THE ANALYSIS OF THE GEOTHERMAL ENERGY CAPACITY FOR POWER GENERATION IN SERBIA

by

Jana S. STOJKOVIĆ [a*], Goran H. MARINKOVIĆ [b], Petar J. PAPIĆ [a], Mihailo G. MILIVOJEVIĆ [a], Maja M. TODOROVIĆ [a], and Marina D. ĆUK [a]

[a] University of Belgrade, Faculty of Mining and Geology, Belgrade, Serbia
[b] Geological Survey of Serbia, Belgrade, Serbia

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An estimate of deep groundwater temperature is necessary for the research and utilization of this geothermal resource. Geothermometers are based on the temperature relation of some chemical reactions or the solubility of some minerals. Researchers mostly use silicon-based (quartz, chalcedony, amorphous silica) and cation-based (Na-K, Na-K-Ca, Na-K-Mg, and so forth) geothermometers. Temperatures of some prospectively abundant geothermal water resources in Serbia are estimated using the silicon-based geothermometers. In the absence of hot water resources, temperature of deep thermal groundwater has to be estimated and considered for power generation with the Kalina or the Rankine binary cycle. Best thermal waters (temperatures from 130 °C to 160 °C) for the purpose are located in the spa of Vranjska Banja, followed by Kuršumlijska, Sijarinska, and Jošanička spas and Bogatić of Mačva. Pumped at the present rate of 200 l/s, the mentioned sources may generate 70 MW_t, of which some 30 MW_t the Vranjska Banja alone. Total power (for the five tested resources) is estimated at about 2200 TJ per year.

Key words: *geothermal water, geothermometer, power generation, Serbia*

Introduction

Chemical and isotopic geothermometers are important 'tools' in the research and utilization of a hydrogeothermal resource. Most of geothermometers are generally based on the chemical equilibrium reactions; the groundwater-mineral reactions are slow in reaching balance at low temperatures, especially due to the rapid movement of water. Thus, water chemistry is reflected on the fluid temperature equilibrium by concentrations of dissolved mineral forms. Geothermometers should be used carefully to avoid misinterpretation of the results. Particular consideration should be given to sampling, especially of fluids hotter than 100 °C. Any separation of vapour from liquid water may alter the water chemistry and greatly affect the use of gas, isotope or some other geothermometer [1].

Temperature of deep groundwater is determined indirectly, because the method involved is fast and inexpensive. Geothermometry is generally used in determining the current and previous temperatures of geothermal fluids. The methods are based on the temperature relations of some chemical reactions or solubility of some minerals. Solution of a mineral in groundwater, which mainly contains silicon, provides information about the temperature condition in rocks at which processes occur or have occurred in the past. Experiments have substantiated that solubility of a mineral depends on temperature; it is proportional with the growing temperature

* Corresponding author; e-mail: janastojkovic@gmail.com

of groundwater, with the exception of calcite for example. Geothermometers are determined on the basis of this dependence (van't Hoff equation). Conventional geothermometers are based on silicon (quartz, chalcedony, and amorphous silica), cations (Na-K, Na-K-Ca, Na-K-Mg, *etc.*) and isotopes. Temperature equation for each geothermometer includes a specific equilibrium constant for the given mineral-water reaction [2].

The literature that treats geothermal waters of Serbia includes many reference units confined either to the estimate of a potential resource or to its exploitation. Geothermal water is usually heat-pumped for heating. Some of references will be mentioned later in this text.

Stojiljković *et al*. [3] describe an installation intended for a drying plant. A pilot plant was installed in the heat-exchange station at the Gejzir Hotel of Sijarinska Banja. The heat power available to the industry was 2.5 MW from thermal water pumped at the rate of only 15 l/s. At the maximum rate of 30 l/s, the available heat power would be 5 MW. Milojević *et al.* [4] consider using geothermal water for heating green-houses near Jošanička Banja. They estimate that the available amount of heat may be used either for heating or for cultivation in an area exceeding 5 ha. On the basis of calculation for available heat amount, the authors concluded that geothermal water could be used either for heating or for cultivation on the area bigger than 5 ha. Milanović *et al.* [5, 6] develop geothermal heating systems for Smederevska Palanka and Debrc. The geothermal flow rate is 2.5 l/s and the water temperature is 48 °C, about 7.5 tons of fuel oil or 82.6 MWh of heat energy may be saved per heating season (assuming the fuel oil heat capacity was 40 MJ/kg.

Methodology

Samples of groundwater were collected for this research during 2011-2012 in the locations selected on the basis of the physical and chemical properties previously analyzed by standard methods in accredited laboratories. Samples of groundwater within the temperature range from 27-111 °C were taken from 23 sources. The samples were chemically analyzed for calculation of the hydrogeothermometers. The estimates of deep fluid temperatures are based on the thermometer equations, which indicated potential of the hydrogeothermal resource.

The first to be implemented was silica geothermometer based on quartz solubility; solubility in water of different silica forms (quartz, chalcedony, and amorphous silica) were measured in relation to temperature and pressure. This geothermometer is used for the fluids hotter than 150 °C. For lower fluid temperatures, chalcedony is used, which controls the amount of dissolved silicon. Many geothermometers have been developed, of which the quartz geothermometer for thermal water most frequently uses the formula [7]:

$$t[^\circ\mathrm{C}] = \frac{1309}{[5.19 - \log(\mathrm{SiO_2})]} - 273.15 \tag{1}$$

Fluid temperatures from 120° to 180° indicated by the quartz geothermometer suggest that the silicon solubility in water is probably controlled by chalcedony, and therefore the formula for chalcedony thermometer is [1]:

$$t[^\circ\mathrm{C}] = \frac{1112}{[4.91 - \log(\mathrm{SiO_2})]} - 273.15 \tag{2}$$

Finally, for the expected temperatures below 100°C, formula for the amorphous silica geothermometer [8] is:

$$t[^\circ\mathrm{C}] = \frac{731}{[4.52 - \log(\mathrm{SiO_2})]} - 273.15 \tag{3}$$

The Giggenbach [9] Na-K geothermometer has formula:

$$t\,[^\circ\mathrm{C}] = \frac{1390}{1.75 + \log\left(\dfrac{\mathrm{Na}}{\mathrm{K}}\right)} - 273.15 \tag{4}$$

Fundamental theory of geothermometers

Silicon is second highest element (first is oxygen) in the Earth's crust. It is a metalloid, under carbon in the Periodic table, between aluminum and phosphorus, having both metal and non-metal properties. It is a very important element in geothermometry, because silicates are extensively distributed natural minerals forming some 75% of the Earth's crust. Silicon is a macro-element of a large number of petrogenic minerals and is therefore widespread in igneous, metamorphic and sedimentary rocks. Silicon concentration is very high before the main stage of a crystallization. It is highest in granites and notably reduced from acid to basic and ultrabasic magmatic rocks. Silicon concentration is also high in granite pegmatites. Plagioclases are the commonest group of silicate minerals in igneous rocks with the highest proportion of silica in the continental crust. Alkali feldspar and quartz also have large distribution; the two groups of minerals and plagioclases are tectosilicates [10].

Silicon occurs in elevated concentrations in geothermal water as well, for example in geysers of the Yellowstone National Park, USA, in which SiO_2 concentrations may be as high as 570 mg/L [8]. Highly alkaline water (pH > 9), a rare natural occurrence, also is characterized by elevated silica. Amorphous SiO_2 (60-80 mg/L at 0 °C; 100-140 mg/L at 25 °C; 300-380 mg/L at 90 °C) is much more soluble than the almost insoluble crystalline SiO_2, quartz in particular (6 mg/L at 25 °C). Solubility of SiO_2, both amorphous and crystalline, grows with the rising temperature, and elevated silicon concentrations therefore occur in thermal waters. The relationship between SiO_2 concentration in groundwater and temperature is extensively used as a geothermometer in examinations of geothermal resources. In addition to temperature, SiO_2 solubility is affected by acidity/alkalinity of solutions and a variety of the salts present. Silica is rapidly dissolving in water of low pH values, such as pit water or water with elevated carbon dioxide. Silica solubility is rapidly increasing in groundwater containing Na_2CO_3, $NaHCO_3$, NaOH or NaCl [11].

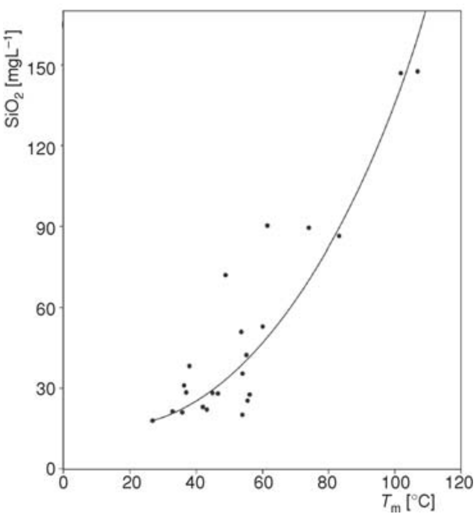

Figure 1. The diagram changes of silica concentrations and measured temperature (T_m °C)

Results and discussion

The silica phases present in geothermal fluids are quartz, chalcedony and amorphous silica. Figure 1 presents the diagram changes of silica concentrations in selected 23 groundwater samples, and measured temperature (T_m °C). It is obvious that high content of silica conditionally increase with temperature. The results of the chemical geothermometry in the most promising locations are given in tab. 1, which also includes temperatures at which electric power may be generated by some generally recognized method (Rankine or Kalina cycle). Naturally, an interpretation of the silicon concentration in water is somewhat uncertain for the unknown solid phase controlling silicon (quartz or chalcedony). Moreover, the mixing with shallow groundwater and the rock-water reaction are very difficult to predict. The quartz geothermometer seems applicable for groundwater below 100 °C because it may long remain oversaturated with respect to quartz.

Table 1. Results of estimated groundwater temperatures on the basis of applied geothermometers

Locality	T_m	$SiO_{2amorphous}$ [°C]	$SiO_{2chalcedony}$ [°C]	$SiO_{2quartz}$ [°C]	Giggenbach [°C]
(1) Vranjska spa (VG-2, VG-3)	111	88	133	160	176
(2) Kuršumlijska spa	63	69	103	131	193
(3) Jošanička spa	74	68	103	131	152
(4) Sijarinska spa	75	69	103	131	193
(5) Bogatić BB-1	60	51	76	105	197

A general comment on the obtained temperature, for selected 23 groundwater samples, is that the temperatures based on amorphous silica are much lower, even below the measured temperatures, than those by other geothermometers (fig. 2). The chalcedony geothermometer temperatures varied from 76-133 °C, but they are probably higher in view of the well depth. The

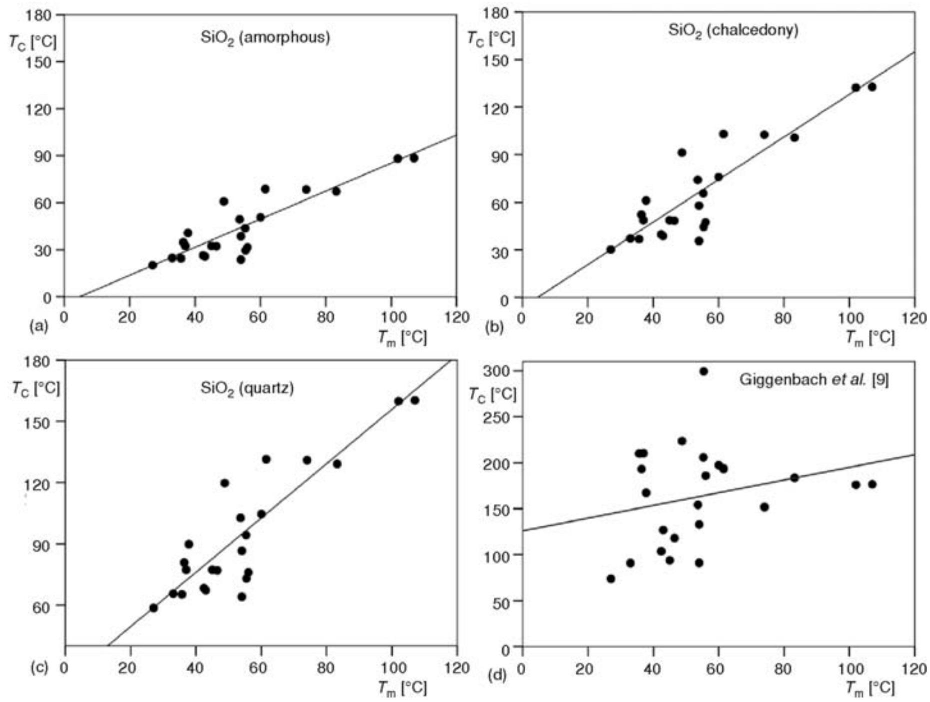

Figure 2. The diagrams of estimated temperatures of geothermal waters (T_c) on the basis of selected geothermometer and measured temperatures (T_m)

quartz geothermometer indicates temperatures between 105 °C and 160 °C. Note that the temperature estimate for all sources is exceeding 130 °C, therefore deep groundwater is available for other uses but heating. Finally, the Giggenbach geothermometer indicated impossibly high water temperatures and thus is not considered, as has been mentioned. An exception is Vranjska Banja (VG-3) for which the temperature estimate was about 176 °C. While sampling, attention was given to preventing calcite deposition as a result of change in the partial carbon dioxide pressure. This gave a more realistic temperature estimate than in other sources, because calcite deposition was prevented which would have given higher fluid temperature [12, 13].

Different researchers reported sensitivity of the Na-K-Ca geothermometer to the partial pressure of CO_2 [14]. Groundwater of Sijarinska spa and Kuršumlijska spa are natural carbonated. For groundwater temperatures less than 200 °C, this geothermometer should be cautiously used with the water rich in CO_2. A diagram (fig. 3) of the Na-K-Mg geothermometer shows the tested groundwater in the field of partial equilibrium, below the complete equilibrium that determines Na/K geothermometer variation by Giggenbach. Scatters towards magnesium peak indicate partial equilibrium or the thermal water mixing with cold water.

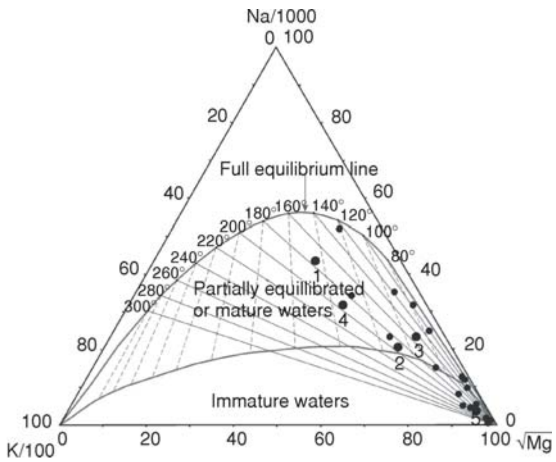

Figure 3. Giggenbach diagram for the selected geothermal water sources (numbers represent locations from tab.1)

Power generation in binary cycle plants

The amount of geothermal energy in the Earth's interior will remain billion of years there, until the sun transforms into a gigantic red star. Unfortunately, this energy is not readily available. The source of geothermal energy is radioactive decay that evolves within the planet some 6730 km under the surface. The Earth's crust is comparatively cold, except for the hot spots where magma is nearer the surface, and grows warmer with the depth. As to the utilization of the planet's heat, the efficiency of heat conversion into a form of beneficial energy as defined by the second law of thermodynamics is limited. An absolutely perfect engine may have thermal efficiency of only 13.6% (input fluid temperature 66 °C and output 20 °C). A few geothermal power plants in the world use the hot spots, where the fluid temperatures are far above 150 °C, but even their engines are not perfect. According to the Energy Information Agency, the mean efficiency of the geothermal power plants in the USA is about 16% [15].

Thermal energy available from geothermal sources is used in different forms, and the capacity of the equipment for use of the produced geothermal energy may be less than 100 kW. There are two systems for conversion of the geothermal energy:

(1) *Single Cycle Geothermal Power Plants*. Generation of power by the conventional steam turbine requires the working fluid temperature of no less than 150 °C. It is available only from very hot geothermal sources or with overheated water flashed to steam.

(2) *Binary Cycle Power Plants*. Water temperature and pressure in many geo- and hydro--thermal power plants are too low for efficient operation of the steam turbine. Dual cycle

"binary plants" have been developed for better use of the low-temperature fluids within the range from 100 °C to 175 °C.

In a binary plant, the hot-water circuit passing through the thermal source is separated from the closed loop working fluid used in the turbine by a heat exchanger. The hot water gives up its heat in the heat exchanger to a working fluid with a low boiling point and high vapour pressure at low temperatures when compared to steam. The working fluid is usually ammonia or some organic compound such as butane, pentane or iso-pentane, which flows through the secondary side of the heat exchanger and evaporates, and steam is used to rotate the turbine in the conventional Rankine cycle electricity generation plant. After the vapourized binary fluid has passed and transmitted its energy to the turbine, it condenses and is fed back for use in the heat exchanger. Having passed through the heat exchanger, water is pumped back through the well into warm rock. This system has an additional advantage that the fluid (mostly salt water from ocean or polluted water from aquifer and hot rocks) never comes into contact with the turbine generator units [16].

Binary cycle power plants are a latest development; they operate with the fluid temperatures as low as 57 °C [17]. This is the commonest type of the geothermal electricity plant constructed at present. Both Organic Rankine and Kalina cycles are used, and the thermal efficiency level of 10-13% is characteristic of this type of power plant.

The examples of most promising locations for electricity generation from geothermal sources in Serbia are given in tab. 2.

Table 2. Most promising locations for obtaining electricity in Serbia

Locality	Q [L/s]	T_m [°C]	T_{quartz} [°C]	T_C [MW$_t$]	TE [TJy^{-1}]	Utilization	System cycle
(1) Vranjska spa (VG-2,VG-3)	50	111	160	29.3	923.3	Electricity	Single
(2) Kuršumlijska spa	20	63	131	9.3	292.8	Electricity	Binary
(3) Jošanička spa	20	74	131	9.3	292.8	Electricity	Binary
(4) Sijarinska spa	30	75	131	13.9	439.2	Electricity	Binary
(5) Bogatić BB-1	20	60	105	7.1	224.2	Heating	

Besides natural discharge of thermal water of the temperatures up to 83 °C, water of 111 °C flows out the wells VG-2 (1064 m) and VG-3 (1470 m) at the rate of 50 L/s in Vranjska Banja. The granitoid intrusion of Surdulica, a product of Tertiary magmatism, is believed responsible for the large hydrothermal potential of the region, and for lithothermal potential; there are other theories that propose the presence of a younger intrusion. Total electric power output from this geothermal resource is 6 MW$_e$, equal to an amount of about 13 000 tons of liquid fuel [18]. According to an estimate by quartz geothermometer based on the expected groundwater temperature of 160 °C, the Vranjska Banja alone possesses a thermal capacity of about 30 MW$_t$, and a total energy of about 920 TJ per year. This latest information undoubtedly indicates a direct system of prospective electricity generation, for which some foreign companies expressed their interest (Canada, Italy).

Second best prospects after Vranjska Banja, according to the estimates, are Kuršumlijska, Sijarinska, and Jošanička spas, and then Bogatić of Mačva with the expected groundwater temperatures between 130 °C and 160 °C. The estimate, based on geotermometry, of the thermal capacity for the present well yield of 200 L/s, is 70 MW_t, of which 30 MW_t in Vranjska Banja alone. Total thermal energy (for five tested wells) is estimated at about 2200 TJ per year. This information sheds new light on the potential geothermal water resource in Serbia.

The highest measured temperature of geothermal water, published in the Geothermal Atlas of Vojvodina, is 82 °C in NE Banat (Vrbica, borehole Vbc 1/H). The potential sources are able to yield groundwater of 100-150 °C temperatures from a depth of 2-3 km. These temperatures regrettably are not based on the geothermometers, but by other methods during the borehole drilling. In any case, the authors of the Geothermal Atlas of Vojvodina conclude that the estimate of the thermal groundwater resources, determined as the total available thermal power, amounts to 72.6 MW_t at the efficiency rate of only 8% [19].

Conclusions

Chemical geothermometers are very useful for investigation, exploitation and management of geothermal resources. Their correct interpretation based on exploratory drilling data may give accurate estimates of fluid temperature in a geothermal reservoir. They are also useful in monitoring, because variation of a geothermometer during the geothermal fluid abstraction indicates a change in the reservoir itself. The use of geothermal fluids depends greatly on how accurate is the interpretation. In the absence of hot water resources, temperatures of deep thermal groundwater had to be obtained by geothermometers and considered for electricity generation in the Kalina or the Rankine binary cycle. The most perspective of the thermal water resources (temperatures from 130 °C to 160 °C) are the spas of Vranjska Banja, then Kuršumlijska, Sijarinska, Jošanička, and Bogatić of Mačva. Pumped at the present capacity rate of 200 L/s, thermal water from greater depths may generate 70 MW_t electric power of which 30 MW_t Vranjska Banja alone. An estimate of the total power output (for five tested sources) is about 2200 TJ per year. This estimate differs in being higher than the previous resource estimates.

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