RADIOACTIVITY OF MINERAL WATERS IN BOHEMIA

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Czech Republic is a country of many mineral and thermal springs. Studies of mineral waters including chemical and radiochemical analyses have been conducted in Czechoslovakia for a long time. Company Aquatest-Stavební geologie (AQ) took part in these activities since early 1960s – new capture of springs, survey drillings, proposition of protective zones. An offer of available radiochemical analytical methods is presented in this paper. Survey of historical data and of analyses of other institutes is listed for comparison. The parallels with some foreign mineral sources are mentioned.

1 Natural radionuclides in mineral water

Mineral and thermal waters are a special kind of ground-waters distinguished by specific chemical and physical properties as, e.g., higher mineralisation, trace elements, dissolved gas, higher temperature or radioactivity. Mineral and thermal waters are usually connected with specific and unique geological and tectonic structures.

From the geological point of view, the average dose equivalent of 0,37 mSv per year is measured on the territory of Czech Republic. In granite massifs and other naturally radioactive rocks or permo-carbon basins higher values of 1,1 – 1,7 mSv per year have been detected. Elements of the uranium- radium family have greater signification than those of the thorium series [1].

A high number of mineral waters in Bohemia is a part of the great European province of carbonated waters, which extends from France over Eiffel, Rhön, Harz to the West Bohemia and to Silesia. Valuable mineral waters appear in Central and East Bohemia [2]. The greatest accumulation of springs and of famous spas is in a relatively small area in the North-Western corner of Bohemia: the biggest Czech spa Karlovy Vary with hot springs, Jáchymov with Radon bath (related to the discovery of Po and Ra), Františkovy Lázně and Mariánské Lázně with their cold springs, moreover Kynžvart, Kyselka, Bílina, Teplice up in North Bohemia.

Karlovy Vary is situated in the Sokolov-basin at the confluence of the rivers Teplá and Ohře. The spa was founded in the 14th century (by the emperor Karel IV). Curative agents: gassy thermal springs of the Na-HCO_3-SO_4-Cl type (Glauber-mineralization type), with higher amounts of F^-, Li^+, H_2SiO_3, mineralisation 6,4 g/l and with temperature reaching 73^{o}C.

Deep tectonics is the basic factor of the genesis of the Karlovy Vary thermal water. The recharge area of thermal water is located in the upper granite blocks on both sides of the rift valley [3]. Heated water ascends from the depth of 2000 to 2500 m along young transversal tectonic lines. The main Hot Spring discharges 2000 L/min of water and 5000 L/min of gaseous CO_2. Heated water in the accumulation area is saturated with ascending juvenile CO_2 and water vapour. A large aragonite mantle has developed around the thermal springs. Karlovy Vary thermal water appeared originally at the lowest level of the valley in the Teplá river bed. In the 16th century shallow wells of the depth of 5 to 8m tapped the water in the aragonite bed on the right side

of the river. These twelve small springs (traditional number) have lower temperature (31 – 63°C) and they have lower yields – about 100 L/min together. In 1974 during the construction of the new Colonnade Spring wild thermal springs in the Teplá river surfaced. They influenced unfavourably the whole usable yield of the spring structure. The company AQ was asked to prepare a complete hydrogeological survey of the spring system and to study the possibilities of deeper capture of thermal water [3]. In November 1982 clay – cement mixture was injected into the Teplá river bed and into the base of the Colonnade Spring. This intervention eliminated the largest wild springs. Parallel with the survey the chemical composition including rare elements and radioactivity was monitored once a month for two years. Some results of this monitoring are presented in Table 1.

Table 1. *Karlovy Vary Springs – Activities of ^{222}Rn and ^{226}Ra*

	^{222}Rn - Bq/L						^{226}Ra - Bq/L				
Year	1905	1961	1979-1981 (AQ)				1978-1979				
Spring	Mache Meyer	CGI	min	max	mean	σ%	min	max	mean	σ	σ%
Sadový	35	130	36	58	44,3	10,4	0,45	1,68	1,21	0,32	26,1
Svoboda	–	74	64	80	69,1	7,3	0,81	3,40	2,12	0,76	36,0
Skalní	56	125	88	144	129	15,7	0,51	2,64	1,69	0,58	34,0
Libuše	–	196	109	169	138	11,2	0,74	2,40	1,62	0,42	26,2
Václav	–	30	31	43	35	10,8	0,59	2,68	1,76	0,53	29,9
Rusalka	51	59	51	79	57,9	6,8	0,51	2,71	1,68	0,58	34,5
Mlýnský	43	45	47	86	74,3	9,9	0,94	2,43	1,73	0,45	26,0
Zámecký	238	–	19	210			0,89	2,61	1,76	0,41	23,0
Vřídlo SVE	12		2	9			0,35	3,71	2,06	0,79	38,6
Vřídlo SVB							0,76	3,69	2,02	0,81	40,0

O. Hynie [2] gives for ^{226}Ra the values 1,3 – 2,0 Bq/L. The average activity of ^{226}Ra estimated by AQ in all small springs in 1978 – 79 was 1,70 Bq/L, in the branches of the Hot Spring – 2,02 Bq/L. The changes of the concentrations of U_{nat} were 0, 0004 – 0,02 mg/L, median 0,001 mg/L. AQ makes analyses of ^{226}Ra and ^{222}Rn by the emanometric method with the accuracy of 90 %. The variability of Ra in Karlovy Vary therma in 1978 – 79 is illustrated in Fig. 1. The Ra content in all the springs fluctuated during the monitoring period. The changes of Ra cencentration show a similar pattern for the small springs in the line Mlýnský – Sadový (Mill – Colonnade) spring. The movement of Ra in Hot Spring is greater and has a shift in relation to small springs. Greater variability of the Hot Spring may be influenced by a larger shift of the thermodynamic equilibrium. Table 1 summarizes comparative estimation of Rn concentration in therma, too. "Historical" radon data (1905) are in good agreement with "modern" observations except cases of new capture of water. The largest Rn-activities in the thermal springs were found in the thinnest springs with a long path from the centre – 397 Bq/l or 535 Bq/l. Radon in every source is analysed in double sampling. The

springs of the therma are pulsating. However, the results in Table 1 show better stability in Rn than in Ra as expressed by the standard deviation. Zámecký Spring is pulsating very strongly, and is influenced by the equilibrium in the Hot Spring [4]. Results of repeated determinations in Zámecký Spring were sometimes very different, e.g. 20 and 200 Bq/L. Relatively high differences in Rn activity were found between the Hot Spring and small springs. Radon can enrich these small springs by passing through the rock environment after branching from the central stem of the therma [6]. The small springs have a little bit lower Ra concentration than the Hot Spring. J. Pěček (AQ) isolated barytes and brown sinter with high Ra activities in this area. Barium produces coprecipitates with Ra. O. Hynie quotes that Ra in waters in Gastein spa (Austria) forms coprecipitates with Mn and Fe. Low concentration of Rn in the Hot Spring could correspond with very high content of gaseous CO_2. However, Rn in the gaseous phase estimated by Mache, Meyer [5] approached the equilibrium with water. The new capture (AQ) of small springs in Karlovy Vary (depth 35 – 60 m) had the purpose of improving the resistance of springs to negative man-related effects. The samples from the "fresh" boreholes had a lower Rn level, later the Rn levels started to rise again.

The springs in Karlovy Vary have enough elevated activity of ^{226}Ra over the limit of standard for drinking water. Therma in Karlovy Vary have similar curative properties as the healing waters of the famous Vichy spa in France. The springs in Vichy have the activity of ^{226}Ra between 0,14 and 0,96 Bq/L [7]. Geological conditions in Karlovy Vary show a resemblance to the Royat spa including a large travertin mantle and the neighbouring tertiary vulcans. The main thermal (34^{o}C) spring Eugénie discharges 1700 L/min of water and 2500 L/min of gaseous CO_2. Ra activity of this water is 2,3 Bq/L with low Rn activity – 16 Bq/L. The small St. Mart spring has the activity of Ra of 1,37 Bq/L, and of Rn 435 Bq/L [8].

Spa Františkovy Lázně is situated at the edge of the Cheb basin. Curative agents: rich sources of minerals waters (24 springs) – sulphate-chloride-hydrocarbonate-sodium-ferrous mineral water type and sulphate-ferrous mud and gas. The mineralisation of waters reaches 1,5 – 27,8 g/L of dissolved solids. Uranium content lies in the range of 0,0002-0,003 mg/L, activity of Ra is <0,1 Bq/L, activity of Rn is low, except for the Glauber IV Spring (deeper bore) – about 60 Bq/L. Waters have a direct relation to wheathered and kaolinised granite zones and are mineralised additionally in the tertiary sediments with intense gasification [10]. The ceiling of water of Františkovy Lázně is created by peat. Sorption ability of the peat can reduce radon content in waters (it is the author's hypothesis not verified by experiment). Radon in Císařský Spring in nearby nature reserve Soos reaches 100 – 177 Bq/L.

The spa town Mariánské Lázně is located at the southern edge of the Slavkovský Les range. The geological topography of Mariánské Lázně is very diverse with a great variety in the chemical composition of the 140 springs found there. Only 40 springs are used for curing purposes and those are hydrocarbonate-sulphate-magnesium-ferrous waters, sulphate- hydro-carbonate-sodium-ferrous water or hydrocarbonate-magnesium-sodium-ferrous waters. All these waters have a low radioactivity: U_{nat} mostly near to the detection limit of 0, 0002 mg/L, ^{226}Ra below 0,1 Bq/L. In several samples Ra only once exceeded 0,2-0,5 Bq/L. Table 2 shows the activity of ^{222} Rn in some springs in Mariánské Lázně. Rn content is stable in the Lesní (Forest) spring with a highest elevation. Greater changes were found in the Křížový (Cross) spring.

The new capture of the Křížový spring or the reconstruction of Colonnade took place several times. The mineralisation of the Křížový spring is 11,6 g/L. The simple acidulous waters in Pottovo údolí obtain 300 mg/L of dissolved solids, activity of Rn 12-55 Bq/L (in 1988). Relatively high Rn activities (145- 118-383 Bq/L) were found in this area in waters from some AQ investigation boreholes in 1990s.

Table 2. Mineral Springs in West Bohemia – Selected Data

Spa Mariánské Lázně						Spa Teplice v Čechách					
Spring	^{222}Rn - Bq/L					Spring	Year	^{222}RnBq/L	^{226}RnBq/L	U_{nat} mg/L	t °C
Year	1905	1980	1981	1987	1988	Pravřídlo	1985	258	0,33	0,008	38
Lesní	63	57	-	56	59	Hynie	1993	65	0,15	0,002	40
Křížový	58	23	13	53	56	Horský	1985	1865	0,53	0,60-1	28
Rudolf	20	15	10	–	22						
Spa Františkovy Lázně						Isotopic Analysis (9)					
Spring	^{222}Rn - Bq/L				Depth – m		Date	^{3}H-T.U.	^{14}C Bq/l		^{14}C Age
Year	1905	1956-60	1982	1983		Pravřídlo	3.6. 76 -	25±6	0,0213±0,0016		14000
František	11	11,5	10,8	14,3	4,4		27. 8. 76				
Studený	5,6	6,3	4,8	6	3,0	Hynie	22. 9. 76 -	0±3	0,0133±0,001		18000
Solný	1,8	–	1,0	2,4	2,8		28. 9. 76				
Natálie	6,5	12,6	8,5	11,4	8,0	Horský	21. 5. 74 -	79±9	–		–
Štěpánka	9,5	10,7	8,0	13,6	3,9		36. 6. 75	154±14			

Jáchymov is situated in a protected valley on the southern slope of Krušné Hory (Ore Mountains) at an altitude of 650 m above sea – level. The thermal springs with a very high content of radon (a rare case in balneology) with the mineral water coming up from the mine are captured at the surface and then piped to the spa buildings. The Jáchymov Ore district has a rich historical past. It became a focus for silver mining in the 16th century (Count Jáchym Šlik) and produced arsenic, lead, cobalt, nickel throughout the 18th and 19th centuries. The uranium ores have been exploited since the middle of the 19th century. The discovery of radioactive thermal springs is closely connected with the mining activities. The unusual thermal spring (28°C), later named Curie Spring, was discovered in 1864 in the Svornost mine. J. Štěp iniciated the first primitive radon bath in Jáchymov in 1906. Štěpovy springs encountered uranium veins. These springs were cold, with a small discharge and with very high activity of ^{222}Rn – over 69 000 Bq/L (as measured by F. Běhounek). The mining has penetrated into metamorphic rocks and has extended rarely into granite [3]. The water occuring in the granite massif has an increased temperature and low redox potential. The discharge of the radioactive thermal water on the 12th level of the Svornost mine forms the actual system of springs.

The radon spa with medical service was founded in Jáchymov in 1920. The Curie Spring fed the spa baths. The primary discharge of the Curie Spring was 400 L/min, the discharge in 1924 was 1451 L/min, in 1940 – 74 L/min, in 1956 – 65 L/min [3], in 1971 – 28 L/min. In the early 1960s the new springs tapped by boreholes (Laboutka at al.) called C-1 and HG-1, later named F. Běhounek Spring. In 1962 it was decided

not to proceed further with uranium ore exploitation. For the time being, if the thermal water is to be exploited, the Svornost mine must be kept open [3] and preserved. At present, the only source serving curative purposes is F. Běhounek Spring, producing the thermal water (about 35°C) at the depth of 97 m bellow the bottom of the 12th gallery of the Svornost mine. The contemporary yield of the well is about 300 L/min. The Jáchymov springs are simple thermal waters with about 0,7 g/L of dissolved solids with the Glauber-type mineralisation and with high activity of ^{222}Rn.

AQ radiochemical analyses (40 samples for each source) in 1972-93 are as follows: Běhounek Spring – average activity of Ra 7,55 Bq/L, max. activity of Rn – 11 100 Bq/L; C-1 spring average activity of Ra 2,48 Bq/L, max. activity of Rn – 13 300 Bq/L; Curie Spring – average Ra 2,36 Bq/L, max. Rn – 6600 Bq/L. Uranium varied in these three springs similarly in the range of 0,01-0,08 mg/L. The springs have a very high excess of Rn in equilibrium ratio Ra:Rn. The equilibrium ratio Ra:U has a shift towards radium. This shift corresponds with low redox potencial of these springs. The mine waters connected with the metamorphic rocks have shift towards uranium. The activity of ^{210}Pb – 1,1 Bq/L – and the activity of ^{210}Po – 0, 76 Bq/L – in Běhounek Spring found in 1998 (AQ) signify a shift towards radon.

The laboratory in the Jáchymov spa controlled Rn content in Běhounek, Curie, C-1 Springs once a month. The automatic equipment records simultaneously the deviations of activity of Rn with the temperature, pressure and the discharge of water at Svornost mine.

The Teplice spa is situated in the basin between Krušné Hory (Ore Mountains) and České Středohoří (Central Bohemian Range). The basis of treatment is from the Pravřídlo spring and the Horský spring with hydrocarbonate-sodium waters, two abundant radioactive thermal springs gushing out from a porphyric stratum deep in the rock [2]. The Pravřídlo spring had the largest discharge and temperature, 49.5°C in 1835. The mine water breakout at Döllinger coal pit in 1879 and further mining activities in neighbourhood caused several times the disappearance of springs. Borehole T28-Hynie is a part of the reparative work. Isotopic analyses in Table 2 show the absence of ^{3}H in T28-Hynie. P. Trýzna [9] concludes, that this new spring is responsive to the original Pravřídlo spring. The content of Rn and especially of uranium is elevated in the branch of Horský and Kamenný springs. This phenomenon can be influenced by cenoman lenticle (explained later). Cenoman in the North Bohemian Cretaceous basin contains deposits of poor uranium ores.

There are several other spas and mineral springs in West Bohemia. Bottled mineral water Korunní and Magnesia have the gross alpha activity <0,1Bq/L and the gross beta activity responding to the content of potassium. Well-known bottled mineral water Mattoni has activity of ^{226}Ra in the range 0,3-0, 9 Bq/L and the gross alpha activity up to 1 Bq/L.

The Poděbrady spa is situated in Central Bohemia in the Labe (Elbe) valley. The activity of Rn of these waters is bellow 10 Bq/L, trace content of uranium, activity of Ra 0,2-0, 5 Bq/L, the gross alpha activity 0,9 – 1,5 Bq/L. These waters are connected with a cenomanian-aquifer with a low redox potential in this locality. The mineral water in the borehole in Dymokury near Poděbrady had Ra activity of 0,94 Bq/L and the gross alpha activity 2,5 Bq/L. M. Poliak (IHE) analysed another sample of Dymo-

kury with a similar difference between activity of ^{226}Ra and gross alpha activity and found radium isotopes from the thorium family.

The Jánské Lázně spa with an indication for the treatment of the after-effect of poliomyelitis etc. lies on the southern slopes of the Krkonoše (Giant Mountains). Simple therma (28°C) contents uranium below the detection limit, activity of ^{226}Ra is <0,05 Bq/L, activity of ^{222}Rn about 2 Bq/L. Krkonoše are mountains with higher radioactivity background. Some fresh waters have Rn activity over 2000 Bq/L here. Santholzer quoting H. Vogt denotes the thermal springs in Janské Lázně as a mystery of balneology.

The laboratory of AQ company analysed numerous mineral waters from resources in the Czech Republic. This paper presents a choice of renowned spas with different curing effects and with different geological environment. The determination of radionuclides in water is necessary with regard to human health. The natural radionuclides can serve as conservative tracers. The level of radioactivity could illustrate changes of water regime.

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