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Hydrochemical study of geothermal reservoirs in Burgas basin (South–East Bulgaria)

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Хидрохимично проучване в геотермични резервоари в Бургаския басейн (ЮИ България)

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Резюме. Бургаският басейн е един от перспективните хидротермални региони в Източна България. В него са открити седем хидротермални находища и десет проявления с температура на водата до 50 °C. Настоящото проучване обхваща три геотермични находища, разположени в северната част на басейна – Айтос, Поляново и Съдиево. Представени са температурните криви, измерени в сондажите в находищата Поляново и Айтос. Химическият анализ на водните образци е направен с модерни аналитични методи след съответна процедура за техния подбор. Обсъдени са резултатите от химичните анализи на водни образци от района, направени в лабораториите на три държави – България, Италия и Индия. Изчислени са дълбочинните температури на находищата на базата на концентрациите на силициев двуокис, натрий, калий и калций. Според получените данни, резервоарната температура на находищата се изменя между 80 и 120 °C.

Ключови думи: хидротермални резервоари, пукнатинна порестост, температурни профили, химични геотермометри.

Abstract. Burgas basin is one of the perspective hydrothermal provinces in Eastern Bulgaria. Seven reservoirs and ten occurrences with water temperature up to 50 °C have been discovered in it. The current study is focused on three reservoirs located in its northern part – Aytos, Polyanovo and Sadievo. Temperature-depth curves measured in the wells are presented for Polyanovo and Aytos reservoirs. Appropriate collecting procedures and modern analytical methods were used to determine the water chemical composition. Water analyses made in three different laboratories in Bulgaria, Italy and India are discussed. Subsurface temperatures have been estimated from the concentrations of silica, sodium, potassium and calcium. All the thermal waters sampled have shown the reservoir temperatures between 80 and 120 °C.

Key words: hydrothermal fractured reservoir, temperature-depth profiles, chemical geothermometers.

Introduction

The territory of Bulgaria has a complex and diverse geological structure. Part of it is affected by young Alpine tectonics. Rocks and formations ranging in age from Precambrian to Quaternary built up the territory of the country. Bulgaria is divided into three major hydrogeological units: Low Danubian artesian basin, Intermediate region and Rila–Rhodopes region (Fig. 1). The studied area is located in Burgas hydrothermal basin, which is situated in the eastern part of the Intermediate region. The basin is presented by unstratifed (fault-fractured), stratified and mixed hydrothermal systems. Water circulation takes place in the fractured massif of granite and metamorphic rocks and in the Upper Cretaceous volcano-sedimentary deposits. Thermal reservoirs are formed also in many postorogenic Neogene–Quaternary grabens filled up with terrigenious deposits.

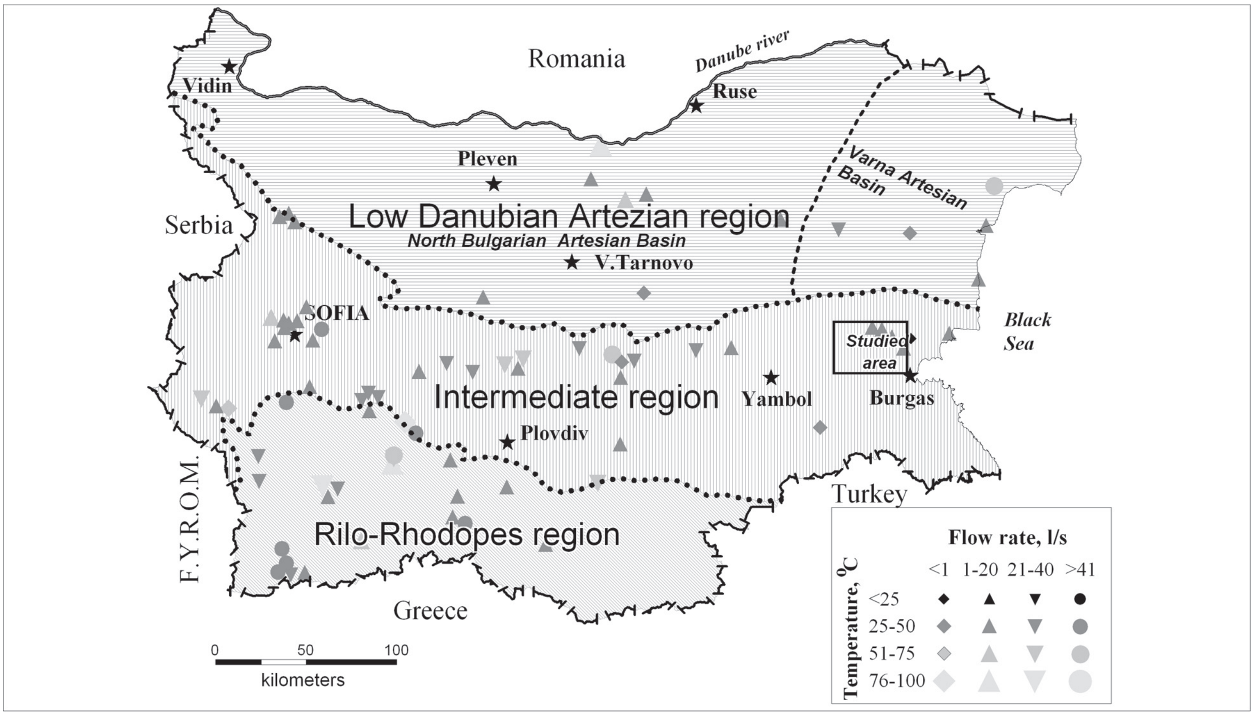

Fig. 1. Map of main hydrothermal regions in Bulgaria (Bojadgieva, Benderev, 2011)

Фиг. 1. Карта на основните хидротермални региони в България (Bojadgieva, Benderev, 2011)

Seven reservoirs and ten occurrences have been discovered in Burgas basin (Vlaskovski et al., 1997). The current study is focused on three reservoirs – Polyanovo, Aytos and Sadievo, located in the northern part of the basin (Karnobat–Aytos graben), along the Aytos fault (Fig. 2) (Bojadgieva et al., 2007). Aytos and Sadievo reservoirs were studied in the period 1969–1985, while Polyanovo was explored after them between 1988 and 1996. Two wells in Polyanovo – 111 and 135 and one in Sadievo – 20 are selected as

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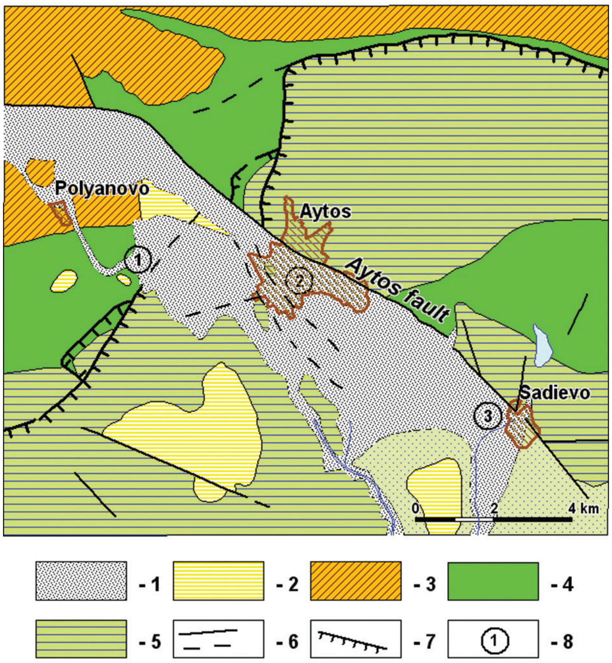
Fig. 2. Location map and geological setting of the discussed reservoirs (by Vlaskovski et al., 1997; Petrova et al., 1994)
1, Quaternary (gravels, sands, clays); *2,* Neogene (clays, sands, gravels); *3,* Paleogene (sands, siltstones, marls, calcareous clays); *4,* Upper Cretaceous (marls, siltstones, sandstones, limestones); *5,* Upper Cretaceous (volcano-sediment rocks); *6,* normal fault (certain, uncertain); *7,* reverse fault; *8,* geothermal reservoirs

Фиг. 2. Карта на местоположението и геоложките условия на изучаваните находища (по Vlaskovski et al., 1997; Petrova et al., 1994)
1 – Кватернер (чакъли, пясъци, глини); *2* – Неоген (глини, пясъци, чакъли); *3* – Палеоген (пясъчници, алевролити, мергели, варовити глини); *4* – Горна Креда (мергели, алевролити, пясъчници, варовици); *5* – Горна Креда (вулканосединментни скали); *6* – разломи (установени, предполагаеми); *7* – възсед; *8* – геотермални находища



monitoring points for ground water quality control in the country.

The existing geological, hydrogeological, geophysical and hydrochemical data are summarized in several publications (Kulaksazov, 1974; Petrova, Simeonov, 1989; Teneva, 1994; Vlaskovski et al., 1997; Georgieva, Vlaskovski, 2000; Bojadgieva, Gasharov, 2001).

The investigation of deep reservoirs structure is impeded due to their complex fracture type water conductivity. The results of magneto-telluric exploration carried out under a joint Indo–Bulgarian project could provide a better understanding of the reservoirs structure.

The aim of the current study is to summarize and analyze the water chemical data available for the studied area and to estimate the deep temperature distribution based on several chemical geothermometers. The water chemical data are provided by the Laboratory for geological analysis Ltd., and Research Institute of Resorts, Physiotherapy and Rehabilitation in Sofia (Bulgaria); University of Florence, Department of Earth Sciences (Italy) and National Geophysical Research Institute (NGRI), Hyderabad (India).

Geological and hydrogeological setting

Fractured type hydrothermal deposits in Bulgaria are less studied compared with porous and karst collectors, both in terms of hydrogeological parameters and structure of the permeable zones. Thermal waters in the studied area are formed, accumulated and circulated predominantly in Upper Cretaceous volcano-sedimentary (alternation of tuffs, tuffites, limestones, sands and marls) and crystalline volcanic (trachites and basaltoids) rocks intersected by tectonic fractures. The water is flowing along deep-seated faults randomly distributed in the area. Polyanovo, Aytos and Sadievo reservoirs are associated mainly with Aytos fault system that marks the northern and eastern borders of the Aytos graben. Aytos fault is of Late Alpine tectonic age and is still active during the Quaternary (Iliev-Brucev et al.,1994).

The major factors controlling the hydrodynamic water conditions are structural, tectonic and morphological ones. The recharge zones are located in the surrounding low mountains chains. The level difference between recharge and drainage zones varies between 30–35 m up to 100–150 m. The Aytos reservoir is drained to the east in the Black sea aquatory, while Polyanovo and Sadievo reservoirs are of local drainage basis.

Prior research

Geological, hydrogeological, geophysical and hydrochemical investigations have been carried out for the three reservoirs. The best studied among them is Polyanovo (Fig. 3). The biggest number of wells (19) is drilled there but they are predominantly shallow compared to those in Aytos (Fig. 4). The reservoirs in Polyanovo and Aytos exhibit the highest water temperature values respectively (49 °C and 50 °C), while in Sadievo the temperature is much lower – about (34 °C), (Table 1), (Vlaskovski et al., 1997). The highest flow rate (20.9 l/s) is measured also in Polyanovo.

The studied reservoirs are situated in a similar geological environment and belong to the South Bulgarian nitrogen hydrothermal mountainous sys-

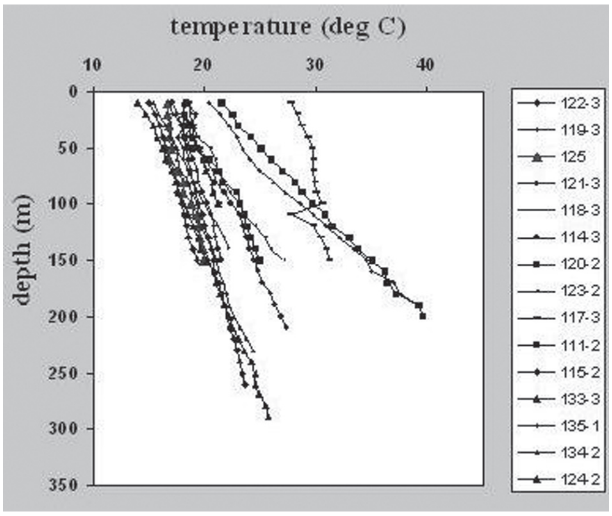


Fig. 3. Temperature logs measured in wells from Polyanovo reservoir

Фиг. 3. Температурни измервания в сондажи от находище Поляново

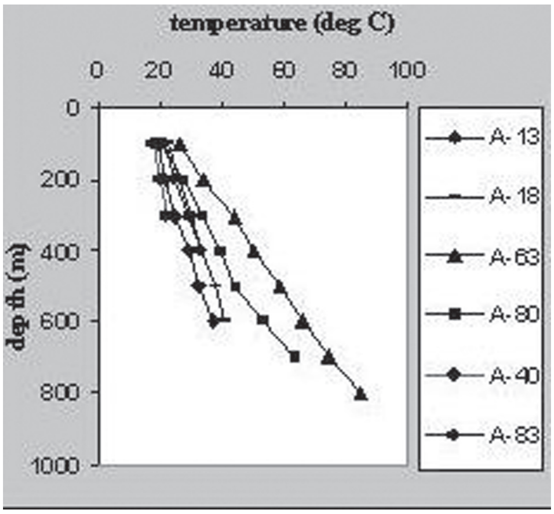


Fig. 4. Temperature logs measured in wells from Aytos reservoir

Фиг. 4. Температурни измервания в сондажи от находище Айтос

Table 1
Summarized data for the studied reservoirs

Таблица 1
Обобщени данни за изучаваните резервоари

N	Reservoir	Number of wells	Depth of wells (m)	Water level (m)	Water temperature (°C)	Flow rate (l/s)	Transmisivity coefficient (m^2/d)
1	Polyanovo	19	100 – 500	9.9 – (+44.9)	15 – 49	5 – 20.9	0.2 – 45
2	Aytos	5	310 – 1200	24.5 – (+10.6)	29 – 50	0.04 – 6.0	3.7 – 50
3	Sadievo	3	185 – 989	38.8 – (+50.3)	29 – 34	3.4 – 16.9	7.2 – 307

Note: (+) – above the surface

tems but they are characterized by different hydrogeological and hydrochemical data and are of different size and thermal potential. According to Vlaskovski et al. (1997) these reservoirs have no hydraulic connection between them.

An extensive geophysical study (well logging and field survey – electric, magnetic and gravity) has been carried out in Polyanovo reservoir only. As a result three parallel tectonic disturbances with west-east orientation have been discovered there (Vlaskovski et al., 1997). The less studied reservoir is Sadievo with only three wells drilled there. Temperature log is available for one of them only – Sadievo 88, which is 300 m deep.

According to Vlaskovski et al. (1997) the most perspective reservoirs in terms of thermal water use are Polyanovo and Sadievo.

Hydrochemical study

Chemical tests of water samples taken from the three reservoirs have been done in Sofia (Bulgaria, 1968–1997), in Florence (Italy, 2005) and in Hyderabad, (India, 2006) for the purposes of various projects. The data from the three sources have been summarized and compared. They show that the water chemical composition remained unchanged in time. Some variations exist in CO_2 and HCO_3 contents only. According to Zhong-He and Armannsson (2006), unreliable results for HCO_3 could be related to a matrix effect introduced by the presence of weak acid in the water sample.

Although the three studied reservoirs are located at a distance of 10 km a change in water chemical content is observed. Water type varies from hydro carbonate – sodium (Aytos, Sadievo) to hydro carbonate-sulfate-sodium (Polyanovo). Also, the chlorine content in Polyanovo (up to 170 mg/l) is much higher than in Aytos (up to 59 mg/l) and is missing in Sadievo. On the contrary, the quantity of K and Na cations in Polyanovo is twice lower compared to the other two sites. These data confirm the assumption that the studied reservoirs are of different structures and recharge zones. The increased values of fluorine (up to 12 mg/l) and methasilisic acid (up to 150 mg/l) are typical for this type of rocks. TDS (total dissolved solids) values are in the range of 0.34 to 0.71 g/l, while pH does not differ considerably (9.0–9.89).

Relatively high dissolved helium content (up to 1330 Pa in 114 Polyanovo) is registered in the studied area, which implies a deep groundwater origin.

Laboratory analysis in NGRI, Hyderabad (India)

Water samples for laboratory analysis in NGRI, Hyderabad (India) were collected from 3 geothermal areas in Burgas basin (Bulgaria) and filtered through a 0.45-μm membrane filter using compressed nitrogen as a non-reactive pressure source. The filtered water samples were stored in acid-rinsed plastic bottles. A portion of the filtered water was acidified with concentrated nitric acid to a pH of 2 in order to keep the divalent cations in solution. Dilution of 10 ml of the filtered samples to 100 ml with distilled deioniser water was done to retard the precipitation of silica.

All the 4 samples were analysed for pH, total dissolved solids (TDS), electrical conductivity (EC) and trace elements. pH was measured using a pH meter with glass electrode, TDS and EC measured using conductivity meter (Table 2). The concentrations of all cations and anions were determined by using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Chemical elements concentration is given in Fig. 5.

Calculations of subsurface temperature

When the water percolates through the subsurface strata, an interaction with the wall rocks is expected. The solution of rock forming minerals and therefore their constituents such as Si, Na, K, and Ca, etc., depends upon temperature-controlled equilibrium. These elements therefore act as geochemical thermometers for the estimation of subsurface reservoir temperature.

Table 2
Electrical conductivity and TDS results

Таблица 2
Резултати за електропроводност и обща минерализация

Sample No	Sample location	EC (µS/cm)	TDS (ppm)
1	Aytos 83	537.1	215
2	Polyanovo bath	646.2	259
3	Polyanovo 111	1012.0	507
4	Sadievo 88	452.4	178

Thus under appropriate condition the chemical composition of the thermal water may give valuable clues to the reservoir temperature. Surface-discharge water from the much more common system with a continuous liquid phase will usually be a sodium chloride solution and may also contain high concentrations of other chemical species. It is possible to derive all the constituents of thermal waters by solution of the rocks through which they flow (Ellis, Mahon, 1964, 1967).

The relationships of the chemical species in solution, when considered in the context of the local geologic setting (Data, Bahati, 2003), can be used to predict the temperature of a geothermal reservoir. In general, the concentrations of all constituents will increase with temperature as the solubility of the minerals increases. Magnesium shows a contrary trend, with higher concentrations at low temperature from the solution of dolomite, amphiboles, or pyroxenes, and lower concentration at high temperature from the slight solubility of chlorite (Reed, 1975).

Various investigators have proposed methods for calculating temperatures from water chemistry. Fournier and Rowe (1966) presented temperature calculations based on the solubility of some of the silica minerals. Experience in several geothermal areas shows that regardless of the silica minerals originally present, quartz is the phase that usually controls the SiO_2 concentration in solution (Mahon, 1966). Temperature calculation from the sodium/potassium ratio (Ellis, 1970) is based on the assumption that the cations in solution are in equilibrium with albite and orthoclase at temperatures above 150 °C. Fournier and Truesdell (1973) developed an empirical method for estimating temperature from the sodium, potassium and calcium concentrations. All the chemical indicators of temperature are based on the assumptions that the water was in equilibrium with the surround minerals in the reservoir and that the water moved to surface rapidly, without reacting at lower temperature on the way to the surface (Fournier, Truesdell, 1974). Mixing of cold, shallow ground water can dilute geothermal water and will often give misleading results for the geochemical thermometers.

Fournier and Truesdell (1974) developed a mathematical method for estimating the amount of mixing of hot water with cold water. In addition, a computer program is available for performing the iterative calculations (Truesdell et al., 1973).

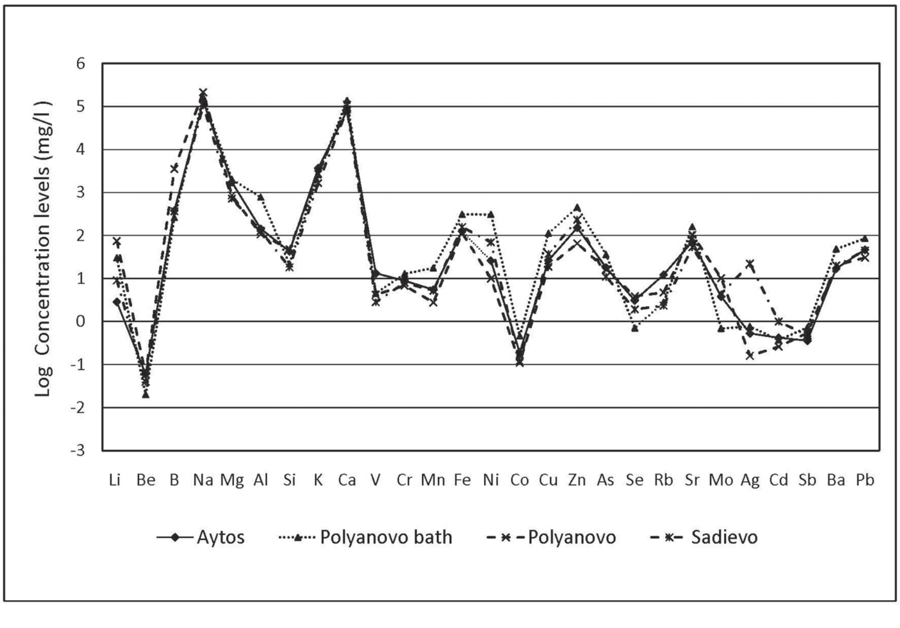


Fig. 5. Chemical elements concentration of geothermal water samples (Burgas basin, Bulgaria)

Фиг. 5. Концентрация на химическите елементи във водните образци (Бургаски басейн, България)

Table 3
Temperatures data of the studied reservoirs

Таблица 3
Температурни данни за изучаваните находища

Sample No	Location	Silica geothermometers temperatures (°C)			Cation geothermomethers temperatures (°C)	
		Cristobalite	Chalcedony	Quartz	Feldspars	$\beta = 1/3$
1	Aytos 83	110.5	102.8	136.2	70.8	143.5
2	Polyanovo bath	117.9	110.7	140.3	37.9	117.5
3	Polyanovo 111	109.1	101.4	135.5	25.9	111.6
4	Sadievo 88	119.7	112.5	141.3	37.7	117.6

In this study, the temperature calculations (Table 3), were made for each water source using the following equations of Fournier.

Calculated temperatures for the solubility of silica minerals:

Cristobalite (SiO_2 in moles/kg)

$$T(^\circ\mathrm{C}) = \left[\frac{-1000}{\log(\mathrm{SiO_2})}\right] - 273.15$$

Chalcedony (SiO_2 in moles/kg)

$$T(^\circ\mathrm{C}) = \left[\frac{-1032}{0.09 + \log(\mathrm{SiO_2})}\right] - 273.15$$

Quartz (SiO_2 in mg/kg)

$$T(^\circ\mathrm{C}) = \left[\frac{1309}{5.19 - \log(\mathrm{SiO_2})}\right] - 273.15$$

Quartz with steam loss from boiling (SiO_2 in mg/kg)

$$T(^\circ\mathrm{C}) = \left[\frac{1522}{5.75 - \log(\mathrm{SiO_2})}\right] - 273.15$$

Calculated temperatures for the solubility of feldspars and empirical equations (cations in moles/kg):

Feldspars (albite and orthoclase)

$$T(^\circ\mathrm{C}) = \left[\frac{777}{0.47 + \log\left(\frac{Na}{K}\right)}\right] - 273.15$$

Empirical Equation

$$T(^\circ\mathrm{C}) = \left[\frac{1647}{2.24 + \mathrm{A} + \mathrm{B}}\right] - 273.15$$

$$\mathrm{A} = \log\left(\frac{\mathrm{Na}}{\mathrm{K}}\right) \quad \mathrm{B} = \beta \log\left(\sqrt{\frac{\mathrm{Ca}}{\mathrm{Na}}}\right)$$

Calculate first for β = 4/3, then if T is greater than 100 °C, recalculate for β = 1/3.

Data analysis

The results based on the graphic analysis are briefly described below:

– Silica geothermometers predict temperature values in a narrower interval compared to cation geothermometers.

– The calculated temperatures for Polyanovo 111 and Sadievo 88 (Fig. 6), by using silica geothermometers (cristobalite and chalcedony), are about 10–20% higher compared to the values calculated for the same wells by Teneva (1994).

– The highest predicted temperature is calculated for Aytos 83 applying cation geothermometers, while according to results from silica geothermometers the highest water temperature should be expected in Sadievo 88. The silica-bearing geological strata in the region exert influence on the temperature estimations obtained by silica geothermometers. Data from more wells located in both reservoirs are needed to get a better understanding of water temperature distribution.

– Among cation geothermometers more suitable for application (Fraser at al., 1986) in the region are Na-K-Ca (for β = 1/3) (Fig. 7). Temperatures, predicted by them are close to the values calculated by cristobalite and chalcedony geothermometers (Table 3). Sadievo and Polyanovo bath have similar temperature values.

Conclusions

1. The best-studied subsurface temperature filed is of Polyanovo reservoir where the highest number of wells exists.

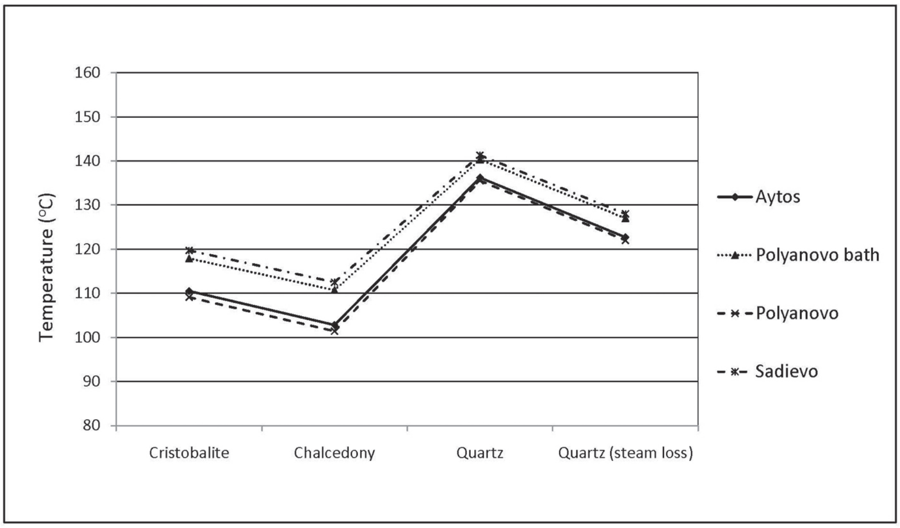


Fig. 6. Estimated temperature from solubility of silica minerals

Фиг. 6. Изчислена температура по разтворимост на силикатни минерали

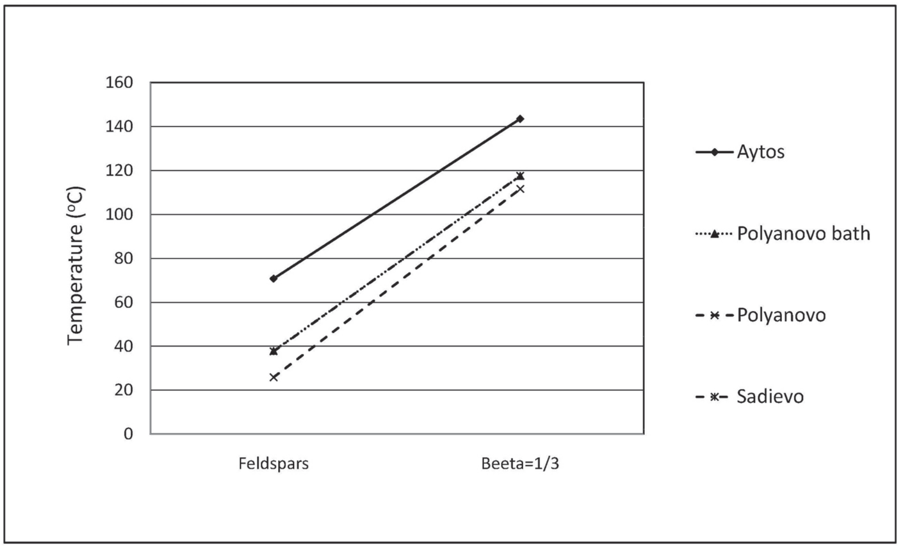


Fig. 7. Estimated temperature from solubility of Na–K–Ca minerals

Фиг. 7. Изчислена температура по разтворимост на Na–K–Ca минерали

2. The highest predicted water temperature is obtained for Aytos 83 well by using geochemical thermometer based on solubility of Na–K–Ca minerals.
3. Chemical analysis of more water samples taken from different points in Polyanovo and Aytos reservoirs would provide more reliable data on reservoir temperature distribution in them.
4. All the thermal waters sampled have shown a reservoir temperature between 80 and 120 °C.
5. The water in this temperature range can be used for industrial or domestic heating and cooling. Due to the high fluorine content (from 2 to 12 mg/l) water is not suitable for bottling without additional treatment.

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