Chemical composition of the thermomineral waters of Jošanička Banja Spa as an origin indicator, balneological valorization and geothermal potential

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Abstract
The chemical composition of the groundwater is directly dependent on the geological structure, hydrogeological and hydrochemical characteristics and as such it represents an output result of all the factors and processes which take place in the environment within which they were formed. The chemical composition of thermomineral waters often represents a crucial factor in determining the origin, balneological valorization and geothermal potential of the resources. This paper presents the analysis of origin, balneological valorization and geothermal potential of Jošanička Banja Spa, on the basis of the results gained through making the analysis of chemical contents of the thermomineral waters which occur in the area. The ratio of concentrations of specific chemical components in the thermomineral waters of Jošanička Banja has served as the basic tool for ascertaining the origin of these waters. On the basis of the analysis of the main anion–cation and gas compositions as well as the contents of specific micro-components, a balneological valorization of these resources has been carried out. Apart from that, this paper also presents the calculation of the expected temperatures in the primary geothermal reservoir, which was carried out on the basis of the results of chemical analysis of thermomineral waters that occur in the area. Geothermal potential of about 4 MWt, and significant contents of balneologically active components of the chemical composition of these waters, open up a possibility for their multi-purpose use, which is also presented in the paper.

Keywords: thermomineral waters, geothermal potential, balneology, massif of Kopaonik, Jošanička Banja Spa, multipurpose use.

The adequate comprehension and analysis of the groundwater chemical contents is the essential tool for determining almost all value characteristics of any water. The starting point in the development and valorization of water resources is reflected in studying the three main components: correct origin ascertaining, multi-parameter valorization and defining the energy potential. A special significance in studying these components is ascribed to spas, in other words to thermomineral waters. A fastened development of both wellness and spa concepts, as basic goals of the spa tourism development, has led to establishing an entire range of new methods which are deployed to define spa potentials in a qualitative way [1,2]. Studying the above-mentioned parameters is also significant for the development of chemical industry when it comes to extraction and industrial use of micro-components from thermomineral waters [3].

Individual analyses regarding the origin ascertaining, balneological valorization as well as defining geothermal potential are analysed as separate cases by many scientists out of a simple reason: there are not so many occurrences on the Earth to which they can apply an integrated approach. Such researches can be found in the following papers [4–8].

Jošanička Banja Spa is a unique case where high-temperature waters can be used in cascades as both an energy resource and spa and sports-recreation wellness factor. Remaining similar cases in Europe can be found in Moravske Toplice (Slovenia) [9], Karlovy Vary (Czech Republic) [10], Baile Herculane (Romania) [11]. The data which describe the methodology and results of multi-criteria analysis are also presented in the mentioned papers.

This paper represents the methods which can be applied as the future general rule of chemical research for the water types similar to that in Jošanička Banja spa. On the basis of the gained results, once again it was confirmed that an adequate analysis and interpretation of chemical analyses cannot be suitably replaced in the contemporary geological, hydrogeological, geothermal and chemical sciences.
Basic characteristics of the study area

Jošanička Banja Spa is located on the northern slope of the mountain massif of Kopaonik (Figure 1) in the valley of the Jošanica river, at the altitude of about 550 m.

Natural discharges of the thermomineral water in the area of Jošanička Banja Spa may be found in two zones. The first one is in “Banjski park”, where a wide discharge zone was formed, with the yield of 14.1–15.4 l/s and temperature ranges from 70.1 to 78.7 °C. The other discharge zone is found on the site “Slanište” which is located in the valley of the Jošanica river, at the distance of 2 km to the west of “Banjski park”. The total yield of a wide discharge zone is approximately 2 l/s, while the groundwater temperature at this source ranges from 36 to 37 °C. Apart from carrying out hydrogeological and hydrogeothermal researches at the two natural thermomineral water sources in the area of Jošanička Banja Spa, 9 study hydrogeological boreholes were also made, out of which the two: B-3 and B-6 is in exploitation.

Besides its significant potential, the groundwater in the area of Jošanička Banja Spa has not still been applied to the adequate purpose. In addition to the balneological valorization and geothermal potential estimates, recommendations for the future sustainable use of this significant resource are also given in this study.

THE APPLIED CONCEPT AND METHODOLOGY OF RESEARCH

The ways of analyzing and researching the potentiality of a site or phenomenon can be multiple and multi-disciplinary. Depending on the needs and purpose, when analyzing the potential of a hydrogeothermal phenomenon, we may analyze geographical factors, geological-hydrological characteristics, hydro-chemical and geothermal features, as well as urban factors and development or economic factors. Each of these factors has its own unique features and is unique in its methodology and output results. The analyses of hydrogeothermal phenomena from the aspect of chemical composition as the main indicator of origin, balneological valorization and geothermal potential, represent possibly the most complex of all the enlisted principles, first of all due to their complexity, bulkiness and number of applicable methods.

The concept of researches which were carried out in the area of Jošanička Banja Spa, is methodologically split into three inter-connected units, whose aim was to evaluate the resources of thermomineral groundwater and afterwards the balneological valorization and geothermal potential of Jošanička Banja Spa thermomineral water (Figure 2).

Geological and hydrogeological features of the area of Jošanička Banja Spa

The area of Jošanička Banja Spa is characterized by a heterogeneous geological structure. It is made of igneous, sedimentary and metamorphic rocks of different age, ranging from the youngest Quaternary alluvial sediments of Jošanica to the oldest Paleozoic schists (Figure 3). The granitoid complex of the rocks in the Kopaonik area, during its embedment performed the metamorphism of the aureole zone which is nowadays represented by marble and a series of fillits and seri-
Figure 2. The applied concept and methodology of research.

Figure 3. Geological and hydrogeological map with a hydrogeological profile.
cite–chlorite schists which are distributed in the central area of Jošanička Banja Spa and are super positionally found “trapped” between granitoid rocks.

Tectonic and neotectonic movements which are occurred in the area of Jošanička Banja Spa provided a good predisposition for the formation, circulation and discharges of thermomineral waters in the area of Jošanička Banja Spa.

From the aspect of the formation of thermomineral waters of Jošanička Banja Spa, the most significant development is that of the fractured aquifer type, which, according to the lithostratigraphic units, can be subdivided into the following subtypes:

- Fractured aquifer type formed within serpentinites and harzburgites;
- Fractured aquifer type formed within schists;
- Fractured aquifer type formed within granodiorites and quartz diorites;

Apart from the fractured aquifer type in the area of Jošanička Banja Spa, we can also classify the intergranular aquifer type formed in the alluvial sediments of the Jošanica river and karst-fractured aquifer type formed within calcite and marble. The origin of the thermomineral waters is related to the fractured aquifer type within schists, granodiorite and quartz diorite.

The fractured aquifer type formed within the schists is distributed in massive tectonic fractures and cracks on the Earth crust. This aquifer is located underneath the local erosion basis which is in the study area represented by the Jošanica river. Generally speaking, Paleozoic schists in this terrain belong to the weakly water-permeable rocks, and here the groundwater can only be formed within some segments of limited dimensions. Generally, the fractures are of small dimensions, but they are not fully filled which enables a better circulation of the groundwater. With the transfer to hornfels and skarns water-permeability of the schists complex is on the increase. Analyzing the results gained by carrying out some tests with the controlled artesian pressure at the borehole B-5, the coefficient of transmissivity, $T$, was calculated: $5.49 \times 10^{-3}-3.30 \times 10^{-4}$ m$^2$/s. This is confined aquifer. The value of hydrostatic pressure at the head of the B-5 borehole is 0.6 bar. Thermomineral water as its path to the terrain surface uses the cracks in the schists rock complex. In the area of Jošanička Banja Spa the discharge of the fractured aquifer type formed within the schists rock complex, takes place by a natural and artificial way. The natural way means that the aquifer is discharged via thermomineral springs with the temperature from 70.1 to 78.7 °C and they are located in the vicinity of the basin of The Jošanica river in the spa park and via thermomineral springs with a lower temperature (36–37 °C) on the site “Slanište” which is located downstream on the left bank of the Jošanica river. The artificial way means that the thermomineral water in the area Jošanička Banja Spa is drained at exploitative boreholes B-3 and B-6 (water temperature is around 52 °C at B-3 and 56 °C at B-6).

Fractured aquifer type formed within granodiorites and quartz diorites spreads over a significant area in Jošanička Banja Spa. These rock masses are mostly distributed in north-eastern, south-eastern and central parts of the study area, and here they are characterized by an expressed anisotropy of effective porosity scaling from 1.6 to 4% [12] This aquifer type plays an important role from the aspect of formation, movement and discharge of the thermomineral groundwater in the area of Jošanička Banja Spa. The heat source of the hydro-geothermal system of Jošanička Banja Spa is represented by granodiorites and quartz diorites which are at certain depths cut by ruptures along which thermomineral groundwater circulates. In some parts of the terrain these rock masses are compact and here they stand as a barrier to the water movement. The thermomineral groundwater of Jošanička Banja Spa is probably partly formed within this aquifer type in granodiorites and quartz diorites, and this is made clear by the calculations gained via the geothermometer method.

**Hydrochemical characteristics of the thermomineral water occurrences in the area of Jošanička Banja Spa**

The results gained by carrying out the analysis of the qualitative features of thermomineral waters (Table 1) in the area of Jošanička Banja Spa indicate that this is a single body of thermomineral waters. The chemical composition of the groundwater from the analyzed occurrences and objects mutually differs according to some parameters of its quality, and this is comprehensible, bearing in mind the complexity of petrological and mineralogical, tectonic, hydrogeological, hydrogeo-thermal, hydrochemical and other features of the study area. The thermomineral water of Jošanička Banja Spa is characterized by a low mineralization with the predominant sodium ion (Figure 4), high contents of silicon acid and an expressed alkaline reaction.

Regarding its organoleptic features, this water is translucent, without colour and with the smell of hydrogen sulfide (HS$^-$$^-$). Regarding some specific components, the thermomineral waters of Jošanička Banja Spa are characterized by the presence of fluoride, lithium and boron.

**The origin of the thermominERAL waters in the area of Jošanička Banja Spa**

In order to define structural–geological and hydrogeological conditions of the formation, movement and discharges of the thermomineral waters in Jošanička Banja Spa, the following methods were applied:

- Lithostratigraphic and tectonic analysis of the inner area of Jošanička Banja Spa;
Analysis of the thermomineral water discharge hydrographs;
- Analysis of the thermomineral waters temperature regime;
- Analysis of the thermomineral waters qualitative characteristics;
- Analysis of geothermal characteristics.

On the basis of the hydrogeological research carried out up to now, within the body formed in the fractured aquifer it is possible to determine the origin of thermomineral waters in the area of Jošanička Banja Spa. A greater part of the analysis of the thermomineral water origin in Jošanička Banja Spa was performed on the basis of the research carried out at the spring “Banjski park”, which is characterized by the biggest yield, highest temperatures and the highest degree of exploration.

Lithostratigraphic and tectonic analysis of the conditions for the formation of thermomineral waters in Jošanička Banja Spa

Thanks to the tectonic and neotectonic activity which took place in the area of Kopaonik region, a considerable number of faults were created. From the hydrogeological, that is hydrogeothermal aspect, in the area of Jošanička Banja Spa there are two most sig-
significant faults. The first one stretches along the Jošanička river basin, generally, in the east–west direction, while the other runs right to it and goes along the basin of the Velestica river in the direction southwest–northeast (Figure 5).

The thermomineral occurrences in the area of Jošanička Banja Spa are related to the overlapping zones of these faults, where a seepage spring of thermomineral groundwater is formed ("Banjski park") and it is characterized by temperatures from 70.1 to 78.7 °C. Going from the above mentioned spring to the west, the thermomineral temperature falls down to 37 °C (Figure 5).

**Analysis of the temperature regime of thermomineral waters of Jošanička Banja Spa**

Groundwater monitoring at the site "Banjski park" was carried out at 6 monitoring spots (Figure 6). The above mentioned monitoring has shown that the water temperature at the spring of "Banjski park" ranges from 70.1 to 78.7 °C (Figure 7). The highest amplitude of temperature fluctuations was registered at monitoring spot 7 and it equalled 1.7 °C, and this indicates a stable temperature regime of the groundwater (Figure 7) and the absence of mixing up thermomineral waters with "cold" surface water.

From the balneological aspect, the thermomineral waters in Jošanička Banja Spa belong to the group of hypertherms, that is the group of waters whose temperature is above the human body temperature. The exception to this is the thermomineral water from the spring of "Slanište" which belongs to the group of homeotherms, that is the group of waters whose temperature is within the human body temperature limits. From the geothermal aspect, this water belongs to hydrogeothermal resources of low enthalpy (t of the fluid is <100 °C).

**Hydrochemical determination of the origin of thermomineral waters of Jošanička Banja Spa**

The formation of physical-chemical and gas composition of the thermomineral water in the area of Jošanička Banja Spa is related to the younger deep igneous rocks and thermo-metamorphic processes caused by them and they took place in the Kopaonik region in the course of Paleogene and Neogene. On the basis of the collected data on the qualitative features of thermomineral waters in Jošanička Banja Spa (Table 1), the analysis of the thermomineral water origin was carried out from different hydrochemical aspects.

**Quality regime**

The regime of the groundwater at spring "Banjski park" is characterized by a significant degree of stability of the basic anion–cation composition and this is indicated by the results of monitoring the basic anion–cation composition in the past 30 years. In the diagram presented in Figure 8, we may see that in the course of the period the basic anion-cation composition did not significantly change.
D’Amore diagram

The six new hydrochemical parameters for determining water groups on the basis of geological characteristics of the main reservoirs are defined by using the basic anions and cations [14]. Applying these hydrochemical parameters, we may come to the answers related to the groundwater origin. Hydrochemical parameters are marked with letters A to F and with the range of +100 to –100 meq/l.

In Figure 9 there is D’Amore diagram of the thermomineral water of Jošanička Banja Spa, whereas Figure 10 is showing the type D’Amore diagram for different water types.

Figures 9 and 10 clearly show that the thermomineral waters of Jošanička Banja Spa, according to their characteristics, are found in between the waters characterized by a metamorphic type and those characterized by a clastic type. Taking into account the geological structure of the terrain and hydrogeological character-
istics, it is more likely that the origin of these waters is related to metamorphic, that is thermometamorphic processes which took place in the area throughout its geological past.

Gas composition

Previous researches which were related to the gas composition of these waters [15,16] showed that the predominant gas in the thermomineral waters of Jošanička Banja Spa is nitrogen with 91% of the volume, then comes O₂ with 5% of the volume, CO₂ with 2.4% of the volume and H₂S with 1.6% of the volume and this points to the fact that the thermomineral waters of Jošanička Banja Spa have a vadose origin and this is also indicated by the presence of nitrogen in the water [15].

When carrying out the terrain researches at thermomineral occurrences and objects of Jošanička Banja Spa, the presence of gases was registered. The smell of the thermomineral water pointed to the presence of hydrogen-sulfide (HS⁻), which is almost non-existent in the air, so it acidifies with the formation of the water and SO₂. At larger depths of the Earth’s crust, hydrogen sulfide is related to thermocatalytic processes of the dissolution of sulphur compounds and reduction of sulfates under the conditions of high temperatures.

Analysis of the contents of genetically relevant chemical components in the thermomineral waters of Jošanička Banja Spa

On the basis of the performed analyses of qualitative features of the thermomineral groundwater from the springs in the Jošanička Banja Spa area, the following conclusions were drawn:

- Silicon dioxide amount (SiO₂) of 1.621 mmol/l is typical for thermomineral water. With the temperature increase, the solvent quality of the water also changes. Under ordinary conditions the solubility of silicon acid is quite low. In high temperatures quite a frequent occurrence is that of silicate-carbonate-sodium waters, and this is exactly the case of Jošanička Banja Spa.
- HCO₃/SiO₂ < 5 (0.161) ratio indicates that the chemical composition of thermomineral waters is related to the silicate dissolution.
- On the grounds of the SiO₂/(Na⁺+K⁺+Cl⁻) < 1 ratio, we may conclude that at larger depths of the aquifer there is an ionic change (Ca²⁺ and Mg²⁺ into Na⁺).
- (Na⁺/Na⁺+Cl⁻) ratio which is bigger than 0.5 (0.889) also points to the ionic (cationic) change.
- (Mg²⁺/Ca²⁺+Mg²⁺) ratio points to the presence of ferro-magnesium minerals (actinolite Ca₂(Mg,Fe)₅Si₈O₂₂(OH,F)₂ which occurs within the chlorite-epidote-actinolite slates). The basic chemical process which takes place in these slates is the process of albitization. The
formation of the albite mineral is related to a retrograde metamorphism of basic plagioclases or recrystal-
ization in the course of metamorphosis, when the ionic change occurs (Ca$^{2+}$ and Mg$^{2+}$ into Na$^{+}$). In metamor-
phites, the change-causing cations can be found in huge amounts and their character depends on the
character of their inner plagioclase. In albite molecules, the plagioclase has about 10% of anorite component,
that are mostly sodium compounds, which as the product when they decompose leaves behind the change-
causing sodium which makes up over 90% ekv. in all the analyzed samples of thermomineral waters.

- The dry residues value which is less than 500 mg/l, as well as the Cl-/anion sum < 0.8 (0.119) concentra-
tion indicate that the chemical composition of thermomineral waters has to do with the silicate
dissolution.

**BALNEOLOGICAL VALORIZATION OF THERMO-
MINERAL WATERS OF JOŠANIČKA BANJA SPA**

The chemical composition of thermomineral waters besides the temperature represents the most impor-
tant balneological component of these resources. The chemical composition of the groundwater may quite
often serve as a significant tool for defining geothermal potential of a specific geothermal system.

The thermomineral waters of Jošanička Banja Spa were formed within a single groundwater body, which
caused a similar chemical composition of thermomineral waters of all the analysed occurrences and objects. According to other analyzed parameters (gas composition, pH value, mineralization and specific
components contents) all the waters were classified within the same category (Table 2).

The thermomineral waters of Jošanička Banja Spa according to the basic anion-cation composition belong
to the group of carbonate-sulphate-sodium waters, while according to the pH value parameter these waters
are classified as the waters characterized by an alkali reaction (Table 2). Out of some specific components, the thermomineral waters of Jošanička Banja Spa are characterized by the presence of silicates, fluorides, lithium, boron and hydrogen sulfide.

Balneological valorization of the thermomineral waters of Jošanička Banja Spa based on temperature,
basic anion composition, basic cation composition, gas composition and micro components contents.

**Temperature**

The temperature parameter is one of the basic determinants of the thermomineral waters of Jošanička
Banja Spa. Hot groundwaters are regarded as useful in the process of treating some rheumatism diseases,
sports injuries and post-surgical processes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Banjški park</th>
<th>Slaniště B-3</th>
<th>Jošanička Banja Spa</th>
<th>B-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hypotherms</td>
<td>t &lt; 36 °C</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Homeotherms</td>
<td>36–37 °C</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Hypertherms</td>
<td>t &gt; 37 °C</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Gas composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Hydrogen sulfide + CO$_3$-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Nitrogen + +</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Nitrogen methane</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<td>Methane</td>
<td>+</td>
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<td>+</td>
</tr>
<tr>
<td>pH value</td>
<td></td>
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</tr>
<tr>
<td>Strongly acid pH &lt; 3.5</td>
<td>+</td>
<td>+</td>
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<td>+</td>
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<tr>
<td>Weakly alkaline pH: 7.2–8.5</td>
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<td>Alkaline pH above 8.5</td>
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<td>+</td>
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</tr>
<tr>
<td>Mineralization</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Low mineralization waters&lt;1 g/l</td>
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<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>Waters of increased mineralization 1–5 g/l</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Medium-mineralization waters 5–15 g/l</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<td>+</td>
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<tr>
<td>Specific components contents</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Therapeutic mineral waters with no specific components or features</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Carbonated mineral waters</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Sulphide mineral waters</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Iron,arsenic waters and waters with the increased contents of Mn, Al, Cu and Zn</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Bromine and iodine waters</td>
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<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Waters with high contents of organic matter</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Silica waters</td>
<td>+</td>
<td>+</td>
<td>+</td>
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</tr>
</tbody>
</table>

**The basic anion composition**

The presence of carbonate ions which are dominant in the thermomineral waters of Jošanička Banja Spa is
caused by some increased pH values. From the balneological aspect, a more significant presence is that of
sulphate ions which can be used for treating a huge range of diseases, from skin infections to respiratory
problems and skin inflammations. Sulphate waters may be also used for treating liver diseases or gastro-intestinal tract issues, as well as for respiratory problems when the inhalation therapy is applied.

**The basic cation composition**

Sodium ions are dominant in the thermomineral waters of Jošanička Banja Spa. The magnesium and calcium ion contents are much lower than the sodium ions amount. Sodium waters are used as an adjuvant tool for treating arthritis diseases and they can also stimulate the lymph system in the body when used for bathing.

**Balneologically relevant gases**

The most significant of all the gases in the thermomineral waters of Jošanička Banja Spa is hydrogen sulphide. Its healing amount is caused by the contents of free hydrogen-sulphide and hydrosulphide ion. These waters are applied in treating skin diseases, rheumatism, mental disorders and vaginal dryness issues and inhalations.

**Balneologically relevant micro components**

**Fluorides.** An increased amount of fluorine can be found in alkali waters which contain lower concentrations of the calcium ion Ca²⁺, which is the case of thermomineral waters in Jošanička Banja Spa (0.24–5.6 mg/l). Generally, the fluorine in thermomineral waters originates from the minerals which contain fluorine (fluorites and apatites). From the balneological aspect fluorides are significant in the prevention of tooth decay.

**Lithium.** The lithium concentrations in the thermomineral waters from the spring in Jošanička Banja Spa ranged from 0.14 to 0.18 mg/l. The lithium in these waters originates from igneous and metamorphic processes which occur in the area. In the igneous rocks formation Li⁺ is gathered in acid rocks, especially at the last stage of the magma crystallization, and then lithium minerals are formed: spodumene and lepidolite, etc. From the aspect of balneological valorization, lithium is significant for the mental disorders treatment.

**Boron.** This micro component belongs to the group of elements which are found in waters in traces only. In the thermomineral waters of Jošanička Banja Spa, boron was found in concentrations 0.55 to 0.68 mg/l. Its origin is related to some volcanic processes which took place in the area of Kopaonik. Balneological valorization of boron is manifested in the skin disease treatment.

**GEOTHERMAL POTENTIAL OF THE THERMOMINERAL WATERS OF JOŠANIČKA BANJA SPA**

The area of Jošanička Banja Spa has always attracted researchers due to its geothermal potential and they have tackled the issue of the thermomineral waters of Jošanička Banja Spa from different perspectives [13,15–19].

The heat sources of the hydrogeothermal system of Jošanička Banja Spa are granodiorites and quartz diorites of the Paleogene and Neogene ages. The manifestations of geothermal energy at the surface of the terrain, as it has been mentioned before, occur in the form of springs created along the basic fault structures. The temperatures of geothermal springs fall are moving in the direction southeast to northwest (Figure 11). Besides the geothermal springs as the main indicators of an area's geothermal potential, there are also paleo-hydrogeothermal occurrences located 10 km to the south of Jošanička Banja Spa. The existence of these phenomena points to the fact that the original outlet of the thermomineral waters was carried out at another location in the altitude range from 600 to 1000 m [20]. After the Jošanica River's basin full formation and neotectonic upraise of the terrain, the outlet of the thermomineral waters “moved” from the original location to the today's site of Jošanička Banja Spa. According to the same author, the total area of this bank is approximately 45 km², and its thickness is about 1000 m.

![Figure 11. The map of hydroisotherms in the area of Jošanička Banja Spa.](image)

In the area which is today regarded as Jošanička Banja Spa, apart from the natural outlet of the geothermal water, there are also two active boreholes. Borehole B-3, 235 m deep, has the artesian pressure with the yield of 1.5 l/s and temperature of 52.2 °C, whereas borehole B-6, which is 294 m deep, owns the artesian pressure of 3.0 l/s and the temperature of 56 °C.

The possibility of finding even higher temperatures of the geothermal waters has not been fully examined still. In the area of Banja there have been made 9 study
boreholes, out of which borehole labelled B-9 is the deepest (596 m). Borehole B-9 is negative, including the other boreholes apart from B-3 and B-6. The measured temperature of the dry rocks at the bottom of B-9 borehole is 81 °C, whereas borehole B-5 (395 m) has the temperature higher by a degree, which is 82 °C. The results of the drilling did not match the expected ones, that is the drilling did not get through to the primary geothermal reservoir (drilling was terminated due to the disaster and the fact that the drilling tools got stuck), so the real (maximum) temperature of geothermal fluids in the primary reservoir was not confirmed.

Due to the impossibility of the direct temperature measuring of the geothermal fluids in the primary reservoir, the method which was applied was that of the chemical geothermometers with a view to providing an empirical definition of the expected maximum temperatures. In practice, up to now, the geothermometer method has played a significant role in researching and managing the geothermal reservoirs of an area. The method of chemical geothermometers is based on the concentration and ratio of certain chemical elements in the groundwater. The most applicable geothermometers are based on the silicon solutions (quartz and chalcedony), then sodium, potassium, calcium, magnesium, lithium, etc. In the course of making calculations, one must bear in mind the limits which each of the aforementioned geothermometers possess, and their mutual comparison leads to a higher degree of the data reliability.

Taking into account the way in which geothermal phenomena appear on the terrain surface as well as their physical manifestations, in order to calculate the expected temperatures in the Jošanička Banja Spa reservoir, silicon geothermometers were used and as a control geothermometer they used the Na/K ratio geothermometer (Table 3). The calculation of the expected temperature in the primary reservoir of geothermal energy in Jošanička Banja Spa was executed on the basis of the chemical composition of the waters in the “Banjski park” spring, since it is a natural outlet and it is the highest ever measured temperature of the groundwater on the terrain surface.

On the basis of the applied method of chemical geothermometers, the expected temperatures in the reservoir move within the range 102–130 °C. The temperature of 130 °C was gained by means of a quartz geothermometer under the conditions of conductive heat transfer without the loss of vapour. If by means of this geothermometer they gain the temperatures 120–180 °C, there is a great possibility that chalcedony could regulate the silicon solubility and it is necessary to use the chalcedony geothermometer as the control one. If the temperature range goes from 100 to 120 °C, when the chalcedony is applied, there is a huge possibility that this is exactly the representative temperature value in the reservoir.

The Na-K geothermometer was used as the control geothermometer, and it provides the most reliable results when the temperatures in the reservoir are high (180–200 °C). Apart from the temperature, the geothermometer’s reliability is also affected by the low contents of Ca (which is the case of the waters of Jošanička Banja Spa), then the negative log value (Ca\(^{12+}\)/Na) = 2.05 (which is not the case of the waters of Jošanička Banja Spa), neutral pH value and belonging to the chloride waters (which is also not the case of the Jošanička Banja Spa waters spa). The application of other geothermometers, such as K-Mg, Na-Ca and K-Ca, in the area of Jošanička Banja Spa is somewhat restricted, since they are applied only if the K and Mg concentrations in the groundwater are high and if by applying Na/K exceptionally high temperatures are gained.

Taking into account all the factors which have an effect on the temperature calculations by the geothermometer method, it may be concluded that the expected temperature of geothermal fluids in the primary reservoir of Jošanička Banja Spa is somewhere about 100 °C, and this result was obtained by means of the SiO\(_2\) (chalcedony) geothermometer.

Knowing the temperatures and yield of geothermal occurrences and objects in the area of Jošanička Banja Spa, it is possible to predict the thermal capacity of geothermal waters. When defining the thermal capacity which is based on the currently available temperatures and yields, the following equation was applied [21]:

\[
\text{Therm. Cap. [MW]} = \text{Flow rate [l/s]} \times (\text{Inlet temp.} - \text{Outlet temp.} [°C]) \times 0.004184 [\text{MW}]
\]

Table 3. Calculation of the expected temperature in the primary geothermal reservoir of Jošanička Banja Spa via the chemical geothermometers’ method; measured groundwater temperature on surface: 70–78 °C

<table>
<thead>
<tr>
<th>Applied geothermometers</th>
<th>Estimated groundwater temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2) (quartz) [25]</td>
<td>≈130</td>
</tr>
<tr>
<td>SiO(_2) (chalcedony) [22]</td>
<td>≈102</td>
</tr>
<tr>
<td>Na/K [23]</td>
<td>≈107</td>
</tr>
<tr>
<td>Na/K [24]</td>
<td>≈126</td>
</tr>
</tbody>
</table>
and Table 4 is presenting the thermal capacity of each spring.

Table 4. The calculation of the thermal capacity of the geothermal waters from the existent springs in Jošanička Banja Spa

<table>
<thead>
<tr>
<th>Occurrence</th>
<th>Parameter</th>
<th>( Q_s ) / l·s(^{-1} )</th>
<th>( t_{sr} ) / °C</th>
<th>( t ) / °C</th>
<th>( E ) / MWt</th>
</tr>
</thead>
<tbody>
<tr>
<td>„Banjski Park“</td>
<td>( \approx 15 )</td>
<td>( \approx 75 )</td>
<td>50</td>
<td>3.15</td>
<td></td>
</tr>
<tr>
<td>„Slanište“</td>
<td>2</td>
<td>( \approx 36 )</td>
<td>20</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>B-3</td>
<td>1.5</td>
<td>( \approx 53 )</td>
<td>30</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>B-6</td>
<td>3</td>
<td>( \approx 56 )</td>
<td>30</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>3.89 ( \approx 4 )</td>
<td></td>
</tr>
</tbody>
</table>

Taking into account the total available thermal capacity of the geothermal waters, which is about 4 MWt in the area of Jošanička Banja Spa, it is possible to heat about 830 households with the average surface of 60 m\(^2\) and average consumption of 80 W/m\(^2\). Currently, the Jošanička Banja Spa groundwater are used for the sake of heating a few public facilities (health centre, school, post office) and for the sake of some outdoor swimming pools in the summertime, and use as such is definitely below the available capacity.

Apart from the heating, geothermal resources of Jošanička Banja Spa have a great perspective within the greenhouse vegetable production. The average energy needed to heat 1 ha per year is about 20 TJ [20]. The energy used in the Jošanička Banja Spa area is about 112 TJ/year [27], and this is enough to heat almost 6 ha of the greenhouse. If one knows that the annual pepper yield is 20 t/ha, tomato yield is 30 t/ha, cucumber yield is 72 t/ha [28] out of the greenhouse production in the area of Jošanička Banja Spa, it would be possible to produce annually 120 t of peppers, 180 t of tomatoes and about 430 t of cucumbers.

For the sake of using geothermal waters for spa purposes, the scope of optimum temperatures goes from 25 to 37 °C. The conditions for the direct use for the aforementioned purposes are fulfilled by the waters of the “Slanište” spring \( t = 36 \) °C, whereas the waters of B-3 and B-6 boreholes and of the “Banjski park” spring need to go through the temperature lowering process, which actually means that they can firstly be used for the objects' heating. Likewise, the groundwater temperatures of the scope 25–27 °C are suitable to be used for sports and recreational purposes (outdoor and indoor swimming pools intended for the unlimited use).

POSSIBILITIES OF MULTI-PURPOSE USE OF THERMOMINERAL WATERS OF JOŠANIČKA BANJA SPA

The thermomineral waters of Jošanička Banja Spa are a significant resource which has not still been adequately deployed. Regarding their yield of about 20 l/s and a wide temperature scope (36 to 78 °C), these waters can be used for different purposes. The main advantage of using these waters resides in the possibility to apply a cascade model of use, which would gain a significant energy efficiency and saving. From Lindal’s diagram [29] (Figure 12), we may see that the possibility of using the thermomineral waters from the

Figure 12. Possible uses of thermomineral waters, depending on the temperature – a modified Lindal’s diagram.
springs in Jošanička Banja Spa is multiple, starting with fish farming which requires the lowest temperatures (20 °C) up to cereal drying (100 °C, the estimated temperature in the primary reservoir of geothermal fluids). If we add to this the healing component of the groundwater of Jošanička Banja Spa, the possibilities of their applications expand to the usage for spa purposes.

**CONCLUSION**

On the basis of the performed analysis of the chemical composition of the thermomineral waters in Jošanička Banja Spa, the origin of the thermomineral waters was ascertained, that is the fact that these waters are genetically related to the masses of crystalline rocks, so the formation of physical and chemical composition as well as the gas contents of the thermomineral waters are connected to the younger deep igneous rocks and thermometamorphic processes caused by them. The thermomineral waters of Jošanička Banja Spa belong to the group of nitrogen, lowly-mineralized silicic thermomineral waters of atmospheric origin. The silica concentration in the groundwater of Jošanička Banja is typical of the chemical composition of thermomineral waters in Jošanička Banja Spa according to the basic anion–cation sum, that is the dry residue value lower than 500 mg/l.

The results of the analysis of hydrogeothermal phenomena of Jošanička Banja Spa from the aspect of chemical composition as the indicator of balneological valorization, point to significant curative properties of the groundwater. The thermomineral waters of Jošanička Banja Spa according to the basic anion–cation composition belong to the group of carbonate–sulfate–sodium waters. The presence of sulfate ions helps to treat skin infections and respiratory issues, as well as diseases connected to the problems with the liver and gastrointestinal tract. Sodium in the waters is used to treat arthritic diseases and to stimulate the lymphatic system in the body. Out of some specific components, the Jošanička Banja Spa thermomineral waters are characterized by the presence of silicates, fluorides, lithium, boron and hydrogen-sulfides. Lithium is significant for treating mental disorders, whereas the balneological valorization of boron is reflected in its application for treating skin diseases.

Apart from considering the balneological potential, the chemical composition of Jošanička Banja Spa waters was analysed with the aim of indicating the geothermal potential of the area. According to the currently available quantities and temperatures of geothermal waters, the heat capacity equals about 4 MW. Applying the geothermometer method, the expected temperature of geothermal fluids in the primary reservoir of Jošanička Banja Spa is about 100 °C, which significantly increases the geothermal potential and opens up the possibility for a potential use of these waters in the binary cycle for the electricity production.

With the research carried out for the sake of this work, a qualitative valorization of the Jošanička Banja Spa thermomineral waters was carried out and the instructions for their sensible use were given. In the forthcoming period, people should take up the research directed towards: proving the geothermal potential indicated by the application of geothermometer method, developing the methodology of multi-purpose use of thermomineral waters in cascades as well as analysing the effects of using these waters for balneological needs.

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**REFERENCES**


IZVOD

HEMJSKI SASTAV TERMOMINERALNIH VODA JOŠANIČKE BANJE KAO INDIKATOR POREKLA, BALNEOLOŠKE VALORIZACIJE I GEOTERMALNOG POTENCIJALA

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