

THE OCCURRENCES OF SULPHUROUS WATERS IN THE POLISH CARPATHIANS

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Abstract: The sulphurous waters from 125 springs recorded within the Polish Carpathians represent mainly acratopegae and fresh waters, while their mineralized varieties are less frequent. Most of the waters studied belong in the geochemical classification to bicarbonate waters. Other types include (in the decreasing order of abundance): carbonated sulphurous waters, chloride-sulphurous waters, and sporadically occurring sulphate-sulphurous waters. The contents of total dissolved solids range between 0.3 and 3.6 g/dm³, and those of hydrogen sulphide from 1 to 160 mg/dm³. Besides hydrogen sulphide, boron and carbon dioxide are additional therapeutic components, found in several springs.

Key words: Carpathians, sulphurous waters, hydrogen disulphide

Introduction

Numerous occurrences of the springs with sulphurous waters were found within the area of the Polish Carpathians (Rajchel 2000). They are the waters that in 1 dm³ contain at least 1 mg of iodometrically determined sulphur ($\text{H}_2\text{S} + \text{HS}^- + \text{S}^{2-} + \text{S}_2\text{O}_3^{2-} + \text{HSO}_3^-$) (Dowgiałło *et al.* 1969). Hydrogen disulphide is a specific component of these waters, and its content above the pharmacodynamic threshold gives them therapeutic properties (Dowgiałło *et al.* 1969, Dowgiałło 1999).

The occurrences of the sulphurous waters were established within the Podhale Flysch as well as the Magura, Dukla, Silesian, Subsilesian, Skole and Zgłobice units. The waters are associated with the flysch sediments with the age spanning Upper Jurassic and Miocene, the prevalent sandstones and shales being accompanied by minor limestones and marls, as well as radiolarites, cherts and gaizes.

The Carpathian region, the recharge and drainage area of the groundwater, shows a considerable diversification of the geological structure considering both its lithofacies development and tectonic character. As a hydrogeological region it is heterogeneous with regard to its lithological and structural conditions and associated reservoir

properties of its rocks (Bober & Oszczypko 1964, Jetel & Rybarowa 1975, Oszczypko *et al.* 1981, Chowaniec 1991).

Sulphurous waters of the Carpathians

The sulphurous waters from 125 springs recorded within the area of the Polish Carpathians (Rajchel 2000) have been classified on the basis of chemical analyses mainly as acratopegae and fresh waters, and subordinately as mineral waters. Their mineralization (TDS content) is 0.3-3.6 g/dm³ (Table 1). The presence of H₂S in the Carpathian sulphurous waters can be attributed mainly to pyrite, the mineral which is very common in the flysch strata in the dispersed form (Mochnacka 1961, Oszczypko 1963, Gucwa & Wieser 1980). At the current stage of investigations a connection of H₂S with the Miocene strata in the Carpathian basement (Połtowicz 1993, 1995, Kotarba *et al.* 1998, Rajchel *et al.* 2002) or with abiogenic processes (i.e. its juvenile origin) cannot be excluded (Rajchel *et al.* 2002).

Content ranges of individual components in the sulphurous waters of the Carpathian springs

Table 1

Tectonical unit	Number of springs analysed	TDS g/dm ³	Q l/min	Temperature °C	pH	H ₂ S mg/dm ³	HBO ₂ ³ mg/dm ³	CO ₂ ³ g/dm ³
Podhale Flysch	9	0.3 - 1.1	0.2 - 2	9.5 - 12.8	7.1 - 7.8	1 - 20		
Magura Unit	53	0.3 - 3.3	0.5 - 20	8 - 13	6.5 - 8	1 - 52.6	6 - 77.2	1.1 - 2
Dukla Unit	3	0.5 - 1	0.5 - 2	10 - 10.9	7.1 - 7.4	1 - 3.5		
Silesian Unit	47	0.3 - 2.6	0.2 - 20	8.8 - 13.2	7 - 8	1 - 43.5	5.2 - 95	1
Subsilesian Unit	3	0.5 - 1.3	1	11	7.1 - 7.3	1 - 160		
Skole Unit	9	0.7 - 3.6	1 - 8	10.6 - 12	7.1 - 8	2.8 - 26	5.2 - 17.3	
Zglobice Unit	1	3	5	15	7.5	2		

The waters recorded represent the following geochemical types:

- bicarbonate-sulphurous waters;
- chloride-sulphurous waters;
- carbonated sulphurous waters;
- sulphate-sulphurous waters.

Bicarbonate-sulphurous waters are characterized by a small discharge, and usually represent fresh waters or acratopegae from a zone of an active, shallow circulation. This is indicated by oscillations of the discharge in relation to rainfall, low mineralization and temperature changes. These waters belong to the upper

hydrogeochemical zone. Their H₂S content should be linked with the presence of iron disulphides, while higher H₂S contents may be of a deep-seated origin as it is indicated by preliminary isotope studies (Rajchel *et al.* 2002).

Chloride-sulphurous waters are characterized by prevalence of chloride ions, significantly higher mineralization and higher H₂S content. Their genesis is disputable. They are probably a result of mixing of infiltration and paleoinfiltration waters as well as waters released from clay minerals during incipient, low-temperature metamorphism (Zuber & Grabczak 1985, 1987, Leśniak & Dowgiałło 1986). The genesis of their H₂S is most probably associated with bacterial reduction of sulphates, present in the Miocene basement of the flysch strata.

Carbonated sulphurous waters are seldom found. These are mineral waters, characterized by the presence of CO₂, metaboric acid and insignificant amounts of H₂S. The genesis of carbon dioxide is still disputable: associated mainly with the processes of Neogene volcanism, locally it can be linked with metamorphic processes or oxidation of hydrocarbons (Świdziński 1965, Dowgiałło 1978, Leśniak & Węclawik 1984, Zuber & Grabczak 1987). Hydrogen disulphide of these waters may be formed by direct reaction of pyrite and carbon dioxide (Macioszczyk 1987). Its deep-seated origin cannot be excluded, as it is indicated by coexistence of high amounts of carbon dioxide and hydrogen disulphide, established during investigations of the “Zuber” water deposits in Krynica (Duliński *et al.* 1999) and preliminary isotope studies (Rajchel *et al.* 2002).

Sulphate-sulphurous waters are very rare. They occur in the marginal zone of the Carpathians, where their chemical composition and hydrogen disulphide genesis are associated with Miocene strata, particularly those of chemical origin. The mode of generation of hydrogen disulphide is the essential feature differing the Miocene-derived carbonated-sulphurous waters from the sulphurous waters of the Carpathians proper. Purely Miocene springs have their H₂S formed by reduction of gypsum by bacteria in the presence of organic substance. Sulphurous waters from the marginal part of the Carpathians reveal some chemical characteristics of waters genetically associated with the Carpathians as well as of waters associated with sediments of chemical origin and of relict waters of the Miocene basin.

Most of the Carpathian sulphurous waters show only small differences in their chemical composition, as these waters were formed under similar conditions and migrated within the strata of similar lithologies. Any changes in the lithology of aquifer are clearly marked in the chemical composition of the water studied.

The Carpathian sulphurous waters (Table 2) differ in their amounts of hydrogen disulphide, ranging from 1 to 52 mg/dm. Two springs, "Aleksander" in Wrząsowice and "Czarne" in Ochojno, are the exceptions as their H₂S content is about 160 mg/dm³. These springs occur in the zone of overthrust of the Subsilesian Unit onto the Miocene of the Carpathian Foredeep, so their waters were formed under different conditions and the genesis of their H₂S was different. The highest amount of hydrogen disulphide outside the marginal zone was found in the "Wspomnienie" spring in Nowy Sącz (52.6 mg/dm³). The latter spring is associated with the Miocene deposits of the Kotlina Sądecka depression and its chemistry was affected by both Miocene and flysch sediments.

Besides hydrogen disulphide, boron and carbon dioxide are specific components in more than 20 springs. Boron occurs as metaboric acid in six springs of the Magura Unit, where its content varies from 6 to 77.2 mg/dm³. In the Silesian Unit metaboric acid was found in nine springs (5.2-95 mg/dm³), and in the Subsilesian Unit in seven springs (5.2-17.3 mg/dm³). Specific chemical features are also imposed by carbon dioxide. Its higher amounts that allow us to classify waters as the carbonated ones occur in three springs within the Magura Unit (1-2 g/dm³) and in one spring from the Silesian Unit (1 g/dm³). The latter spring represents the easternmost occurrence of carbonated waters that form a small enclave in Rabe near Baligród (the Bieszczady Mts region).

The discharge of the sulphurous springs is diversified and ranges between 0.2 and 20 dm³/min. The springs with the highest discharges occur within the Magura Unit in Złatna, Lipnica Wielka, Lipnica Mała, Nowy Sącz and Wapienne; within the Silesian Unit in Polichy near Ciężkowice, Folusz, Pielgrzymka, Myczkowce and Uherce Mineralne; within the Skole Unit in Straszyle, Lubenia and Nieborów near Hyżne.

Hydrochemical types of sulphurous waters within the distinguished geological units of the Polish Carpathians

Table 2

Unit	Two-ion waters	Three-ion waters	Four-ion waters
A	HCO ₃ - Na	HCO ₃ - Ca - Na HCO ₃ - Ca - Mg	HCO ₃ - Ca - Na -Mg
B	HCO ₃ - Ca HCO ₃ - Na HCO ₃ - Na, HBO ₂	HCO ₃ - Ca - Na HCO ₃ - Ca - Mg HCO ₃ - Cl - Na HCO ₃ - SO ₄ - Na HCO ₃ - SO ₄ - Ca HCO ₃ - Na - Ca CO ₂ + HCO ₃ - Ca -Mg	HCO ₃ - Cl - Na - Ca HCO ₃ - Cl - Ca - Na HCO ₃ - SO ₄ - Ca - Mg HCO ₃ - Ca - Na - Mg HCO ₃ - Ca - Mg - Na HCO ₃ - Cl - Na - Ca, HBO ₂ HCO ₃ - Na - Ca - Mg HCO ₃ - Ca - Na - Mg, HBO ₂ CO ₂ + HCO ₃ - Cl - Na - Ca, HBO ₂ CO ₂ + HCO ₃ - Na - Ca - Mg, HBO ₂
C	HCO ₃ - Na HCO ₃ - Ca	HCO ₃ - Na - Ca	
D	HCO ₃ - Na, HBO ₂ HCO ₃ - Ca	HCO ₃ - Ca - Na HCO ₃ - Ca - Mg HCO ₃ - SO ₄ - Ca HCO ₃ - Na - Ca, HBO ₂ HCO ₃ - Ca - Na, HBO ₂ HCO ₃ - Cl - Na, HBO ₂ Cl - HCO ₃ - Na, HBO ₂ CO ₂ +HCO ₃ - Cl - Na, HBO ₂	HCO ₃ - Ca - Na - Mg HCO ₃ - Na - Ca - Mg HCO ₃ - Cl - Ca - Na HCO ₃ - Cl - Na - Ca, HBO ₂ HCO ₃ - SO ₄ - Ca - Mg HCO ₃ - Cl - Na - Ca Cl - HCO ₃ - Na - Ca Cl - HCO ₃ - Na - Ca, HBO ₂
E	HCO ₃ - Ca		SO ₄ - HCO ₃ - Ca - Mg HCO ₃ - SO ₄ - Ca - Na
F	HCO ₃ - Na, HBO ₂	HCO ₃ - Ca - Na Cl - HCO ₃ - Na, HBO ₂ HCO ₃ - Cl -Na, HBO ₂	Cl - HCO ₃ - Na - Ca, HBO ₂ HCO ₃ - Cl - Na - Ca, HBO ₂
G			SO ₄ - HCO ₃ - Ca - Na

A - Podhale Flysch; B - Magura Unit; C - Dukla Unit; D - Silesian Unit; E - Subsilesian Unit; F - Skole Unit; G - Zgólbice Unit

The temperature of these springs changes from 8 to 9.5°C. The springs with lower discharges and their outlets well insulated have their temperatures higher.

Concluding, sulphurous waters may be formed under closely specified lithological and tectonic conditions. Their hydrogen sulphide content depends on the presence of iron sulphides and organic substance, and is also associated with disjunctive tectonic regime that affects the genesis of the Carpathian waters.

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