IODINE-BROMIDE WATERS IN THE UPPER SILESIAN COAL BASIN - PROPERTIES AND PERSPECTIVES FOR UTILIZATION

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ABSTRACT:

Southern part of the Upper Silesian Coal Basin (USCB), situated at the borderland of Poland and Czech Republic, is an area where valuable groundwaters of potential medicinal use occur. These connate waters, containing significant concentrations of I and Br ions, often fulfilling standards for medicinal waters, are present in Tertiary and Carboniferous formations of the area.The paper presents chemistry, perspectives for utilization, and the mining influence on the groundwaters of potentially medicinal use in the Upper Silesian Coal Basin (USCB). Conflicts between mining industry, and groundwater preservation, were particularly sharp in case of a Polish health resorts, which lost its groundwater resources, due to the impact of intensive drainage. Despite the negative changes, waters from Badenian, of TDS up to 35 g/dm^3, contain I and Br at the levels making possible their therapeutic application in the Spa of Darkov in Czech Republic. Evolution of mining industry within the USCB, may enable future exploitation of the waters, safe from qualitative degradation and diminishing of their resources. Health resorts revitalization, basing on local iodine-bromide waters, becomes again possible in this Region.

Keywords: Groundwater, iodine-bromide waters, medicinal waters, mining drainage

INTRODUCTION

The Upper Silesian Coal Basin (USCB) covering the area of 7500km^2 (fig.1) was developed as Variscian intermontaneous depression, and finally formed in Alpine orogenesis (Kotas, 1985). Its main part, comprising the borderland of Poland and Czech Republic, is situated within the range of Carpathian foredeep. This structure is filled with Tertiary sediments, overlaying Carboniferous coal-bearing formation. Mining activity, lasting for over 200 years, enabled local hydraulic contacts between Quaternary, Tertiary and Carboniferous aquifers. Mining drainage, reaching the depth of 1200m, caused partial depletion of the nonrenewable groundwater resources, and in consequence led to conflicts between mining industry and spas, which were basing on iodine -bromide waters utilization.

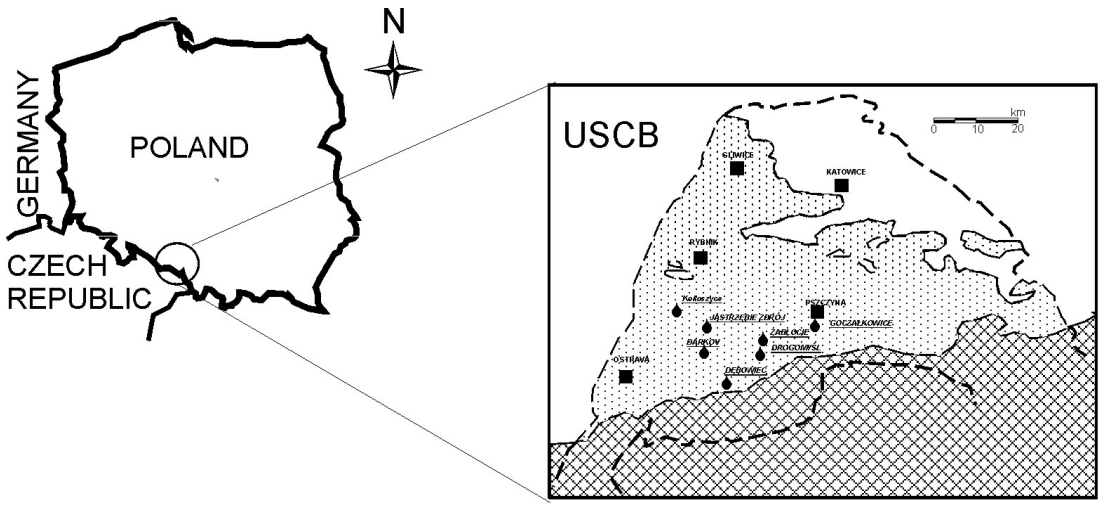

***Figure 1**. The Upper Silesian Coal Basin - map of localities with medicinal waters exploitation. Explanations: 1 - Tertiary overburden; 2 - Carpathians; 3 - places of medicinal waters exploitation; 4 - towns; 5 - borders of the USCB*

HYDROSTRUCTURE AND CHEMICAL COMPOSITION OF WATERS

The main primary aquifers of the area are the following: Quaternary sandy aquifers, groundwater horizons of Early Badenian, Upper Carboniferous aquifers. The most interesting in terms of iodine-bromide waters resources are Tertiary and Carboniferous aquifers. Iodine-bromide waters of peliticTertiary facies occur in two horizons (from -50m to +50m, and from -450 to -400m below the sea level, respectively) formed by complexes of thin lenticular sandy bearings within monotonous measures of impermeable clacareous silts. These connate waters of Cl-Na type contain also methane, which is believed to originate from organic matter decay. The content of iodine vary from 3 to 75mg/dm^3 depending on the depth (Grmela, 1998). Mean chemical composition of these waters, presented after Kurlov's formula is the following (M - mineralization and specific components in g/dm^3):

$$M = 28 \div 60 \frac{99Cl\ 1HCO_3}{88Na + K\ \ 7Ca\ \ 4Mg} (0.04Sr, 0.09Br, 0.024I, 0.004Ba). \quad (1)$$

Waters of this type are utilized for therapy in the Spas of Darkov and Klimkovice near Ostrava in Czech Republic.Fossil connate waters were also found in sandy and gravel sediments, and breccias of detritial facies of Lower Badenian. These sediments (from dozens up to 268m thick) are present in central parts of deep morphological depressions of the roof of Carboniferous complex. The groundwaters are reach in biogenic methane and in chemogenic CO_2 in the most south-western part of the USCB. Chemistry and vertical zoning of the waters, is altered by the decrease of their piezometric heads, caused by mining activity in underlying Carboniferous complex. Representative chemical composition of these waters, is presented below:

$$M = 39 \frac{100Cl}{85Na + K\ \ 9Ca\ \ 6Mg} (0.1Sr, 0.11Br, 0.017I, 0.006Ba) \quad (2)$$

Waters of this type were utilized for therapeutic salts production in Poland, in Zabłocie and Dębowiec (fig.2), however their concentrations of iodine were much higher, reaching: 129 and 131mg/dm^3 respectively.
Average chemistry of waters from Carboniferous fissure-porous aquifers of Czech part of the USCB is characterized below (Grmela, 1998):

$$M = 82 \frac{100Cl}{80Na + K\ 13Ca\ \ 7Mg} (0.25Sr, 0.15Br, 0.01I, 0.007Ba). \quad (3)$$

The main part of the discussed fragment of the USCB is insulated from the surface. Low mineralised, poly-ionic waters (TDS up to 4g/dm^3), are found only in the areas without insulating cover of impermeable Miocene strata. The less deep zone of waters of types Cl-Na, with TDS between 50 and 100, and above 100g/dm^3, was ascertained in the Chwałowice thrust (Poland), at the depths of 250 and 500m respectively (Różkowski, 1971; Różkowski et al., 1985). Waters from the Carboniferous are utilized in the Spa of Goczałkowice (Poland). In the past they were also exploited in the former Spa of Jastrzębie and in Moszczenica (fig.2). The waters from Drogomyśl are especially reach in iodine - 140mg/dm^3 (Dowgiałło et al., 1969).

Table 1. Chemical analyses of waters of potential medicinal use - examples

"Jankowice" Coal Mine - Analysis nr: 25			
Sampling depth: 565m Sampling date: 2002 03 19			Mineralization: 5,48 %
Stratygraphy: Upper Silesian Sandstone Series - Upper Carbonoferous			Water type: Cl-Na+Br+J
Symbol mg/dm^3	Symbol mg/dm^3	Symbol mg/dm^3	Symbol mg/dm^3
Na^+	NH_4^-	Cl^-	HCO_3^-
16163	-	35450	20,0
K^+	$Fe_{ogólne}$	Br^-	NO_3^-
169,51	0,09	119	8,4
Ca^{2+}	Mn^{2+}	J^-	CO_3^{2-}
1483,1	0,5	4,6	-
Mg^{2+}	Sr^{2+}	SO_4^{2-}	F^-
981,9	86,0	1,0	-
TDS:			54769 mg/dm^3
"Pniówek" Coal Mine - Analysis nr: 8			
Sampling depth: 705m			Mineralization: 6,95 %
Stratygraphy: Upper Silesian Sandstone Series - Upper Carbonoferous			Water type: Cl-
Sampling date: 2002 02 07			Na+Br+J+Mn
Symbol mg/dm^3	Symbol mg/dm^3	Symbol mg/dm^3	Symbol mg/dm^3
Na^+	NH_4^-	Cl^-	HCO_3^-
21207	-	43072	4,1
K^+	$Fe_{ogólne}$	Br^-	NO_3^-
245,3	0,39	226	0,9
Ca^{2+}	Mn^{2+}	J^-	CO_3^{2-}
3062,7	1,41	20,6	-
Mg^{2+}	Sr^{2+}	SO_4^{2-}	F^-
1480,5	67,8	97,0	-
TDS:			69546 mg/dm^3

Examination of chemical properties of groundwaters sampled in mine workings within the Upper Carboniferous formation, proved the possibilities of medicinal use of the waters. Groundwaters occur at the depths of 500 to 860m, their TDS values vary between 5.48 and 11.38g/dm^3, and they contain 4.1 -21.7mg/dm^3 of iodine and 64-380mg/dm^3 of

bromine (Labus, 2002). The question of technology and economy of capturing of groundwaters in the mine workings remains open, however the interest in alternative ways for development of Silesian coal mining industry is increasing.

ORIGIN OF THE WATERS

Waters of the Miocene formation in the Polish part of the USCB, with isotopic composition close to SMOW, were recognized as fossil connate waters (Pluta et al. 1993). Connate brines from Miocene of the Czech part (Darkov) are probably a mixture of marine and meteoric waters (Labus et al., 2002). Waters in Carboniferous formation are formed into the following genetic types: palaeoinfiltrative waters of hot climate - their salinity is explained by rocks weathering in Rotliegende, mixed Quaternary and meteoric waters, and meteoric Tertiary waters. The process of brines mixing is controlled by the mining activity (Zuber and Pluta 1989). Podio (1960) set forth a theory on the origin of brines from Carboniferous formation, describing them as fossil waters of Miocene sea, transgressing onto bare, older sediments. The theory was rejected by Pluta et al. (1993), who said that the waters in Miocene formation contain higher concentrations of I, Br and B, while the waters from Carboniferous are relatively enriched with Ba. There are several interpretations of factors influencing the hydrochemical environment of the analyzed area. Pałys (1964) finds a directly proportional dependence of mineralization in the Carboniferous formation, on the thickness of the Tertiary cover. The same author (Pałys, 1966) interprets also the occurrence of waters of HCO_3-Na type, as the result of juvenile CO_2 (connected withTertiary magmatism) reaction with groundwaters. According to Różkowski (1995) the chemistry and mineralization of waters are determined by: incomplete insulation of Carboniferous aquifers by impermeable Tertiary formation, tectonics, decrease of permeability of aquifer-rocks with the depth, and by the phenomena caused by mining activity. Underground exploitation of coal causes the stress relief, resulting in the increase of rocks permeability, leading consequently to hydraulic contacts between waters of different types. Deep exploitation and intensive drainage lead to widening and deepening (to 450 - 650m, and maximum to 850m below the ground surface) of recharge zones, and zones of Quaternary waters mixing with brines.

HISTORY AND PERSPECTIVES FOR UTILIZATION

Existence of iodine -bromide waters within the Czech part of the USCB has been known since XIII century. The waters are used in therapy against rheumatism, arteriosclerois, female, dermatic and nervous diseases Waters from pelitic Miocene strata were captured in 1862 and became the basis of therapy in the Spa of Darkov. Extensive coal mining activity in 50 ad 60-ties of 20th century, and most of all the founding of a new colliery "Darkov" in the proximity of the Spa, led to decrease of resources of its medicinal waters. In consequence, in order to substitute the collapsing Darkov, a new Spa - Klimkovice has been set out in the most south-western part of the USCB. The Spa of Klimkovice was opened in 1994, but on the other hand the traditional Darkov has remained operational, due to rapid decrease of Upper Silesian coal mining at the end of 20th century (Hufova, Vašičkova, 2001).

Coal industry transformation had also a negative influence on the waters utilization. In the "Frantisek" mine the iodine-bromide waters (drawn from Miocene overburden) have been used for the production (1000kg/day) of so called Darkov Salt since 1922. The colliery is closed nowadays and the salt production has been stopped. Medicinal waters of Darkov, containing 11.6 to 75mg/dm^3 of iodine, are drawn from 10 boreholes, from the depth of 392 to 512m. Waters utilized in Klimkovice are captured by 4 pairs of boreholes, 124 to 513m deep - iodine concentrations vary from 7 to 60mg/dm^3. The history of medicinal waters exploitation in the Spa of Jastrzębie (Poland) begins similarly as in the case of Darkov. In the second half of the 19th, century iodine-bromide waters were found in Badenian, and Upper Carboniferous formation, in coal exploration boreholes. Waters characterized by TDS at the level of 17.5g/dm^3, containing 9.2mg/dm^3 and 38.2mg/dm^3 of I and Br respectively, drawn from several boreholes supplied the sanatoria of Jastrzębie. Five collieries were built here in 1962-1974, and the valuable waters of Jastrzębie begun to be drained into the mine workings. The Spa does not exist presently, and the hydrogeological data describing the disastrous drainage process are unavailable.

Goczałkowice Zdrój is nowadays the only one operational spa in the Polish part of the USCB. It bases on iodine- bromide waters found in 1856 in Upper Carboniferous sandstones, during halite deposits exploration. The highly mineralized water (TDS - 72g/dm^3) containing 185.0 and 22.85 g/dm^3 of Br and I, respectively, is drawn from four boreholes.
Drogomyśl, Zabłocie and Dębowiec have not became health resorts, however their waters fulfill the standards for medicinal waters. Waters of Drogomyśl, found in Miocene and Carboniferous strata, in 1949, were never utilized in balneology. Iodine-bromide waters were found in Zabłocie and Dębowiec in 1902 and 1947, respectively. These iodine-reach waters occur in Badenian sediments, and they were used in medicinal salts production in the past (tab.2 and 3).

Table 2 Localities with iodine-bromide waters resources - utilization of groundwaters

Locality	I and Br [mg/l]	Past	Presence	Future
Darkov	I - 9.24mg/dm^3 Br - 38.2mg/dm^3	Founded in 19th century, Endangered by mining drainage in the middle of 20th century Therapeutic Salt production.	Operational Spa, production of salt is closed down	Continuous activity of the Spa.
Klimkovice	I - 9.24mg/dm^3 Br - 38.2mg/dm^3	Opened in 1994	Operational Spa	Continuous activity
Jastrzębie	I - 9.24mg/dm^3 Br - 38.2mg/dm^3	Founded in 19th century Destroyed by mining drainage in 70-ties of 20th century	The spa does not exist	Revitalization is possible basing on foreign water resources
Goczałkowice	I - 22.85mg/dm^3 Br- 185.0mg/dm^3	Founded in 19th century	Operational Spa	Continuous activity
Zabłocie	I - 129.1mg/dm^3 Br- 125.3mg/dm^3	Waters found in 1902 have been used for medicinal salt production till 1980.	Private property since 2003; inactive	Probably salt production; iodine production is economy dependent
Drogomyśl	I - 140.2mg/dm^3 Br- 158.3mg/dm^3	Waters found in 1949	Inactive	Unknown; iodine production is economy dependent
Dębowiec	I - 67-131mg/dm^3	Waters found in 1947, used for medicinal salt production, experimental scale of iodine production	Private property, preparation to start salt production	Salt production planned; iodine production economy dependent

Table 3. Chemical properties of medicinal salts from Zabłocie (Papierkowski, 1959) and Darkov

Constituents[g/kg]	Zabłocie (Poland)	Darkov (Czech Republic)
Ca	21.2	39.2
Mg	11.5	13.3
Na	28.7	321.3
K	2.23	4.0
Cl	516.2	600.1
Br	2.51	3.4
J	2.0	0.5
SO_4	0.09	0.07
Fe	0.007	0.03
Mn	traces	0.03

CONCLUSIONS:

Health resorts revitalization, basing on resources of local iodine-bromide waters, becomes again possible in the South-Western part of the Upper Silesian Coal Basin. The best conditions for such actions exist in the localities of former health-resort structure. Other localities, famous for their natural and historical values could serve in future as a centers of balneotherapy and recreation. Main works aiming the creation of smaller balneotherapeutic points should include: indication of the localities predestined to the function (basing on their natural values); precise definition of the future balneotherapeutic function of the locality, its need for resources, and the source of them; protection and monitoring of the areas of prospected occurrence of groundwater resources – medicinal waters, muds, etc. Proposed actions may also result in maintenance of heritage and supporting the cultural role of localities with valuable natural resources as well as in a growth of employment in health and recreation services.

Iodine-reach groundwaters of the Miocene formation are also a valuable raw material for iodine production. They are more stable in chemical composition, and less subjected to pollution than waters drawn from mine workings, draining Carboniferous aquifers. The reserves of I in the brine deposit situated by Dębowiec and Zabłocie, (of 50km^2 in area) were estimated at the level of 25 to 126Gg (Chajec, 1966). Iodine refinement is obviously dependent on the economical and to a less extent - technological factors.

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