation of mixed oxic–anoxic zone, caused by an unsuitable pump work scheme and groundwater abstraction regime, also favors the rapid clogging. Propagation of the clogging process in and around the well and the mixing of different geochemical zones are explained in following separate section.

The concentrations of dissolved oxygen are also important for iron-related bacteria. The results of IRB BART tests indicated that bacterial aggressiveness was high in 16 %, mediate in 36 % and low in 48 % of the samples. Low aggressiveness means that the bacterial population is too small (or that it has very low activity), whereas mediate indicates that there is either a moderately active or modest population of the targeted bacteria. High aggressiveness was shown only by the bacterial consortium sampled on the 1st of September 2011. The most important iron-oxidizing bacteria found in water samples and encrustations, were *Gallionella ferruginea*, *Leptothrix* sp. and *Siderocapsaceae*. According to Roden *et al.*,¹⁹ Fe(II)-oxidizing bacteria dwell in micro-aerobic environments of low oxygen concentrations (Table I, values less than 1 mg L^{-1}), but Vet *et al.*¹⁶ concluded that *Gallionella* spp. can grow under neutral pH and aerated conditions when chemical iron oxidation is inhibited by low water temperature (about $13 \text{ }^\circ\text{C}$) and suppression of auto-catalytic iron oxidation.

The concentration of iron in the groundwater is also important for the formation of encrustations. Usually, drinking water has a relatively small concentration of dissolved iron. In the case of the Trnovče water supply source, the aver-

age concentration of total iron was 1.79 mg L^{-1} , while the maximum value was 18.8 mg L^{-1} (Bnz-1, before the regeneration). The values of the dissolved iron concentrations are given in Table I. The concentrations of iron in the groundwater could vary over the year, depending on the mode of aquifer charging. During the summer or drought periods, the groundwater feeds the Velika Morava River.²⁰ Charging of the aquifer is slower and the groundwater comes from the upland. Generally, groundwater from deeper part of the aquifer is anoxic and iron is present as dissolved ferrous iron. In contact with dissolved oxygen, the Fe(II) is rapidly oxidized to Fe(III). Pham and White noticed that the rate at which Fe(II) is oxidized to Fe(III) is critical in determining the fate of iron and its bio-availability in many natural waters.²¹ In the particular case of Trnovče, this means that bacteria have to compete with rapid chemical oxidation.

The values of the conductance were higher for the Bnz-1 well than for the other wells. Bnz-1 well is located in the hinterland while the other three wells are closer to the riverbed. The values of the redox potential also indicate the mixing of different geochemical zones.

XRPD analysis detected low-crystalline (hydr)oxides and kaolinite in the sample collected from the Bn-5 well (Fig. 3).

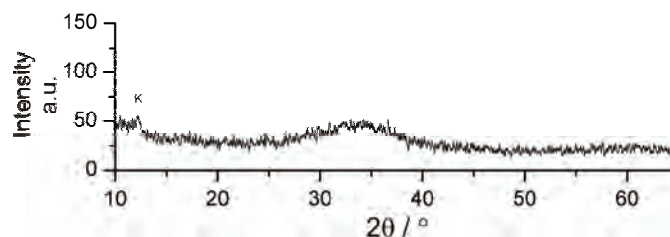


Fig. 3. XRPD pattern of encrustation from Bn-5 well.

Chemical analyses of the encrustations sampled from the water supply wells (Bn-5, Bnz-1, Bn-6 and Bn-9G) performed by EDS revealed the presence of iron and manganese (hydr)oxides. The proportion by weight of manganese (hydr)oxides in the well deposit samples ranged from 0.3 to 21.3 wt. %, while that of iron-(hydr)oxides was from 62.6 to 76.2 wt. %. In addition to these (hydr)oxides, there were also carbonates (5.4 wt. % on average), phosphates (4.3 to 7.2 wt. %) and silicate grains (clay and sand), drawn in from the alluvial matrix through the screen slots. The chemical oxidation of manganese is slower than that of iron. Compared to iron, the rate of manganese oxidation is at least 10^6 times slower in waters with a pH value close to neutral.²² Chemical oxidation of manganese accelerates with increasing pH value ($\text{pH} > 8$).²² The joint occurrence of low-crystallinity manganese and iron (hydr)oxides in the deposits of Trnovče wells can be explained by the microorganisms present in the environment.¹⁴ It is well known that the iron-oxidizing bacteria *Leptothrix* sp. are also able to oxidize manganese(II).

Propagation of clogging around the Trnovče wells

Assessments of well clogging rates need to address the groundwater retention time in the near-well region (gravel pack). The Bn-5 well, which exhibited the poorest performance at Trnovče, was selected for detailed analysis. Its drilling diameter is 500 mm, the diameter of the screen 219 mm, and the screen length 7 m. In order to explain the iron hydr(oxide) precipitation process in and around the well screens, leading to screen slot clogging in shallow alluvial aquifers, four phases can be distinguished.²⁴ These phases illustrate the formation of ferric deposits and a discharge loss for the Bn-5 well.

In the first stage, prior to the development of the water supply source, the underground environment was undisturbed; the aquifer is sub-artesian and the groundwater was anoxic (Fig. 4).²⁴ In this stage, the concentration of dissolved O_2 was much lower than in stages of exploitation. Following the commissioning of the wells during the second stage, a cone of depression is formed and the front of the potential blending of traces of groundwater with different geochemical zones moved downwards. The initial capacity of the studied well was $Q = 15 \text{ L s}^{-1}$ (in 1999), lasting over a relatively short time, only until 2001. The third stage of the life cycle of the well began as early as 2002, when its capacity dropped to $Q = 7 \text{ L s}^{-1}$ (46 % of its initial capacity). In the period 2002–2008, the number of production wells at Trnovče increased to 18; the dynamic groundwater level reached the upper zone of the screen (Figs. 1 and 4), moving the redox front to the water-receiving part of the well. Iron-(hydr)oxides were deposited on the walls of the well screen and casing. As soon as iron-(hydr)oxides were present on the screen slots, the oxidation reaction accelerated and, besides homogeneous oxidation, heterogeneous oxidation also occurred.^{1,3,8,23,24} The first regenerations at this site were conducted in 2004, combining mechanical cleaning with the chem-

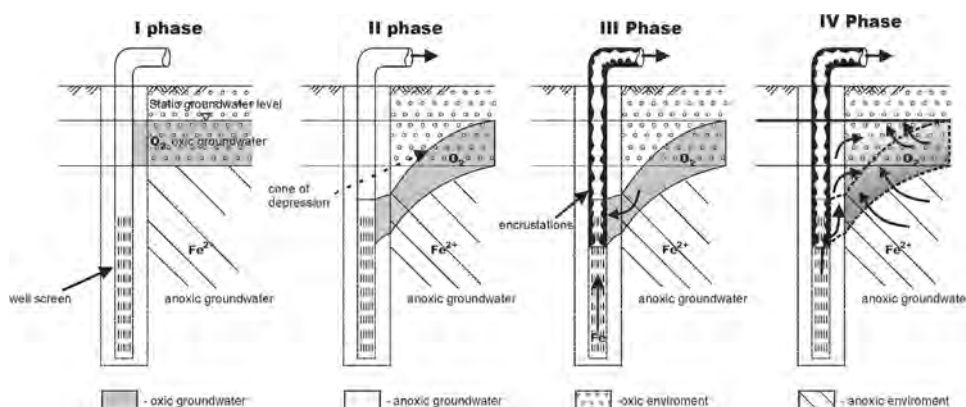


Fig. 4. Stages of well clogging due to blending of oxic and anoxic ground waters²⁴ with permission from IWA Publishing.

ical action of hydrochloric acid and citric acid as an inhibitor. This procedure increased the capacity of the well to $Q = 12 \text{ L s}^{-1}$ (Fig. 5). The next regeneration of water supplying Bn-5 well was undertaken in 2008, when the capacity of the well had dropped to 2 L s^{-1} . The same method was applied and the discharge was increased to 8 L s^{-1} .

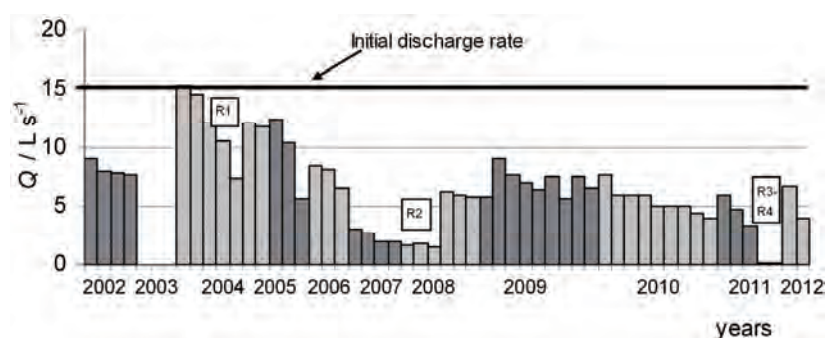


Fig. 5. Declining discharge of Well Bn-5 over 10 years of service.

At stage four, iron was precipitated in the well itself and over an extended area around the well. Insoluble (hydr)oxides were deposited on the grains of the pack in the near-well region, as well as further afield from the well, on alluvial sediment grains. In near-well region, coated grains were found in 2010 during drilling for piezometers near the wells Bnz-1, Bn-5 and Bn-6. Deposition of iron (hydr)oxide on sediment grains reduces porosity and change the entrance velocities in the screen slot. In connection with the problem of a general decline of the groundwater level over the wide area of the Trnovče source, the pumps were occasionally stopped. During the pumping stops (from several hours to more than one month), there was sufficient time for the iron species that remained within the column of water within the well to be oxidize and the screen and casing were encrusted.

This final stage of the life cycle of the well resulted in complete shutdown of the well.

CONCLUSIONS

The exploitation wells at the Trnovče water source are jeopardized by the clogging process. Variations in values of chemical parameters, such as the concentration of Fe(II), dissolved oxygen and redox potential, are the result of an unsuitable pumping scheme and general declining of the groundwater levels. As the groundwater level dropped to the screen zone, the redox front shifted to the water-receiving part of the well. Mixing of water containing oxygen with anoxic groundwater reaching Fe(II) led to mineral encrustations, especially iron (hydr)oxides.

At pH values around 7, as is the case of the Trnovče water source, the chemical oxidation of Fe(II) is strongly pH dependent. Small variations in the measured values could significantly change the oxidation rate. The conditions present in the groundwater are favorable for the rapid oxidation of dissolved iron. Iron-oxidizing bacteria could accelerate this process. The role of bacteria in clogging process depends on the availability of dissolved iron and the concentration of dissolved oxygen.

In alluvial aquifers, variable amounts of ions, catalysts, inhibitors, bacteria and minerals could be present simultaneously. The definition of an exact rate law for such a complex aquatic system is very difficult.

During the precipitation, newly formed precipitates coat older ones. Preliminary results showed high contents of low-crystalline iron and manganese (hydr)oxides inside the water supply wells. With time, if the regeneration methods were not proper, the early formed iron deposits will be re-crystallized into a variety of stable iron oxide end-products. This could be expected in the extended area around the well.

Due to the poor design of the well casings (small diameter and short tail-pipe), the pumps were housed inside the screen and this additionally accelerated precipitation. Iron oxidation did not occur solely inside the well; the process tended to extend into a much wider zone, beyond the well. Especially vulnerable is the well pack, but the process propagates further when there are considerable fluctuations of the groundwater level in the extended zone of the Trnovče water supply source. An adequate exploitation scheme could reduce these phenomena and extend the life of the wells.

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ИЗВОД

ЕФЕКАТ ОКСИДАЦИЈЕ ГВОЖЂА У ПОДЗЕМНИМ ВОДАМА АЛУВИЈАЛНОГ АКВИФЕРА ВЕЛИКЕ МОРАВЕ НА КАПАЦИТЕТ БУНАРА ЗА ВОДОСНАБДЕВАЊЕ

БРАНКИЦА МАЈКИЋ-ДУРСУН, АНЂЕЛКА ПЕТКОВИЋ и МИЛАН ДИМКИЋ

Институција за водопривреду "Јарослав Черни", Јарослава Черни 80, 11226 Београд

Процес оксидације дивалентног гвожђа из подземне воде на филтрима и потисним цевоводима бунара који каптирају плитке алувијалне средине, доводи до формирања бунарских талоба. Основни циљ овог истраживања био је утврђивање разлога брзог колмирања бунара за јавно водоснабдевање. У конкретном случају, талоба чине хидроксиди гвожђа (62,6 до 76,2 мас. %). Прекомерна експлоатација бунара доводи до мешања различитих геохемијских зона и формирања редокс фронта. Током две године истраживања, концентрација раствореног кисеоника у подземној води варирала је у широком опсегу од 0,1 до 7,1 mg L⁻¹ као последица неодговарајућег експлоатационог режима. Теренска мерења температуре подземне воде, концентрације раствореног кисеоника, рН вредности, као и лабораторијске анализе раствореног гвожђа, показала су да измерене

вредности погодују таложењу гвожђа и формирању наслага, у условима прекомерне експлоатације подземних вода.

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