SCALING POTENTIAL OF GEOTHERMAL WATER FROM THE WELL A-2 AT VRANJSKA BANJA (SERBIA)

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Geochemical and physicochemical characteristics of geothermal water from A-2 well are investigated in order to estimate its tendency towards the formation of scale in the pipe installation. Based on the geochemical analysis of major elements and groups, as well as triangular plots, this geothermal water can be classified as Na-Alk-SO₄ type. The ternary diagram classifies it as steamheated-peripheral water. A-2 has a good utilization capacity of 1 L s⁻¹ at the water temperature of 84 °C. Regarding this, SI values are determined as the measure of tendency to form deposits. A positive SI value of calcite (0.14) and aragonite (0.03) at the temperature of 84 °C suggests a very low tendency to form scale, as well as the possible occurrence of a minor proportion of carbonate minerals. XRD mineralogical and SEM analyses of the scale have confirmed its calcite composition. SI values for the temperature of 25 °C indicate the safe silicate minerals deposition due to the positive temperature coefficient. The obtained SI values indicate that the A-2 geothermal water in Vranjska Banja is suitable for use in piping installations because it shows poorly pronounced tendency to form deposits.

Keywords: Geothermal water, A-2 well, Scale, Saturation index, Calcite

Introduction

Hydrogeochemical processes in groundwater are controlled by physicochemical interactions. These interactions depend mainly on pH value, temperature and partial pressure of CO₂. Monitoring of these parameters provide the important information on the scaling potential of geothermal water. In groundwater studies, these parameters are usually combined by saturation index (SI). SI is applied to examine the possibility of precipitation of certain minerals, for evaluating the chemical equilibrium between fluid and rock and for predicting the presence of reactive minerals, as well as estimating the mineral reactivity [1]. Also, this index can be used for estimating the reactive surface area [2]. Physicochemical parameters and concentrations of major ions need to be included to calculate SI. In order to speed up, the calculating process software program (EQ3/6 for example) is most commonly used. The use of the program reduces the cost of testing the potential formation of sediment but does not exclude the occasional practical verification of the mineralogical composition.

Vranjska Banja Spa is located in the Serbian Crystalline Core region, 12 km away from the town of Vranje. The oldest rocks in the wide area of Vranjska Banja Spa are from Proterozoic age (gneiss, crystalline schist and metamorphosed volcanite rocks) with Paleozoic, Mesozoic and Cretaceous-Paleogene granitoid rocks [4]. A geological map of the wide area of Vranjska Banja Spa is showed in Figure 1.

Figure 1. Geological map of the wide area of Vranjska Banja Spa ([4])

A-2 is a well with the depth of 44 m, located near the borehole VG-3. From this well 1 L of water with the temperature of 84 °C is obtained. It consists of granodiorite, with occurrences of pyrite in shallow layers and amphib-

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olite shale. Today, geothermal water in the Spa Vranje is used for bathing needs, for heating the individual objects in the spa and for greenhouses and poultry farms.

Experimental

The experimental methods/techniques have already been described earlier [6]. The groundwater sample was collected in high density polyethylene bottles followed by deionized water (0.1 μS) and then rinsed two to three times before sampling by using sampling water. Before the analysis, the samples were filtered by using Econo-filter 0.45 μm RC cellulose membrane. Field measurements of pH were done using a multi water quality probe (HANNA RS-232, Portugal). Electrode calibration was made by using a standard solution of HI 7071S (HANNA-Calibration solution).

Bicarbonate was determined with neutralization titration and chloride with the precipitation method (Mohr's Method). The gravimetric method was applied in the determination of sulphate.

Inductively Coupled Plasma-Optical Emission Spectrometry. Cations that are present in the water samples were analyzed by ICP-OES Spectro-Arcos (1.4 kW; 12 MHz).

Scanning Electron Microscopy (SEM) works were carried out by using a Jeol JSM-35 electron microscope equipped with a Tracor TN2000 energy dispersive X-ray spectrometer. Operating conditions for the energy-dispersive analyses were 25 keV accelerating voltage, 0.1 μA beam current and a beam spot diameter of approximately 3 μm .

X-ray powder diffraction (XRD) analysis. This analysis was used for the mineral identification of collected samples, using Ragaku Ultima IV powder diffractometer. The X-ray beam was nickel-filtered $\text{CuK}\alpha_1$ radiation ($\lambda = 0.1540$ nm, operating at 40 kV and 40 mA). XRD data were collected from 5 to 90° (2 θ) in a continuous scan mode with a scanning step size of 0.02° and at a scan rate of 5° min⁻¹. The phase analysis, accompanied with Rietveld refinement, was done by using the PDXL2 software (version 2.0.3.0).

Total uncertainty (including accuracy error) of the analysis is less than 5%.

Results and discussion

Geochemical and physicochemical characteristic of A-2 geothermal water

Na^+ and HCO_3^- represent the dominant ions (880 and 380 mg L^{-1} ; Table 1). Cations concentrations that are present in the water samples decreases in the following order $\text{Na}^+ > \text{Ca}^{2+} > \text{Al}^{3+} > \text{Mg}^{2+} > \text{Sr}^{2+} > \text{Fe}^{2+}/\text{Fe}^{3+}$ and anions: $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. At pH value of 7.4, dissolved carbonates occur predominantly in the form of HCO_3^- ion. According to temperature, total hardness and pH, this water belongs to hyperthermal, very soft and moderately alkaline (Table 1.).

Table 1. Concentration of major ions in A-2 geothermal water [mg L^{-1}] and its physicochemical parameters.

IONS		PARAMETERS	
Na^+	880	T [°C]	84.0
K^+	10	pH	7.4
Mg^{2+}	1	pHs	7.0
Ca^{2+}	15	L.S.I.	0.4
Al^{3+}	1	R.S.I.	6.6
$\text{Fe}^{3+}/\text{Fe}^{2+}$	<0.01	Total hardness [°dH]	2.3
Si^+	15	Dry residue [g L^{-1}]	1.8
HCO_3^-	380	Conductivity [S cm^{-1}]	1.4
Cl^-	55		
SO_4^{2-}	365

Figure 2. Triangular plots of: a) Ca^{2+} - Mg^{2+} -(Na^+ + K^+) and b) HCO_3^- - SO_4^{2-} - Cl^- for A-2 geothermal water

The concentrations of major cations (Na^+ , Ca^{2+} , K^+ , Mg^{2+}) and anions in mg L^{-1} were plotted in the triangular plots (Figure 2) to evaluate the hydrochemistry

of geothermal water. Plots show the relations of different hydrochemical variables which are relevant for the hydrochemical evolution and the groundwater flow dynamics. Geothermal waters from Vranjska Banja can be classified as of Na-Alk-SO₄ type. Based on the ternary diagram, this water is classified as steamheated-peripheral water (Figure 3). This classification is consistent with the classification of VG-2 and VG-3 geothermal water in Vranjska Banja [7].

Figure 3. Cl⁻-SO₄²⁻-HCO₃⁻ ternary plot for A-2 geothermal water (based on [8])

Table 2. SI of carbonate and evaporate minerals in the A-2 geothermal water at the temperature of 84 °C and 25 °C

Mineral	Temperature	
	84 °C	25 °C
Albite	-1.96	1.20
Alunite	-6.79	2.30
Anhydrite	-1.60	-2.25
Anorthite	-1.77	-0.29
Aragonite	0.03	-0.69
Ca-Montmorillonite	-1.22	5.88
Calcite	0.14	-0.54
Chalcedony	-0.63	-0.05
Chlorite	-0.02	-7.43
Chrysolite	-3.64	-9.26
Dolomite	-0.64	-1.93
Gypsum	-1.88	-1.95
Halite	-6.00	-5.94
Illite	-1.67	-5.02
K-feldspar	-2.17	1.59
Kaolinite	1.09	6.87
Quartz	-0.35	0.38
Sepiolite	-9.73	-9.37
SiO ₂	-1.30	-0.89
Talc	-0.59	-5.66

Scaling

Langelier's Saturation Index (LSI) value of 0.4 indicates a slight tendency towards corrosion but not to-

wards scaling. This assumption is confirmed by its Ryznar's Stability Index (RSI) value of 6.6 (Table 1), based on interpretations of Ryznar [9]. Newer interpretation of RSI values based on Carrier, 1965, indicates the possibility of little scale. In order to clarify these concerns, the determination is done by using the SI index EQ 3/6 software program based on the concentration of present ions. By using SI index EQ 3/6 program, the ionic activity Q corresponding to different minerals in the brine was calculated and it was compared with the theoretical solubility, K, of the respective minerals. When Q<K, the saturation index is negative and the solution is undersaturated with respect to the mineral considered. When Q>K, the solution is supersaturated and when Q=K, the solution is exactly saturated or in equilibrium with the mineral in respect. Based on the values of Q and K, the obtained SI is calculated by the following equation: $SI = Q \log\text{-log } K$. SI of A-2 was calculated for carbonate and evaporates minerals (Table 2).

Figure 4. XRD spectrum of calcite from geothermal water A-2

Figure 5. SEM of sediment formed by deposition of A-2 water in pipe installations

Based on Table 2, SI values of calcite and aragonite have low positive values indicating the possible occurrence of small amounts of carbonate minerals. Indeed,

in the multi-year inflow of a A-2 water in Banjska Reka at the flow rate of 1 L s^{-1} , the output tubes result in the formation of minor amounts of scale ($<100 \text{ g}$; Figure 4). Figure 4 shows XRD data analysis that confirms the scale SI assumptions for minor amounts of calcite occurrence in pipe installations at the temperature of 84°C . Calcite scale SEM is shown in Figure 5.

Silica scaling is probably the most troublesome scaling encountered in geothermal systems due to its stiff crystalline structure. Silica scaling is mainly dependent on pH, temperature and silica concentration. Silica scaling will occur only when SI is greater than 1, even to 1.4, depending on the temperature [10]. Compared to the carbonates that have a negative temperature coefficient of solubility of CaCO_3 in water, the coefficient solubility of silicate is positive [11-13]. Therefore, carbonates are formed on a higher and silicate at a lower temperature of the geothermal water. With the decrease of the water temperature to 25°C , scaling silicate minerals (Table 2) are expected with SI values higher than 1.4. Of course, such a scenario would be carried out in case that geothermal water A-2 is practically used for industrial and energy purposes rather than freely flowing into Banjska Reka.

Conclusion

In this paper, geochemical and physicochemical characteristics of geothermal water A-2 are investigated in order to determine its tendency towards the formation of scale in the pipe installation. Based on the analysis of major elements and groups, as well as triangular plots, this geothermal water can be classified as Na-Alk-SO₄ type. Based on the ternary diagram, it is classified as steamheated-peripheral water.

The calculated SI values at the temperature of 84°C indicate the occurrence of a minor scale in the form of carbonates (mainly calcite). These data were confirmed by XRD analysis of practical scale. SI data obtained for the temperature of 25°C indicate the deposition of a number of different silicate minerals. Obtained SI, LSI and RSI values indicate that the A-2 geothermal water in Vranjska Banja is good to use for pipes in the installations because it shows a low tendency to form deposits.

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Izvod

SKLONOST KA STVARANJU KAMENCA GEOTERMALNE VODE IZ BUNARA A-2 SA LOKALITETA VRANJSKA BANJA (SRBIJA)

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Proučavane su geohemijske i fizičko-hemijske karakteristike geotermalne vode iz bunara A-2 u cilju procene njene sklonosti stvaranju kamenca u cevnim instalacijama. Na osnovu geohemijske analize glavnih elemenata i grupa, kao i na osnovu trougaonih dijagrama ova geotermalna voda se može klasifikovati kao Na-Alk•SO₄ tip, dok se na osnovu termalnog dijagrama klasifikuje kao pregrejana vodena para. A-2 poseduje dobar kapacitet iskorišćenosti od 1 L s⁻¹ na temperaturi vode od 84 °C. Pri ovim uslovima, SI vrednosti se određuju kao mera sklonosti ka stvaranju kamenca. Pozitivne SI vrednosti kalcita (0,14) i aragonita (0,03) na temperaturi od 84 °C ukazuju na veoma nisku tendenciju ka stvaranju kamenca, kao i na mogućnost pojave manjih količina ovih karbonatnih minerala na cevnim instalacijama. XRD analiza sastava kamenca potvrdila je pretpostavku o nastanku kalcita. SI vrednosti za temperaturu od 25 °C ukazuju na nastanak silikatnih minerala zbog pozitivnog temperaturnog koeficijenta. Dobijene SI vrednosti ukazuju da je A-2 geotermalna voda pogodna za upotrebu u cevnim instalacijama jer pokazuje slabo izraženu tendenciju ka stvaranju kamenca.

Ključne reči: Geotermalna voda, A-2 bunar, Kamenac, Saturacioni indeks, Kalcit