

BROMIDE CONCENTRATION IN MINE WATERS FROM THE WIELICZKA SALT MINE AS AN INDICATOR OF THEIR ORIGIN AND MIGRATION OF FLOW PATHS IN THE SALT DEPOSIT

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Abstract: The subject of this study is the chemistry of waters contained in the salt deposit of Wieliczka. The bromide content determined in relation to the chloride one, using the evaporation curve or the Cl/Br ratio, point to dissolution of chloride minerals as the main process in the origin of mine waters. Because of a number of processes involved in the circulation of waters within the deposit, the Br content in mine water depends on three factors: concentration of salts associated with leaching of the deposit, Br content in the salt, and dissolution - evaporation cycles on the water migration paths. The diagram Br vs. Cl or vs. density is used to explain these factors.

Key words: brine, mine waters, bromine, Wieliczka Salt Mine, South Poland.

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INTRODUCTION

The concentrations of all the major elements in waters reflect the processes that affect their chemical composition, origin, and migration. The particular ionic proportion might be a result of either just one chemical process (such as halite dissolving), or several factors. The analysis of proportions among the contents of individual elements reveals whether the brine composition is original and primary, associated with the sedimentation processes (the elision stage), or secondary, *i.e.* associated with the dissolving of salt minerals by infiltrating waters (the infiltration stage). In waters inherently associated with the salt sedimentation processes, the proportions of major elements are roughly the same as in ordinary seawater or in seawater following some processes (e.g., evaporation). Waters that differ in their composition are probably infiltrating waters leaking to the deposit where they uptake minerals due to the dissolution of salts, mostly halite. The chemical composition of such waters reflects the concentrations of major elements in salt minerals and their solubility. Sedimentation waters are those that accumulated in the deposit at the time of its formation, while infiltrating waters leaked to the deposit from the surrounding salt rocks.

WATER LEAKS IN THE SALT DEPOSIT OF WIELICZKA

195 leaks were reported in the Wieliczka salt mine (2002) at all 9 levels of the mine. There are also several leaks in mine shafts. Water influxes of variable flow rate (from trickles to effluents in excess of 100 l/m) leak from the surrounding rock strata, mostly including the Chodenice beds that occur at depth north of the boundary of the salt deposit. The water-bearing capacity of these beds is rather low, but water is often contained in sandstone intercalations within various clay rocks (Garlicki & Wilk, 1993). A thorough analysis of leak locations and the geology of the salt deposit leads to a conclusion that some of the leaks are probably the influxes from the overlying Tertiary series (leaks in the mine shafts and at the levels above), and from basal layers of the Skawina beds, bordering the salt deposit on the south. In the central part of the salt deposit brines of still unknown origin occur. These are probably the leaks from higher levels or influxes from abandoned, sunk goafs. Waters contained in the salt deposit of Wieliczka are generally infiltration waters, what is confirmed by isotopic analysis and measurements of the tritium content (Zuber *et al.*, 2000).

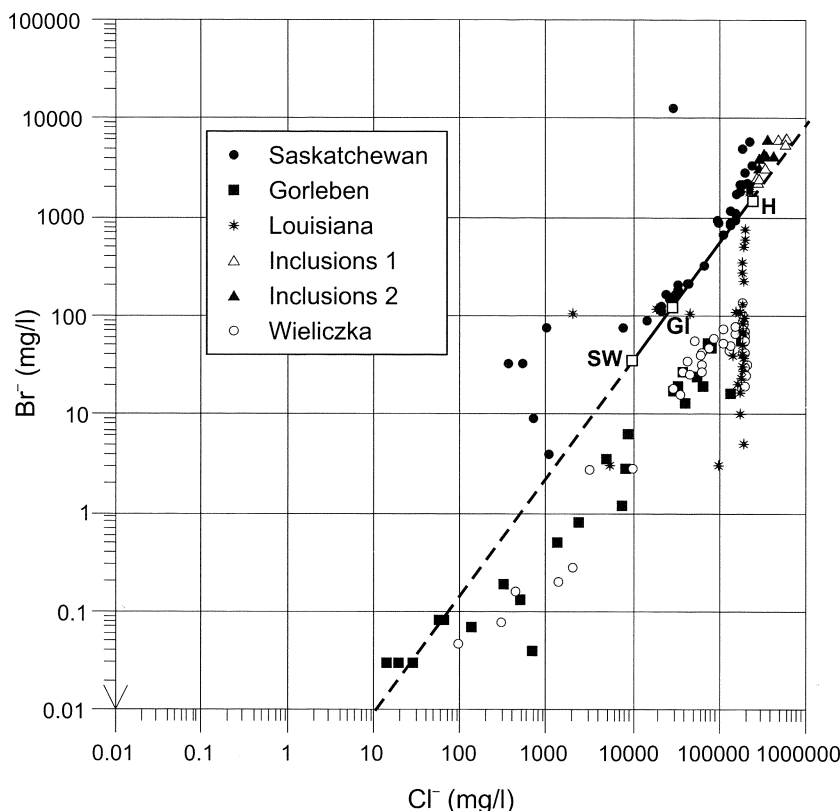


Fig. 1. Br vs. Cl values compared with the evaporation curve (after Fontes & Matray, 1993), Saskatchewan (after Wittrup & Kyser, 1990), Gorleben (after Kloppman *et al.*, 2001), Louisiana (after Kumar, 1993), inclusion 1 (after Horita *et al.*, 1996), inclusion 2 (after Das *et al.*, 1990)

Waters contained in the salt deposit in Wieliczka are essentially Cl-Na brines. The extensive chemical analysis of samples collected from 40 selected water leaks (Winid, 2003) reveal that they are chiefly Cl-Na brines (according to the Kleczkowski's classification, 1979), though fresh waters (Ca-SO₄-HCO₃), (Na-Cl-HCO₃-SO₄), brackish waters (Na-Cl-HCO₃), (Cl-SO₄-Ca-Na) (Na-Ca-Cl-SO₄), and brines of the type (Na-Cl-SO₄) are also reported.

No clear sedimentation waters were found in the salt deposit of Wieliczka. The isotopic composition of fluid inclusions is a good indicator of the presence of such waters. In the salt deposit of Wieliczka no inclusions were found which could be the product of ordinary seawater evaporation. Brines in fluid inclusions in the green salt deposits are the mixture of evaporated seawater and pre-Pleistocene continental waters. Brines in the inclusions from the Crystal Cave are of meteoritic origin (Duliński *et al.*, 2000). It shows that the deposit was not wholly confined and isolated before the beginning of salt mining and, as a result, sedimentation waters are continuously changing into infiltration waters.

BROMIDE CONCENTRATION AS AN INDICATOR OF BRINE ORIGIN

The concentration of Br ions is a major hydrochemical parameter useful in determining the origin of salt waters. In

the sedimentation process during the evaporation of seawater, this element does not form any mineral phase of high solubility. Some portion of Br is admitted to the sediment producing an isomorphic admixture with chlorides and precipitated halite, though a major share of bromides will remain in the solution. In the process of seawater evaporation till it is saturated with Cl-Na, the Br content increases up to 510 ppm. The Br content in the earliest halite crystals falls between 65 and 75 ppm (Holser, 1979). As the evaporation process continues, the Br content in halite will increase. Potassium salts: silvine and carnallite are abundant in Br (about 2000 ppm), its content in halite being only 200 ppm. The solutions produced when salts are dissolved in infiltration waters are depleted in Br when compared to the original brines. Halite crystals formed in the process of re-crystallisation of the same solutions have decidedly lower Br contents. Rock salts (halites) containing more than 400 ppm Br are regarded as primary rocks formed in the process of mineral crystallisation from seawater. Halites containing less than 20 ppm Br are regarded as secondary crystals, formed when primary

salts were dissolved by infiltration waters (Holser, 1979). During evaporation of seawater the concentration of bromides increases and so does the chloride content. The Br content changes linearly with the increase of Cl concentration right to the moment when Cl salts begin to precipitate; then the Cl/Br ratio starts to decrease. The bromide content determined in relation to the chloride can be interpreted as an indicator of brine origin, using the evaporation curve (Fig. 1) that shows the content of a given component (Br) as a function of Cl concentration during the process of seawater evaporation. On the plot of Cl vs. Br contents, the seawater-derived brine will be found on the evaporation curve or in its direct vicinity (Fig. 1). Below that curve, there are points representing brines formed by dissolution of chloride minerals, *i.e.* those depleted in Br when compared to seawater (Collins, 1975; Fontes & Matray, 1993). The positions of points representing the Wieliczka brines (Fig. 1) show them to be infiltration waters. The waters in all the analysed leaks are depleted in Br when compared to ordinary, evaporated or diluted seawater. The first point on the evaporation curve is that representing the content of major elements in seawater (designated as SW), further points correspond to their relevant concentrations at the instant when gypsum (GI) and halite (H) begin to precipitate.

The leak data for Wieliczka have been compared with the contents of major elements in the leaks from salt mines in the diapir deposits of the southern Louisiana (Kumar, 1983), waters from diapirs in Gorleben, Germany (Klopp-

man *et al.*, 2001), and leaks from potassium salt deposits in Saskatchewan, Canada (Wittrup & Kyser, 1990). On the plots, there are also points representing the specified elements contained in fluid inclusion brines in the Prairie group – inclusions 1 (Horita *et al.*, 1996), and the Michigan Basin – inclusions 2 (Das *et al.*, 1990). On account of the specificity of their deposition, they are likely to have been formed as sedimentary deposits.

The simplest technique to evaluate the Br vs. Cl ratio value consists in calculating the weight ratio Cl/Br, and this indicator proves to be the most useful in determining the brine origin. The average value of Cl/Br for seawater is about 300. Identical values are obtained for primary sedimentation waters and for halite precipitation. In infiltration waters, highly mineralised due to the dissolution of rock salt, this value ranges from 500 to 3,000 (Vengosh & Rosenthal, 1994). When Cl/Br ratio value is lower than 400, the brines are regarded as primary (formed during sedimentation); the brines with 400–1,000 are regarded to be of mixed origin. When the Cl/Br ratio is in excess of 1000, we call them secondary (infiltration) brines (Matray & Fontes, 1990). The lower value of the Cl/Br ratio for deposit waters is diagnostic of evaporation processes, compaction or absorption of bromides in the diagenesis of organic sedimentary deposits (Edmunds, 1996).

The Cl/Br ratios for the effluents in Wieliczka mine are within the range of 926–10,666 (Fig. 2). The Cl/Br ratio plotted against the seawater evaporation curve in the coordinate system or expressed as the quotient of their respective weight ratios (the hydrochemical indicator Cl^-/Br^-) provides vital information about the origin of Wieliczka brines.

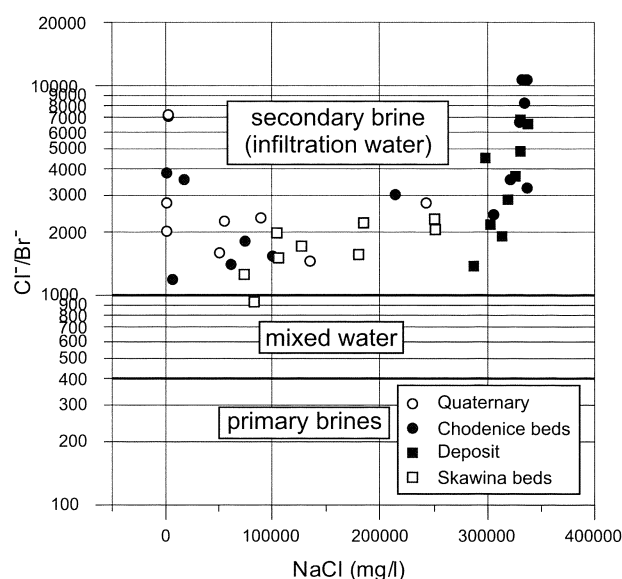


Fig. 2. Cl/Br ratio value vs. salt content in effluents from the Wieliczka mine

PROCESSES DURING THE WATER INFLUX AND MIGRATION WITHIN THE DEPOSIT

The mineralisation of effluents in the Wieliczka salt mine is a result of deposit leaching. At the instant the effluents get saturated, minerals which have phase imbalance will precipitate. In the case of lower-concentration brines, the precipitation processes are caused by evaporation. The content of Br ions in ordinary underground waters is usually low, and slightly increased levels are reported from Wieliczka (chiefly due to the leaching process). Hence, the water circulation within the salt deposit is interpreted as a process of modification of effluent chemistry in terms of Br ions concentration.

The values of Br content in Wieliczka halite are reported in the papers by Garlicki and Wiewiórka (1981), Garlicki and Wali (1981), and Toboła (1999). The Br content in the earliest salts ranges from 40–50 ppm, and in one sample collected from the earliest salt group it would be as high as 221 ppm. Generally speaking, the Br content increases with an increase of Cl. The Br content attains 24–48 ppm in green salt deposits, 22–46 ppm in salts collected near the fore shafts, 50–67 ppm in lower spiza salts, and 30–80 ppm in upper groups of salts near the fore shaft (Garlicki & Wiewiórka, 1981). In the rock salt body deposit section, the Br content ranges from 9.95 ppm (salt fibres) to 34 ppm (large crystal salts) (Toboła, 1999). For convenience it can be said that the Br content in the Wieliczka deposit ranges from 10 to 80 ppm, similarly to rock salt deposits in Bochnia, where the Br content ranges from 10 ppm to more than 50 ppm (Bukowski, 1997). Typically, the Br content varies from 15 to 30 ppm (Toboła, 2000). The range of Br content in salts might be expressed as Cl/Br ratio or its inverse $Br \times 10^3/Cl$, often used for rock salts. The variability range of this indicator is shown in Fig. 3 (after Garlicki & Wiewiórka, 1981).

It is readily apparent that the Br content variability range is considerable. The indicator Cl/Br (derived from the ratio value $Br \times 10^3/Cl$) falls between 5,000–33,000; only in one case the value of 2,000 was reported. This variability range is consistent with the values obtained for the analysed effluents from the Wieliczka salt mine, pointing to the infiltration origin of the brines and demonstrating how much the Br content might vary for waters that dissolve the salts. The Br content in the salt rocks of Wieliczka falls within the interval of 20–221 ppm. The Br concentration profiles for salts are regarded as regular or common irregular. The Br content distribution depends on the conditions of sedimentation processes and it is an indicator of the sedimentation cycle (Garlicki & Wiewiórka, 1981). The content of Br in the analysed effluents from the Wieliczka salt mine would change from 0.046 to 135 mg/l, depending on the brine concentration and Br contents in salts leached by the given effluent.

The circulation of waters within the deposit involves a number of processes. Waters showing increased concentration due to the dissolution of evaporated minerals tend to permeate the Wieliczka deposit. This process is followed by circulation of slightly undersaturated or saturated brine in

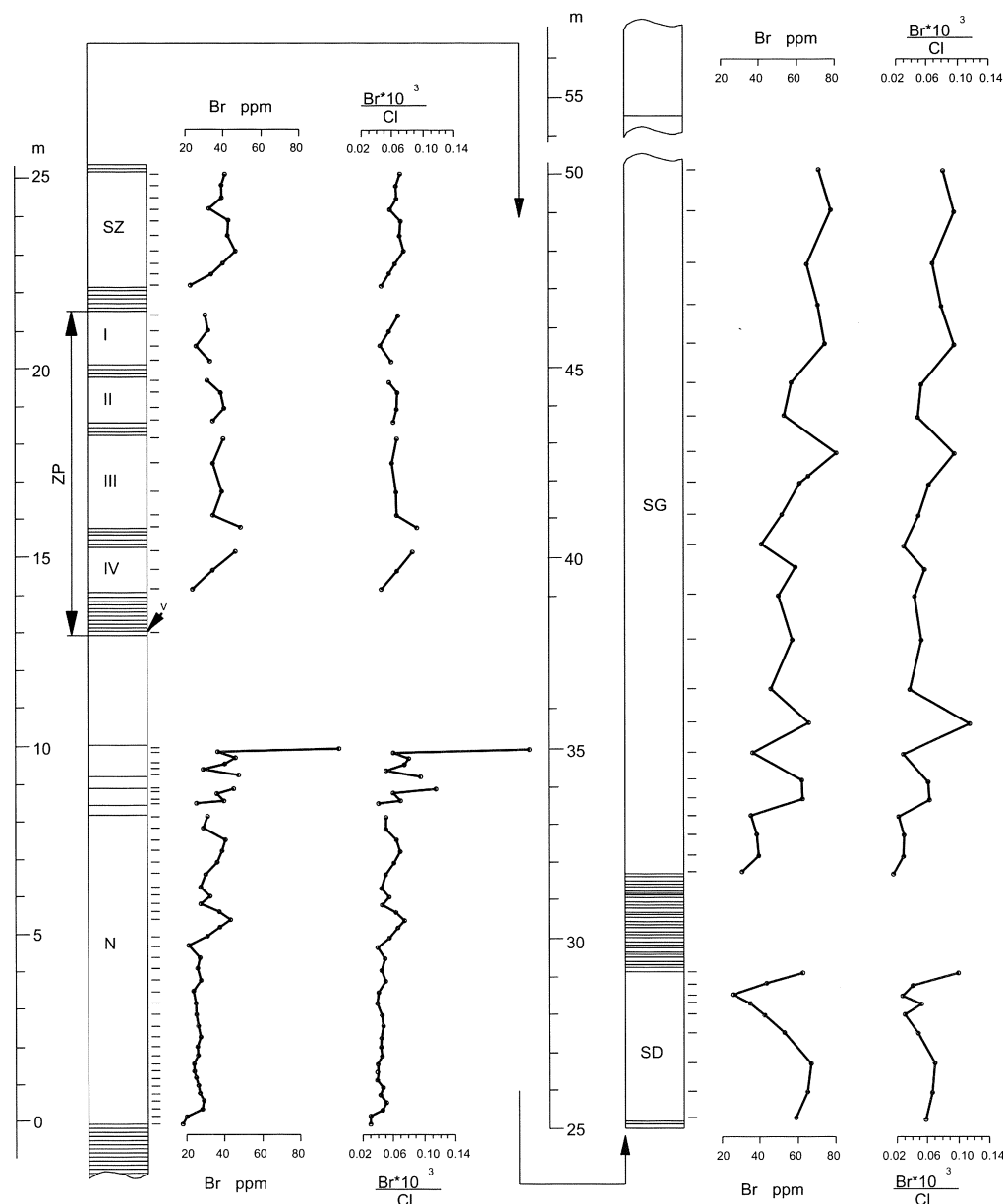


Fig. 3. Br profile of salt layers in the Wieliczka deposit (after Garlicki & Wiewiórka, 1981): N – oldest salt, ZP – set of green salts, number I–V, SZ – shaft salt, SD – lower spiza salt, SG – upper spiza salt

the deposit, and at that stage some mineral phases start to precipitate. In not fully isolated deposits, the water streams from the outside contribute to the already circulating waters, sometimes even saturated, to a degree that cannot be precisely evaluated. The rate of variation of the Cl/Br ratio value can be used as a measure of the intensity of this process.

Apparently, the Br content tends to change more rapidly. When fluctuations of the index value $\text{Br} \times 10^3/\text{Cl}$ for halite is considerable, the indicator Cl/Br in brines changes dramatically, too (Fig. 2). In waters showing lower salt concentration (with respect to saturated brines), the variability range will depend – to a certain degree – on the concentration of the solution.

The factors affecting the Br content in mine waters include:

- concentration of salts associated with leaching of the deposit,
- Br content in the salt,
- dissolution–evaporation cycles on the water migration paths.

The first of these factors can be easily quantified by determining the amounts of chlorides. In the second case, a detailed petrographic-geochemical analysis would be required. The last factor seems to be the least known. The processes affecting the Br content in brine, being the result of halite dissolution, are most complex. The concentrations of Br and Cl ions are plotted on Figures 4 and 1. The variability range of Br concentration in slightly undersaturated or saturated waters (Cl content being close to 180 g/l) is almost as wide as in non-saturated effluents (Fig. 4). This seems to be the evidence of water migration within the salt deposit,

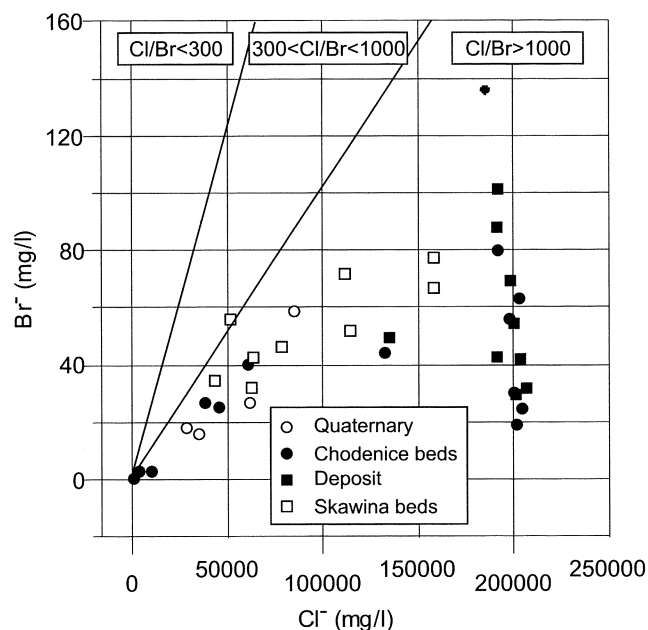


Fig. 4. Br content vs. salinity of mine waters in Wieliczka

accompanied by dissolution and precipitation of halite which are responsible for a lower Br content.

The description of water circulation within the area of the Salar de Uyuni and Coipasa, Bolivia (Retting *et al.*, 1980) provides a better insight into the processes of migration of slightly undersaturated brines and influx of meteoritic waters highly mineralised due to the dissolution of halite. Salars are evaporated sediments of continental origin. They might be inactive hydrogeologically and covered by dry salt crust, or there are influxes of surface or ground waters, which give rise to the evaporation processes (Alonso, 1999).

The salar Uyuni is the largest salt flat in the world (10,000 km²) which has remained a closed basin since the last glacial stage (about 10,000 years ago). It is situated in the central Andean Altiplano (Bolivia). Water contributions come from the Delta of the Rio Grande River, from small lakes in the south (though to a minor degree only), and from underground waters. The water reaching the central part of this salar consists mostly of brine containing re-dissolved halite. The conditions are ripe for secondary precipitation of NaCl and other mineral phases. The salar contains huge amounts of brine locked inside a porous NaCl crust, nearly 10 m thick. During the rainy season the salar is sunk in brine 25 cm deep, while in the dry season the brine will evaporate, leaving only the salt crust on the surface. While investigating the relationship between the Br ion content and volumetric weight (γ_o), which may be used as a measure of the degree of mineralisation (in this case salinity), one can easily distinguish two groups of brine analyses. In the first group, the relationship is given as an exponential function and major fluctuations of the two relevant parameters are reported. In the second case, the Br ion content is variable, though the Cl content and volumetric weight remain unchanged. The first group of samples includes those from the Delta of Rio Grande, which had no direct contact with the

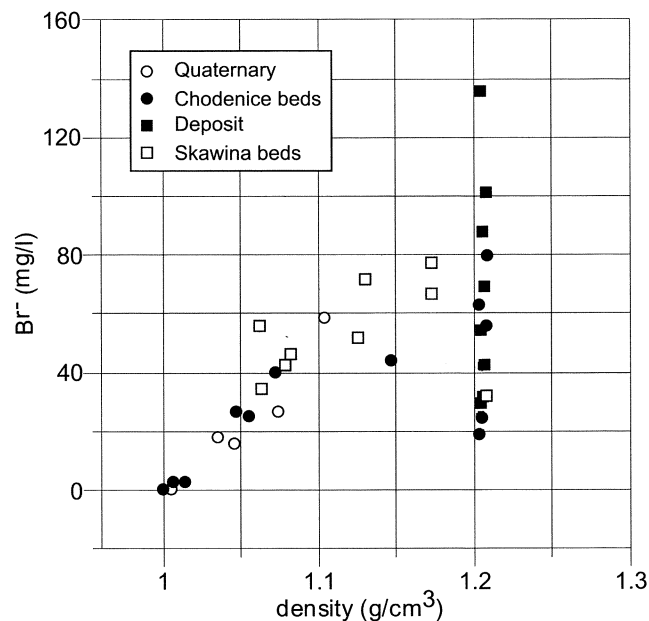


Fig. 5. Br content vs. mine water density in Wieliczka

salt crust. The other group includes samples from the central part of the salar. The difference within the brine analyses and the relevant relationships between their density and Br content are accounted for as follows. The group of variable density and Br content found in the samples from the Rio Grande delta clearly evidence the process of single regular fractionation accompanying the continuous concentration of the solution. The group of the wide range of bromide concentrations with nearly constant chloride content and the narrow density range (1.20–1.21 kg/dm³) is interpreted to reflect variable or cyclic halite re-solution, resulting in progressive depletion of Br due to the inflow of less mineralised waters (Retting *et al.*, 1980).

These relationships were also investigated in mine waters from the Wieliczka salt mine (Fig. 5), yielding very similar results. The analysed effluents are divided into two groups. The first group includes 24 effluents in which the relationship density vs. Br content is linear. The other group includes 18 effluents of the density > 1.2 g/cm³ and bromide content ranging 25–136 mg/l. In this case, the relationship between brine density and Br content can be approximated by a straight line perpendicular to the Y-axis. Apparently, the water leaking to the deposit from the Chodenice beds underlying the Skawina beds, and from the Tertiary overburden dissolves the halite raising the NaCl concentration in the solution. The Br content is associated with dissolved halite: the higher the brine concentration, the greater the bromide content. These are essentially waters rich in chlorides and sodium; consequently, the actual density depends on the NaCl concentration and the Br content is proportional to the brine density. The brine inside the salt deposit (marked in black), saturated or slightly undersaturated with respect to NaCl, is responsible for variable or cyclic solution of halite. Minerals differ in the Br content depending on the actual phase of the cycle and on the salt primary or secondary origin. Considering the relationships between the Br

content and density, the brine analyses are divided into two groups, depending on their density: $\gamma_o < 1.2 \text{ g/cm}^3$ and $\gamma_o > 1.2 \text{ g/cm}^3$, where $\gamma_o = 1.2 \text{ g/cm}^3$ is taken as the critical value. The first group of brines includes chiefly waters leaking from the surrounding strata (the Chodenice beds underlying the Skawina beds, and from Tertiary overburden) which are contacting to a lesser degree with the deposit than other waters. The second group includes all effluents localised in the salt deposit and effluents from the Chodenice beds, fully saturated with NaCl. The waters of the first group are mostly incoming freshwaters, highly mineralised due to halite dissolution outside the salt rock. The waters of the other group contain significant amounts of chlorides formed in the process of re-solution of rock salt deposit, which might be accompanied by repeated precipitation of minerals. The increase of Br ion content in the course of progressing mineralisation is indicative of the origin of these ions: they are the result of dissolution of salts, mostly halite. There is no direct correlation between Cl and Br contents in the second group of samples, and this fact is attributable to the variable Br content in halite. The migration of waters within the Wieliczka salt deposit involves the influx of poorly mineralised waters which, flowing through the surrounding strata and the salt rocks, will take up the ions that pass to the solution as a result of leaching. The ion concentrations increase till the equilibrium is reached; subsequently the crystallisation of secondary minerals will change the chemistry of the resultant brine which might again leach various constituents along the flow path. Apparently, water is mineralised till it becomes saturated. In the conditions of slight undersaturation, the cyclic processes of dissolution - crystallisation takes place.

The processes of brine influx and its migration within the salar and the salt deposit in Wieliczka are comparable, despite differences in their geological settings. In both cases the processes are relatively "fresh" in relation to the actual age of the sediments. The mine waters of Wieliczka were formed during the post-sedimentation infiltration phase. Similarly, the process of water migration inside the salar is relatively new. The waters circulating in the central part of the salar and in the Wieliczka mine are mixed with poorly mineralised infiltration waters. Their amount cannot be determined precisely, since the salt deposit in Wieliczka is not confined and isolated. In both cases, we analyse waters abundant in Cl and Na which determine the brine density. Hence, the processes involved can be easily represented by plotting the Br content vs. parameters associated with the degree of water mineralisation: volumetric weight /density (Fig. 5) or salinity (Fig. 4).

CONCLUSIONS

1. The bromide content in the total amount of substances dissolved in mine waters from the Wieliczka salt mine is relatively low when compared to bromide concentrations in ordinary or evaporated seawater.

2. The relationship between the Br and Cl contents confirms that these brines are chiefly infiltration waters containing dissolved halite.

3. The Br content in non-saturated effluents goes up with an increase of solution concentration.

4. The Br content in effluents showing the composition close to saturation point is variable due to the variations of Br contents in salt rocks being dissolved. It depends also on the cyclic dissolution and precipitation of halite responsible for the reduction of Br content in re-crystallised minerals and, hence, in the brine, too.

5. The Cl/Br indicator is of little use in assessing the risk of flooding because of migrations and exchange of waters, whereby most sedimentation solutions are replaced by infiltration water.

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Streszczenie

**ZAWARTOŚĆ BROMKÓW W WODACH
KOPALNIANYCH ZŁOŻA SOLI WIELICZKA
WSKAŹNIKIEM ICH POCHODZENIA
I CYRKULACJI W ZŁOŻU**

Bogumiła Winid & Stanisław Witczak

Bromki, a raczej oparty na ich zawartości wskaźnik chlorowo-bromkowy (Cl/Br) jest klasycznym wskaźnikiem hydrogeochemicznym wykorzystywanym przy ocenie genezy wód podziemnych, w tym wód towarzyszących złożom soli. W eksploataowanym złożu solnym pozwala zazwyczaj odróżnić wody infiltracyjne, grożące rozługowaniem złoża (Cl/Br > 1000), od wód sedimentacyjnych zachowanych w ciele solnym (Cl/Br < 300), których dopływ nie stanowi takiego zagrożenia.

Jak wynika z przeprowadzonych badań w złożu wielickim, w trakcie obiegu litogenicznego, nastąpił proces daleko posuniętej wymiany wód sedimentacyjnych na wody infiltracyjne, czemu sprzyja stosunkowo płytko położone ciało solne i stosunkowo duże gradienty hydrauliczne generowane przez urozmaiconą morfologię terenu. W złożu nie stwierdzono obecności wód, których wartości wskaźnika genetycznego Cl/Br wynosiłyby poniżej wielkości charakterystycznych dla wody morskiej. Na skutek procesu wymiany wód sedimentacyjnych na infiltracyjne, wartości wskaźnika chlorkowo-bromkowego w zasolonych wodach krążących w złożu oraz w wodach dopływających o niepełnym zasoleniu są tego samego rzędu.

Badania zawartości bromków w wyciekach wód występujących w Kopalni Soli Wieliczka wskazują, że mineralizacja wody następuje na skutek ługowania minerałów złoża solnego. Różnice w wartościach wskaźnika Cl/Br wynikają głównie ze zmiennej zawartości bromków w różnych typach soli.

Mechanizm powolnej wymiany wód złożowych z sedimentacyjnymi na infiltracyjne rozpoczyna się dopływem wód słabo zmineralizowanych, których mineralizacja wzrasta dość szybko na skutek rozpuszczania minerałów ewaporatowych. Następnie ma miejsce proces krążenia po złożu solanki w stanie bliskim nasycenia lub w stanie nasycenia, podczas którego może dochodzić do wtórnego wytrącania minerałów solnych. W czasie wielokrotnego cyklu rozpuszczania i wytrącania minerałów solnych na drodze przepływu, dochodzi także do obniżenia zawartości bromu w minerałach wtórnej krystalizacji. Przebieg procesów można przedstawić na wykresach uwzględniających zależność jonów bromkowych od parametrów związanych z mineralizacją wody (ciężaru objętościowego lub zasolenia). Widoczna na wykresie (Fig. 4 i 5) zależność jest uwarunkowana: zasoleniem związanym z ługowaniem złoża, zawartością bromu w soli oraz cyklem rozpuszczania – wytrącania minerałów solnych na drodze przepływu.

