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Potential of corrosion and/or deposition of solid phases in the thermal waters in the region of Sofia Valley, Bulgaria, depending on their chemical composition

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The thermal waters in the region of Sofia Valley were essential for the emergence and development of the city. There are over 70 water sources with a total flow of 110 l/s and a temperature of 21 °C to 81 °C. They are used for bottling, balneology, as a source of heating energy, spa tourism and others. Waters are formed in rocks with different composition and age, which affect the chemical composition. Therefore, it is essential to evaluate the probability of corrosion of pipes and equipment or the deposition of solid phases in them. The first step is to determine the "Langelier Saturation Index" and the "Ryznar Stability Index". To assess the probability of deposition, the saturation indices for different solid phases are determined. The obtained results make it possible to classify the thermal waters in Sofia Valley according to the possibilities of negative processes in their use and to extract conclusions concerning the significance of the geological and hydrogeological factors.

Keywords: thermal water, scaling, corrosion, saturation index, geochemical modelling, Sofia Valley

INTRODUCTION

The emergence and development of the city of Sofia is highly related to the thermal waters. Along with the natural springs located on the territory of the city and its adjacent territories, thermal waters are revealed in different age and composition rocks through many drillings [1-4]. Geological and hydrogeological conditions are the reason for their different composition and temperature. Waters are used for various purposes – drinking and industrial water supply, bottling, heating, prophylaxis and balneology, sports, recreation. By the time water reaches the user, due to a change in the physicochemical conditions (temperature, pressure, redox potential, etc.), after its surface discharge, there are conditions for corrosion processes and solid phase formation on the pipes and equipment used. The purpose of this study is to evaluate the probability of occurrence of these processes for different types of water, according to their diverse chemical composition and temperature.

CHARACTERISTICS OF THERMAL WATERS IN THE SOFIA VALLEY

Sofia Valley is one of the largest geothermal fields in Bulgaria. It is located in the western part of the country and has got a territory of 1180 square kilometres (Fig.1). The length of the graben is of about 60 km and the width is up to 20-25 km.

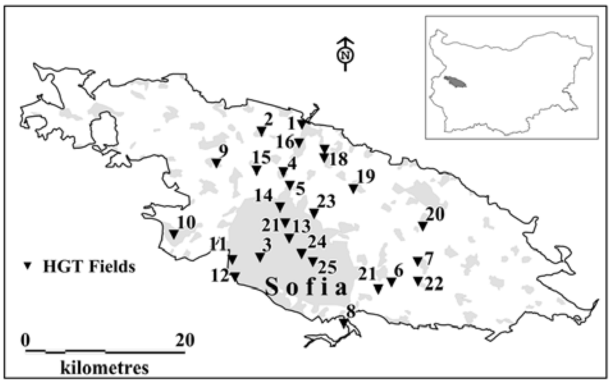

Fig.1. Location of the hydrothermal sources in Sofia Valley (HGT) [1, 2]

The valley represents a tectonic graben structure, striking northwest-southeast [1-2]. The depression is outlined as a closed zone of enhanced thermal potential [1-6]. There are many natural geothermal springs: Sofia-centre (the ancient Thracian settlement was established around it), Ovcha kupel, Knyazhevo, Gorna banya, Ivanyane, Bankya, Pancharevo (nowadays these are quarters of Sofia city or villages at its vicinity) and others (Fig.1, Tab.1). During the period of 1960-1990 a lot of boreholes were drilled and many new geothermal sources were discovered: Kazichene-Ravno pole, Svetovrachene, Novi Iskar, Trebich, Chepintsi and others (Fig.1, Tab.1). The temperature of mineral water currently flowing from geothermal boreholes and natural springs located within the frame of Sofia Valley varies

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from 21 ºC to maximum 81 ºC (borehole P-1 Kazichene). The total approved exploitation resource up to now by the Ministry of Environment and Water, now amounts to approximately 110 l/s (second largest geothermal basin in Bulgaria after Velingrad). Thermal water is partially used only in several areas in Sofia Valley. Bottling of mineral water (Gorna banya, Ivanyane) is a leading application and accounts for about 61% of the total use, followed by treatment and recreation (35% - Ovcha kupel, Bankya) and relaxation and sanitary needs (4% - Pancharevo, Kazichene). Special attention is paid to the further possibilities of geothermal water utilization in the Valley.

Table 1. Characteristics of major hydrothermal sources [1-4]

N on Fig.1	HGT	Rocks	Geolog. index	Flow rate	T
				dm^3/s	°C
1	Novi Iskar	sandstones	P	0.8	25
2	Dobroslavtsi	sandstones	T_1	0.8	40-41
3	Ovcha kupel	limestones	T_2	4.5	32
4	Trebich	limestones	T_2	1	51
5	Ilientsi	limestones	T_2	<2	47
6	Kazichene	limestones	T_{2-3}	5.8	80
7	Ravno pole	limestones	T_{2-3}	6.2	50-58
8	Pancharevo	limestones	T_2	12.5	44-48
9	Kostinbrod	limestones	J_{2-3}	~55	25-31
10	Bankya + Ivanyane	andesites	K2	25	24-38
11	Gorna banya	andesites	K_2	8	19-44
12	Knyazhevo	andesites	K_2	5.5	23-26
13	Sofia - centre	andesites	K_2	16	46
14	Svoboda distr. - Sofia	sedim. form.	K_2	7.2	50
15	Mramor	sands	N_1	1.5	42.6
16	Kumaritsa	sands	N_1	1.3	36-41
17	Gnilyane	sands	N_1	0.9	42
18	Svetovrachene	sands	N_1	5	45
19	Chepintsi	sands	N_1	6	50
20	G. Bogrov	sands	N_1	1.1	44
21	Kazichene	sands	N_1	1.4	39-60
22	Ravno pole	sands	N_1	4.4	51-52
23	Birimirtsi	sands	N_1	0.4	30
24	Lozenets distr. - Sofia	sands	N_2	2.8	33
25	Sofia 4th km.	sands	N_2		23

Water is discharged on the surface by springs and boreholes of depth in the range of 200 to 1200 m. Most of the wells have been drilled more than 30 years ago and are in poor technical condition. The majority of the sources are state owned. According to the amendments to the Water Act, after 2011 six hydrothermal sources were granted free of charge for management and exploitation to Sofia Municipality for a period of 25 years - Sofia center, Sofia-Serdica, Sofia-Lozenets, Sofia-Svoboda, Sofia-Ovcha kupel, Pancharevo.

Geological and hydrogeological background

As it was mentioned above, Sofia Valley is a graben structure, bounded by mountains. The graben basement is built of Mesosoic formations. They consist of andesites, volcano-sedimentary and sedimentary rocks of an Upper Creatacous age in the southwestern part and of carbonate and terrigenous rocks of Triassic, Jurassic and Upper Cretaceous age. The graben is filled of Neogene rocks mainly sands, clay, sandstones and lignite seams at some places. The total thickness of the Neogene complex varies in the range of 100 m to 1142 m. The thickness of the Quaternary cover is mostly between 50 m and 100 m.

The graben structure is complicated by many fault displacements that form internal small horsts and depressions [5]. They provide paths for water circulation and create links between different water bodies. The geological structure is complicated by many faults, some of which are still seismically active.

Three types of reservoirs are presented in the Sofia basin - porous, karstic and fractured. The reservoirs are parts of the basement rocks and of the Neogene and Quaternary formations [6]. They have specific hydrogeological characteristics related to the depth of occurrence, lithological type and structure of the host rocks and the conditions of natural recharge and draining.

The geothermic field of Sofia Valley is strongly disturbed by the mineral water flow. The thermal depression is outlined as a closed zone of enhanced thermal potential on the heat flow map of Bulgaria. The estimated average conductive heat flow is about $80x10^{-3}$ W/m^2 and the average geothermal gradient is of 4.7 ºC/100 m [7]. The highest heat flow density is calculated for Kazichane geothermic anomaly – $140x10^{-3}$ W/m^2 (south-eastern part of the basin).

Chemical composition of thermal waters

The analysis of the results of water samples taken from different water sources of thermal waters in Sofia Valley [3-4, 8] shows that they are characterized by a different chemical composition. The main reasons for this are the different rocks (Fig.1) in which they are formed as well as the local hydrogeological and geothermal conditions.

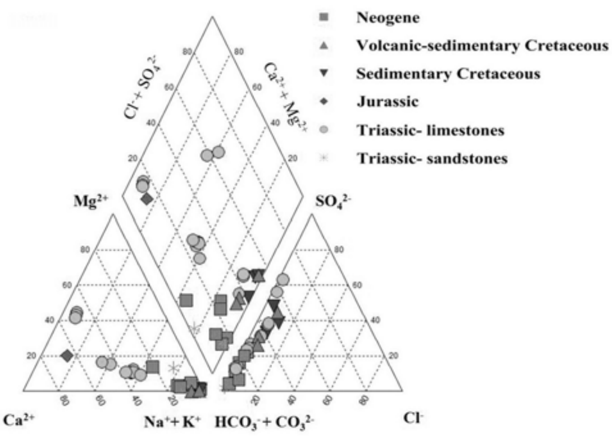

Fig.2. Piper diagram of thermal water sources formed in different rocks

The waters with the highest TDS (total dissolved solids) are formed in the oldest rocks, sandstones, conglomerates, aleurolites and argillites of Permian age – 5 g/dm^3. It is hydrocarbonate, sodium-potassium type and is characterized by high content of free CO_2 and increased radioactivity – 226Ra (220 mBq/dm^3).

The thermal water in the Lower Triassic sandstones is hydrocarbon, sodium, slightly alkaline (with pH about 8), with TDS ranging from 1 to more than 3 g/dm^3. Waters in Triassic limestones and dolomites are reached by boreholes in separate blocks beneath the Neogene deposits, filling Sofia Valley, mainly in the northern part. In addition, there are natural springs in the southern part – Pancharevo, and water conducted by active fault in Ovcha Kupel. In the deep parts, the water is with higher TDS (more than 3 g/dm^3 (Trebich). The lowest TDS is in Pancharevo – 0,5 g/dm^3. Generally predominant are waters with pH of 7.1-7.6. In some of the water sources, along with nitrogen, CO_2 can also be found. The predominant type of water – hydrocarbonate-sodium and hydrocarbonate-sodium-calcium, the relatively high contents of H_2SiO_3, as well as some microcomponents, are indicative of the deep-water recharge of the thermal waters. The waters with different composition are conducted by an active fault in Ovcha Kupel. They are sulphate-hydrocarbonate-sodium-calcium.

Kostinbrod heated water (21-30 °C) of Upper Jurassic limestones have a composition of typical karst waters – hydrocarbon-calcium-magnesium with TDS of 0.5 g/dm^3, which shows connection with the waters of a large mountain karst region, located in the northern edge of the valley.

The most important for Sofia city are the thermal waters formed in Upper Cretaceous volcanic rocks – mainly andesites. These rocks have a wide area of distribution, mainly in the southern part of the valley and are connected to most of the natural thermal springs by faults. These are waters with nitrogen in their gas composition, with low TDS of 0.1-0.3 g/dm^3, relatively high pH values – above 9, and are hydrocarbonate-sulphate-sodium.

Thermal waters are revealed by boreholes in sedimentary rocks of Upper Cretaceous age in the northern part of Sofia (Svoboda district). They have a higher TDS– more than 15 g/dm^3, low alkaline (pH about 8), and are hydrocarbon sulphate-sodium.

In the sand layers of the Neogene sediments, filling the Sofia graben, thermal waters are revealed in many places by boreholes. Their chemical composition is mainly formed by mixing waters from the bedrock with the cold waters as a result of surface recharge. This gives a direct relation to the diverse hydrochemical parameters in the different parts of Sofia Valley. In some areas, the presence of CH_4 and CO_2 can be found, which is a result of coal deposits in the Neogene materials and the relatively difficult movement of groundwater.

MATERIALS AND METHODS

The widespread use of thermal waters in Sofia Valley for various purposes necessitates assessment and prediction of the probability of corrosion and solid phase formation in pipes and equipment. The main factors influencing these negative processes are physicochemical: pH, pressure and temperature change, gas and chemical composition. Comparatively simplified approaches have been developed, aiming at the interaction of waters, mainly with metal pipes, and the probability of formation of carbonate and silicate minerals [9-12]. The ’’Langelier Saturation Index’’ (LSI) and the “Ryznar Stability Index” (RSI), introduced by Carrier (1965) [13], are also used in this study.

$$LSI = pH - pHs \qquad (1)$$

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

where:

pHs is the pH value of water when it is fully saturated with $CaCO_3$. It is estimated by the following formula:

$$pHs = (9,3 + A + B) - (C + D) \quad (3)$$

where:

$$A = (\log(TDS)-1)/10 \quad (4)$$

$$B = (-13.12 \log (T^{o}C + 273)) + 34.55 \quad (5)$$

$$C = (\log (\text{calcium hardness})) -0.4 \quad (6)$$

$$D = \log (\text{alkalinity}) \quad (7)$$

For the purpose of more detailed identification of the various mineral phases that may be formed, the Saturation Index (SI), which is best defined by Garrels, Christ in 1965, is applied. [14] Its determination was made by using the VISUAL MINTEQ software, which is a freeware chemical equilibrium model maintained by Jon Petter Gustafsson at KTH, Sweden. [15] This code allows calculating of saturation indices of a large number of mineral phases as well as the forms of presence of chemical elements in the water.

One of the main problems in the processing of results is the quality of the data from the thermal water analyses. Until now, many samples of thermal waters in Sofia Valley have been taken, some of them were published [5, 8, 16-17]. For the present study only 40 of them, from different water sources, were taken under consideration. The selection requirement was that these samples were analyzed in a comparable manner and that different hydrochemical parameters were analyzed by different methodologies, including field determination of the main changing physicochemical parameters. These conditions are met by some unpublished results, as well as analytical data published by Pentcheva et al. [8] carried out in the laboratory of the University of Antwerp (Belgium).

RESULTS AND DISCUSION

Using the data from the obtained analyzes and the Eqs.(1-2) for each of the tested water sources, the Langelier Saturation Index (LSI) and the "Ryznar Stability Index" (RSI) were determined. The results are grouped according to the characteristics of the water-bearing rock and are mapped on Figs.(3, 4). On the same graph, these results are assigned to the relevant water group, as suggested by Carrier [13] LSI and RSI indications.

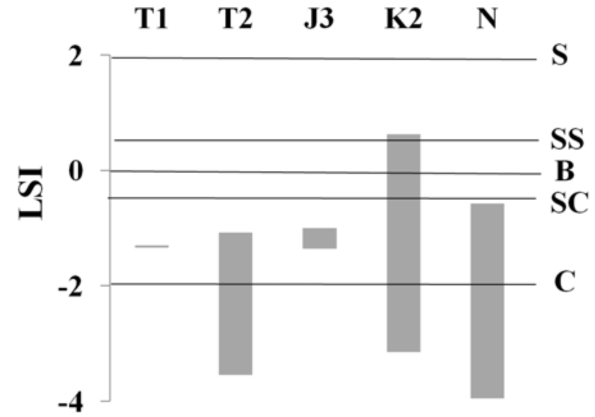

Fig.3. Range of variation of LSI values in different age rocks and their comparison with the suggested by Carrier indications [13] (C - Serious corrosion, SC - Balanced but pitting corrosion possible; SS - Slightly scaling and corrosive; S - Scale forming but not corrosive)

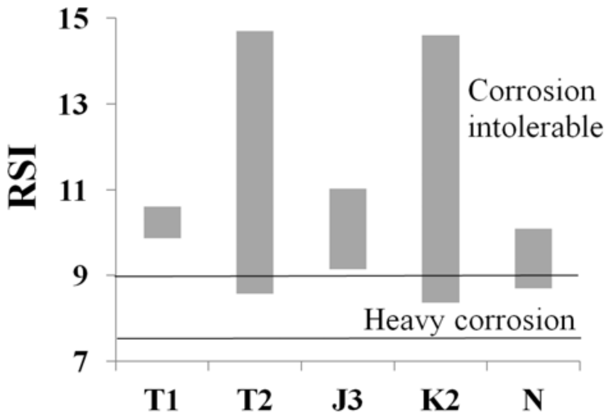

Fig.4. Range of variation of RSI values in different age rocks and their comparison with the suggested by Carrier indications [13]

The obtained results show that in most cases the probability of corrosion of the pipes is higher than the scaling of the carbonate substance. Regarding the LSI prevailing for the whole Sofia Valley, the thermal waters are in the range between Slightly corrosive but non-scale forming and Serious corrosion indications. The waters formed in Triassic carbonate rocks, Upper Cretaceous volcanic rocks and secondary retentive thermal waters in Neogene sediments, which are above Serious Corrosion Index, have a significant presence. Some of the waters formed in the Upper Cretaceous volcanic rocks, which are of major importance for the users are different in nature. A substantial part of these are related to Balanced but pitting corrosion possible and partly to Slightly corrosive but non-scale forming. According to RSI, most of the thermal waters in the study area are Corrosion intolerable.

It should be noted that the proposed by Carrier method [13] mainly characterizes the probability of deposition of carbonates on the pipes and equipment. The specific chemical composition of each individual water source determines the probability of deposition of other mineral phases. This is evaluated for about 200 mineral phases using the values of the respective water saturation indices calculated with the Visual MINTEQ 3 software. The results obtained with regard to the mineral phases, which according to the past practical experience have the greatest significance for deposits on pipes and equipment (carbonate minerals and forms of SiO_2) show that for the thermal waters in Sofia Valley this probability is small. In most cases, saturation indices indicate that under natural thermodynamic conditions the waters are unsaturated to equilibrium with respect to these mineral phases (Fig.5).

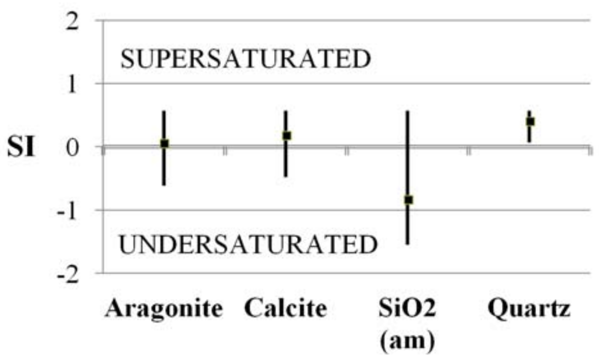

Fig.5. Saturation Index values for thermal waters relative to the major forms of $CaCO_3$ and SiO_2

Along with the major mineral phases, for which there is a risk of solid phase formation (scaling) on pipes and installations, thermal waters are likely to convert into solid state and other mineral phases. These are mainly compounds and minerals for which higher saturation index values were calculated. For example, in all samples in which phosphorus and fluorine is determined, saturation index values for FCO_3-Apatite are high – in the range of 3 to 6.5. Elevated saturation index values for some forms of aluminum hydroxides and silicates have been frequently found. Some of the water sources have high values of the saturation index of phases containing some elements, that are in very low concentrations in thermal waters – Ag, Cr, Cu, Pb, Se, Sn, V, Zn and others. Even if these mineral phases convert into solid state, their amount will be negligible and cannot have a significant effect on the exploitation of the thermal waters.

The evaluation of the probability of deposition of different mineral phases refers to the natural thermodynamic conditions. When the groundwater reaches the surface, so-called geochemical barriers [18] appear – zones in which there is rapid change of the natural conditions leading to a change in the physicochemical conditions. One of the most important factors is the change of thermal water temperature. By simulating such changes for the hottest water source in Sofia Valley –the borehole P1 – Kazichene, it was found that in the case of a sudden drop in the water temperature, the saturation indexes values for carbonate minerals are reduced and they increase in regard to phases containing silicon and aluminum. Another important factor that changes when the thermal water reaches the surface is pH. Considering the type of water in the studied area, its values depend on the state of the CO_2 - HCO_3 - CO_3^2 - system [19]. As a result of a change in the partial pressure of CO_2 on the surface, pH values may increase. This helps the deposition of carbonate materials at the mouths of the boreholes. These processes are relatively less important for the most significant thermal waters in the region, formed in Upper Cretaceous volcanic rocks, which are sulphate-hydrocarbonated.

CONCLUSIONS

Sofia Valley is one of the most important hydrogeological structures in Bulgaria with regard to the formation of thermal waters. The geological structure predetermines their formation in different by composition and age rocks, and consequently their chemical composition is also different. Taking into account the importance of the thermal waters for the city of Sofia, it is necessary to predict the probability of solid phase formation and corrosion on pipes and equipment. Therefore, the probability of these processes with respect to water formed in different rock collectors has been assessed. It is found that for most of the water sources there is a risk mainly of activating corrosion of metal pipes. Relatively less dangerous in this respect are the facilities through which the thermal waters formed in Upper Cretaceous volcanic sediments, which have the highest flow rates and are most used

(Bankya, Gorna banya, Knyazhevo, Sofia centre, etc.). Solid phase formation can only be expected in the areas of rapid temperature drop and the possibility of releasing CO_2 from the water. The obtained results have an important role for a more complete utilization of the hydrothermal resources in Sofia Valley.

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