Physicochemical and geochemical characterization of geothermal waters sedimentation tendency at Sijarinska spa and Vranjska Spa (Serbia)

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Abstract

A comprehensive analysis of physicochemical parameters in geothermal waters from the sites in Sijarinska spa (drill hole B-4) and Vranjska spa (drill hole VG-2) in order to investigate their tendency to form deposits in the pipe installation is presented. Both drill holes, B-4 and VG-2 possess utilization capacity of 30/27 L s^{-1} with water temperatures 75–90 °C. VG-2 water does not show any tendency of (or shows very little) sedimentation compared to the B-4 water. The behavior of the geothermal water from the B-4 hole was examined in real conditions of water flow through the pipe installation in Sijarinska spa. The results of geochemical analysis of B-4 water show that aragonite is the predominant mineral in the sediment (98%) with small amount of calcite, vaterite and anhydrite.

Keywords: geothermal water, LSI, RSI, sediment, aragonite.

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Geothermal waters have significant energy potential and therefore represent a potential future source of energy. Considering overall savings in energy, large supplies and less harmfulness to the environment, the use of geothermal energy has an even more significant role and a great advantage compared to the energy sources based on fossil, non-renewable fuels, in which the release of CO_2 (and other gases that affect global warming) is much greater.

What sedimentary mineral will occur in the water from a hydrothermal source during cooling process depends on the mineralogical composition of parent rock, the nature and composition of the solution and its subsequent genesis. Flowing through pipe installation water creates sediments, which is a massive problem for using geothermal energy since sediments reduce the flow; decrease the inner diameter of the pipe and therefore the transfer of heat energy to the pipe wall [1–3]. As a measure of water's tendency to create sediments (precipitation of $CaCO_3$), Langelier's Saturation Index (LSI) and Ryznar's Stability Index (RSI), are used. A positive LSI value indicates that the examined water does not dissolve the protective carbonate layer of (mostly $CaCO_3$) and has no tendency to corrode [4–6]. An RSI value below 7, indicates that the examined water has a strong preference for carbonate deposition. These parameters were used for comparison with the actual behavior of the geothermal water during flow through the pipe installation in the experimental conditions and in the pipe installations itself.

Sijarinska spa and Vranjska spa are located in Southern Serbia and are rich in geothermal water wells. Despite the large number of geothermal wells (15 in Sijarinska spa and 4 in Vranjska spa), only some of them, after pouring and cooling to ambient temperature, showed sedimentation. The reasons for examining the sediments content in these waters are mainly related to energy and economical costs. In regards to this, the object of this analysis is the sedimentation of waters from drill hole B-4 (Sijarinska spa, depth 1232 m) and drill hole VG-2 (Vranjska spa, depth 867 m). Although these locations are relatively close by, geographic characteristics and chemical composition of these waters are different and they have different physicochemical parameters [7-11].

EXPERIMENTAL

Experimental procedure

Water analyses were performed at a flow of geothermal water in installations in Sijarinska spa and Vranjska spa. Laboratory analyses were performed for the flow through a glass tube of "snake" form, 230 cm in length and 10 mm diameter tube, for 6 h, keeping water temperatures identical to the temperatures in drilling holes B-4 and VG-2 (75/90 °C). The flow of geothermal water was achieved by using peristaltic pump Tesa S. A. (Renens). Rotations per minute of the peristaltic pump were regulated by a potentiometer Symmetry SK 313, power 400 W, voltage 230 V and frequency 50 Hz (Figure 1). Thermoregulation was performed by temperature controller device Symmetry SK 302. The flow of water through this pipe was 10 times

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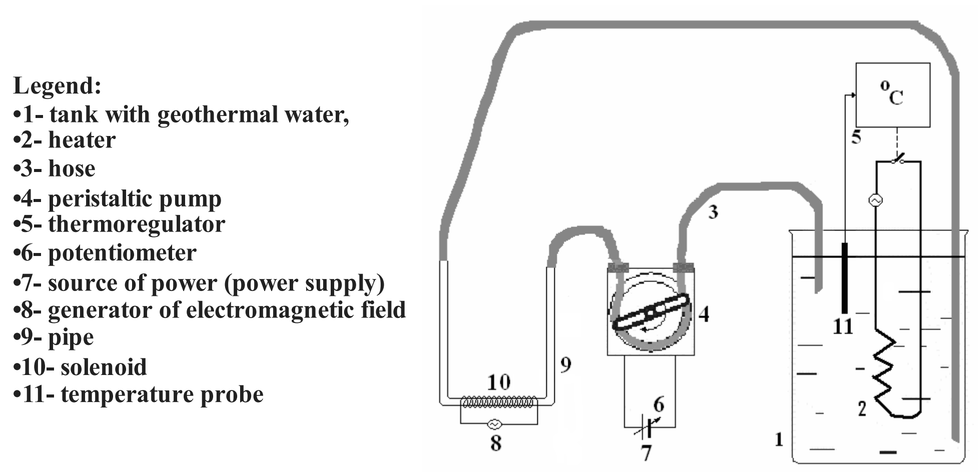


Figure 1. Apparatus for sedimentation in the laboratory conditions.

lower than the flow in pipe installations (0.015 compared to 0.15 L s^{-1}). These parameters were used for comparison with the actual behavior of the geothermal water during flow through the pipe installation in the experimental conditions and in the pipe installations itself. Installations on the tube B-4 in Sijarinska spa included setting a new 1 m-long pipe, diameter 3/4'' (for this study), for determining the sedimentation of geothermal water in the real conditions.

Concentrations of HCO_3^-, Cl^-, SO_4^{2-} and NH_4^+ and turbidity were calculated in accordance with SRPS ISO/IEC 17025:2006 standard.

Analysis of sediment

Powdered rock was treated (12 h) with acetate buffer (acetic acid (1 M)/sodium acetate (1 M) solution at pH 5.0) [11,12] to remove most of the carbonates. This method ensures that carbonate fraction is solubilized. It appears that the treatment of sediments with the acetic acid/sodium acetate is the most efficient and simple method for removing carbonates with a minimal damage to other minerals present [13]. The analysis was performed in order to determine quantitative content of carbonates in comparison to total sediment content.

Analytical methods

Scanning electron microscopy (SEM)/Energy dispersive spectrometry (EDS). All SEM/EDS work was carried out using a Jeol JSM-35 electron microscope equipped with Tracor TN2000 energy dispersive X-ray spectrometer. Operating conditions for energy-dispersive analyses were 25 keV accelerating voltage, 0.1 µA beam current and a beam spot diameter of approximately 3 µm.

X-Ray diffraction (XRD). XRD analysis of the Sijarinska spa sediments was performed by Philips diffractometer (PW 1050/25) equipped with proportional counter and discriminator, using N-filtered Cu radiation at 40 kV and 20 mA.

Inductively coupled plasma-optical emision spectrometry. Major ions in the water and in the whole-rock sample and its carbonate fraction were analyzed by ICP-OES. A Spectroflame ICP-OES instrument was employed and Ar was used as the plasma gas. Total uncertainty (including accuracy error) of the analysis is in the range 5–20%.

RESULTS AND DISCUSION

The results of the analysis of examined major ions and physicochemical parameters of the geothermal waters B-4/VG-2 are given in Tables 1 and 2. Table 1 shows the individual concentrations of ions present in the B-4 and VG-2 waters. Based on the results it can be concluded that the B-4 water has high ion content.

Table 1. Concentration (mg L^{-1}) of major ions in B-4 and VG-2 waters

Component	Sample	
	B-4	VG-2
Na^+	1050	880
Ca^{2+}	45	20
Sr^{2+}	1	1
Mg^{2+}	15	<5
Fe^{3+}/Fe^{2+}	<1	<1
HCO_3^-	2800	400
Cl^-	85	40
SO_4^{2-}	90	60
NH_4^+	<1	<1

The high content (>90%, specification of major carbon species depending on pH) of HCO_3^- compared to H_2CO_3 and CO_3^{2-} is due to pH value of the environment (7.5/7.3) which explains its high concentration (Table 1) and total hardness of water (Table 2). The high content of major ions (Table 1) affects the physicochemical characteristics and leads to increased electrical conductivity (Table 2).

Table 2. Physicochemical parameters of B-4 and VG-2 waters

Parameter	Sample	
	B-4	VG-2
pH	7.5	7.3
Temperature, °C	75	90
Total hardness, °dH	9.2	3.4
Permanent hardness, °dH	1.0	0.6
m-Alkality, mL 0.1 M HCl L^{-1}	460	67
Electrical conductivity, μS cm^{-1}	4370	1240
Turbidity, NTU	3	1.3
Solids, mg L^{-1}	2980	1050
pHs	6.05	6.86
LSI	1.45	0.44
RSI	4.60	6.42

Geothermal waters B-4/VG-2 show moderately basic chemical reaction and based on the temperature values (Table 2), these waters qualify as hyperthermal geothermal waters. Judging by the values of electrical conductivity and total dry residue mass, they fit into mineral waters with high mineral content (Table 2) category. According to the values of total hardness (Table 2) these waters fall into the moderately hard waters. Among cations, the most abundant is Na^+ and of anions HCO_3^- (Table 1). The difference in the total hardness can be explained by the difference in HCO_3^-, Ca^{2+} and Mg^{2+} content (Table 1). The difference in m--alkality (Table 2) is also an indicator of different behavior of geothermal waters B-4/VG-2.

Based on the obtained pHs value, LSI and RSI were determined. The value of pHs, which is in line with the saturation pH was determined using a nomogram [4,5,7], and according to Eq. (1):

$$pHs = f[t] - f[Ca^{2+}] - f[A] + f[R] \quad (1)$$

where: $f[t]$ – the dependence on the temperature of the geothermal water, °C, $f[Ca^{2+}]$ – the dependence on the concentration of Ca^{2+}, mg L^{-1}, $f[A]$ – the dependence of m-alkalinity, cm^3 0.1 M HCl L^{-1} and $f[R]$ – the dependence of the total content of dissolved substances, mg L^{-1}.

Determined LSI and RSI values, according to the Eqs. (2) and (3):

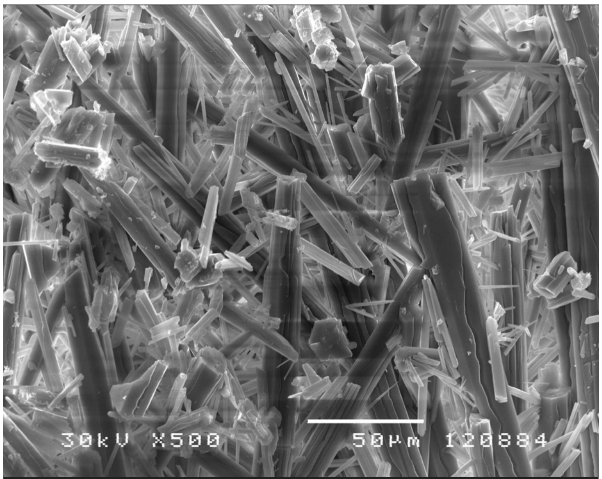
$$LSI = pH - pHs \quad (2)$$

$$RSI = 2pHs - pH \quad (3)$$

A positive LSI value (Table 2) indicates that B-4/VG-2 examined waters show no tendency to corrosion. RSI value (Table 2) indicates that B-4 water has a strong preference for deposition of carbonates, in contrast to VG-2, whose tendency to sedimentation is very low. Unlike carbonates, other minerals present in these waters do not show a marked tendency to deposition on the pipe walls. These results were confirmed experimentally by the actual behavior of the geothermal water during the flow through the pipe installation that is in use in Sijarinska spa and Vranjska spa, as well as in laboratory conditions. In laboratory conditions, during the flow of geothermal water B-4, the development of sediment took place, while in the case of VG-2 water no sedimentation occurred. During the flow of water B-4 through the pipe installation, set on the spring place in real time in Sijarinska spa, for a period of 10 days in 1 m long tube (setup of a new tube done in order to be studied for this paper), was established that total sediment content of 157 g, corresponded to difference in tube mass before and after sedimentation.

In the B-4 hole itself the measured CO_2 concentration in geothermal fluid was high (7.9 g L^{-1} [7]. Therefore, it causes a negative temperature coefficient of solubility of $CaCO_3$ so that a decrease in temperature increases the solubility [14]. By cooling the water from the B-4 hole to 20 °C, and by subsequent filtering and drying, 3.6×10^{-2} g L^{-1} of sediment was obtained. On the basis of measured sediment in the pipe (which is 157 g) during 10 days and the flow of geothermal water of 0,15 L s^{-1}, the calculated value is 1.2×10^{-3} g L^{-1}. By comparing the content of sediments in the B-4 water at 20 °C (3.6×10^{-2} g L^{-1}) and the amount that was settled in the pipe installations (1.2×10^{-3} g L^{-1}) 3.3% of deposit is formed on the walls of the tubes (Figure 2). These results are the total amount of sediment that was settled by the B-4 water cooling as opposed to the results received when the water did not flow through pipe installations.

The mineralogy of the B-4 sediment (SEM/EDS/X--ray) in pipe installation and laboratory conditions is the same and relatively simple. $CaCO_3$ is the principal components (>99%) along with minor amount of $CaSO_4$ (anhydrite, <0.5%, Figure 3). $CaCO_3$ mineralogy studies have indicated that aragonite is the predominant mineral in the B-4 sediment (98%) with lesser amount of calcite and vaterite (>1%, Figure 3). The presence of Sr cations (Table 1; Figure 2) causes formation of aragonite and explains its dominance in the sediment. Due topresence of Sr^{2+} in aqueous solution, the surface energy term in nucleation is modified, leading to possible metastable nucleation of aragonite [15].



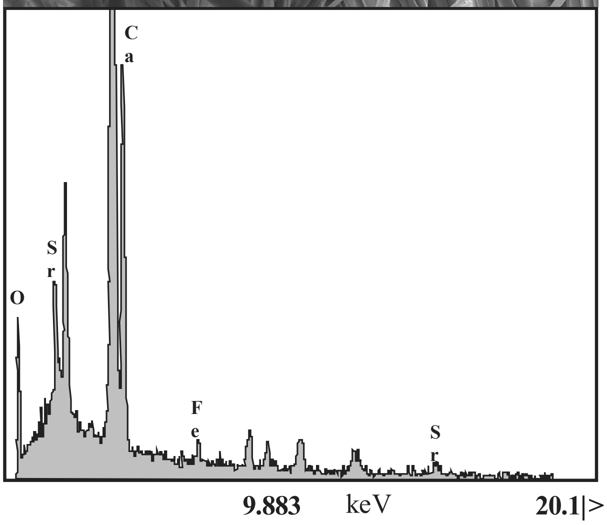


Figure 2. SEM and EDS of sediment formed by deposition of B-4 water in pipe instalations.

CONCLUSION

In this paper, the chemical composition and physicochemical characteristics of geothermal waters B-4 and VG-2 are investigated in order to determine their tendency towards formation of deposits in the pipe installation. Geochemical analysis revealed the concentration of major ions in the samples whose presence causes sedimentation and certain physicochemical properties. LSI 1.45/0.44 and RSI 4.60/6.42 values for B-4/VG-2 explain geochemical behaviour of these geothermal waters. During the flow of geothermal water B-4 the deposits were created, which coincides with the behavior of the same water in real conditions in the installation. In experimental conditions of flow through the pipe installation of geothermal water from the VG-2, the formation of deposits did not take place. Obtained LSI and RSI values indicate that the geothermal water of Vranjska spa (VG-2) is more favorable for use in piping installations because it exhibits less tendency to form deposits. Indeed, the results of mineralogical and geochemical analyses of B-4 water and sediment show the presence of Sr^{2+} (1 g L^{-1}) in the B-4 and VG-2 waters, which in the case of B-4 causes the formation of aragonite (98% of the total sediment). Also, results show 3.3% of deposits on the pipe walls from the total mass of sediment that would be settled by B-4 water cooling as opposed to the results received when the water did not flow through pipe installations.

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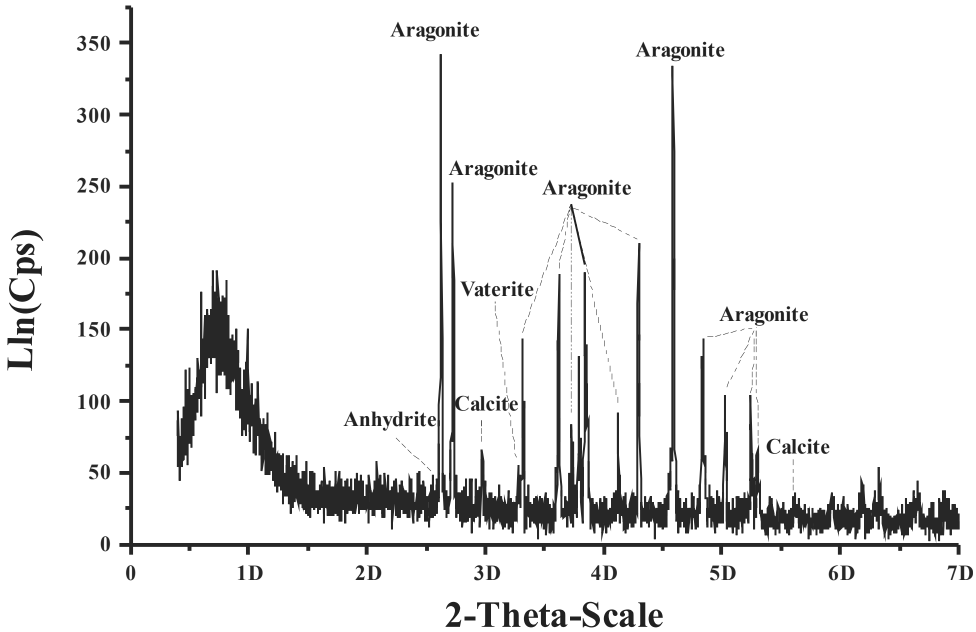

Figure 3. XRD of sediment formed by deposition of B-4 water in the laboratory conditions.

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IZVOD

FIZIČKOHEMIJSKA I GEOHEMIJSKA KARAKTERIZACIJA SKLONOSTI KA SEDIMENTACIJI GEOTERMALNIH VODA SA LOKALITETA SIJARINSKA BANJA I VRANJSKA BANJA (SRBIJA)

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(Stručni rad)

Predstavljena je sveobuhvatna analiza fizičkohemijskih parametara u geotermalnim vodama sa lokaliteta u Sijarinskoj Banji (bušotina B-4) i Vranjskoj Banji (bušotina VG-2) u cilju ispitivanja njihovih sklonosti ka stvaranju naslaga u cevnim instalacijama. Bušotine B-4/VG-2 imaju kapacitet iskorišćenja 30/27 L s^{-1} sa temperaturama vode 75/90 °C. S tim u vezi, određene su pHs vrednosti a onda su izračunate LSI i RSI vrednosti, kao mere sklonosti ka stvaranju naslaga. Rezultati analize pokazuju da bušotine B-4/VG-2 imaju LSI 1.45/0.44 i RSI 4.6/6.4, što znači da VG-2 voda ne pokazuje (ili pokazuje vrlo malu) sedimentaciju u odnosu na B-4 vodu tako da je povoljnija za korišćenje u cevnim instalacijama. Ispitivano je i ponašanje geotermalne vode B-4 u realnim uslovima u Sijarinskoj Banji, protokom kroz cevnu instalaciju. Ovi rezultati su provereni i potvrđeni geohemijskom analizom. Rezultati geohemijske analize B-4 vode pokazuju da je aragonit dominantni mineral u sedimentu (98%) sa manjim količinama kalcita, vaterita i anhidrita. Dominantnost ovog minerala u odnosu na druge oblike $CaCO_3$ uslovljena je prisustvom katjona Sr^{2+} u B-4 vodi. Takođe, rezultati ovih analiza pokazuju količinu od 3,3% sedimenta na cevnim instalacijama u odnosu na sediment koji bi nastao hlađenjem B-4 vode bez njene energetske iskoristivosti.

Ključne reči: Geotermalne vode • LSI • RSI • Sediment • Aragonit