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SELECTED HYDROCHEMICAL RATIOS OF WATERS FROM INFLOWS AT LEVEL VI IN "WIELICZKA" SALT MINE

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Abstract: Relationships between major ions, such as Cl^-, SO_4^{2-} and Na^+ and some microelements, may serve as good indicators of genesis and chemical transformations occurring during groundwater flow. The chemical composition of water from inflows at the level VI of "Wieliczka" Salt Mine is formed mainly by the dissolution of different types of salts caused by waters circulating in complicated systems of semipermeable rocks and fractured sandstones. This complicated geological structure is additionally disturbed by seven centuries of mining activity. Individual inflows are recharged by different flow systems, thus water/rock contact times are different. The authors analysed basic hydrochemical ratios: sodium/ chlorides (rNa^+/rCl^-), sulphides/chlorides ($rSO_4^{2-} \cdot 100/rCl^-$) and chlorides/iodides (Cl^-/I^-). The obtained results proved that hydrochemical ratios may serve as a supporting tool for better assessment of water threats in the western part of "Wieliczka" Salt Mine.

Key words: mining hydrogeology, hydrochemical ratios, "Wieliczka" Salt Mine

INTRODUCTION

The interpretation of various different hydrochemical ratios is one of the methods commonly applied by hydrochemistry. Calculating the relations between the concentrations of particular ions or groups of ions in water allows for deliberations on water genesis and transformation which the chemical composition of water was subjected to. It also enables to compare the chemical types of water for facilitating the discovery of certain deposits.

Most frequently hydrochemical ratios are calculated as an equivalence ratio (e.g. $r\mathrm{Na}^+/r\mathrm{Cl}^-$) or as a weight ratio (e.g. $\mathrm{Cl}^-/\mathrm{I}^-$).

The "Wieliczka" Salt Mine is a worldwide unique tourism, culture and museum attraction visited by over one million tourists every year. At the same time it is a mining plant with a seven-hundred year history. Mining excavations at the "Wieliczka" Salt Mine are located on nine exploitation levels reaching 330 m deep, at a total length of 350 km. During the period of mining operations approximately 2,000 chambers of a total estimated volume of 7.5 million m^3 (Brudnik et al. 2010) were excavated. A complex including ca 300 chambers and a network of connecting corridors of a total length ca 50 km is today recognized as a historic monument protected by law.

Due to the complexity of the geological structure of the Miocene salt-bearing formation the rock mass, during the period of exploitation, was extremely disturbed by mining excavations, both chambers as well as corridors. Investigating the geological and hydrogeological conditions occurred mainly during the exploitation of mining excavations conducted in search for salt. As a result of difficult to foresee human errors the natural insulation of the salt deposit was penetrated at many points initiating numerous and sometimes voluminous groundwater flows into the mine. During the period of its existence several catastrophic floods occurred in the mine. The most serious penetration of water into the mine occurred in 1992 in the region of the Mina traverse. Fortunately, this threat has already been contained.

Currently, one of the most profusive water leakages creating the greatest hazard for the mine is the leakage on level VI in the western section of the mine. This area is located in the vicinity of the northern boundary of the deposit. The average inflow of leakage water in 2012 amounted to 64.5 dm^3/min, i.e. 24% of all the inflows to the mine (Brudnik & Stecka 2013). These leakages supplied water of an average NaCl concentration amounting to 209 g/dm^3.

Samples of water were taken at four points of inflow in 2010. In 2011 samples were once again taken at the same points as well as at six additional inflows in the area of chambers Z-24, Z-26, Z-28 and Z-32. The location of the sample points is presented on the map (Fig. 1). The chemical analyses of the water samples drawn at the points of the leakage were performed in the laboratory of the Department of Hydrogeology and Engineering Geology at the Faculty of Geology, Geophysics and Environmental Protection of the AHG University of Science and Technology in Krakow. ICP-OES spectrometer (Perkin-Elmer,) was used for Na, Ca, Mg and Fe determinations. Concentrations of other metals were determined using ICP-MS (Perkin-Elmer, Elan 6100).

RESEARCH AREA CHARACTERISTICS

Geological setting (Fig. 1)

The rock salt deposit in the area of Wieliczka is part of the Miocene salt-bearing formation running along a narrow belt in the vicinity of the fore-Carpathian basin beginning in the Upper Silesian region via the area of Krakow towards the eastern borders of Poland.

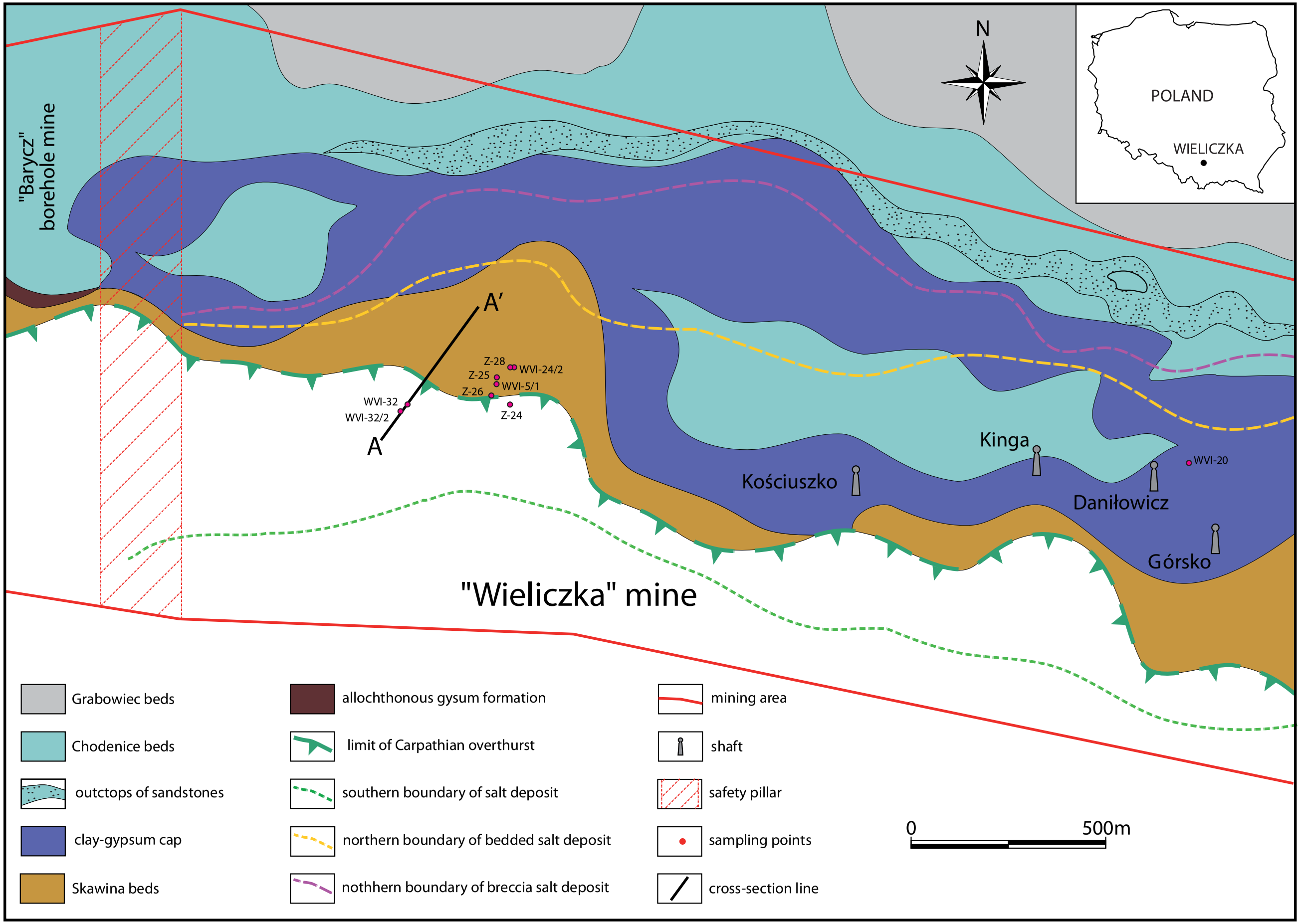

Fig. 1. Geological map of western part of Wieliczka salt deposit (after Brudnik et al. 2010)

The deposit extends in the east-west direction over a length of ca 10 km while the width of the belt in the area of the "Wieliczka" Salt Mine amounts to ca 1.2 km.

The deposit is divided into two parts: the boulder (breccia) deposit and the stratiform (bedded) deposit. In the breccia deposit the salt formations are strongly dislocated, whereas in the bedded deposit, despite tectonic disturbances, the continuity and sequence of the layers is generally maintained. The thickness of the saliferous formation is approximately 350 m.

Three lithostratigraphic units are identified in the discussed succesion (Gaweł 1962):

1) the Skawina beds,
2) the Wieliczka beds (salt series),
3) the Chodenice beds.

The Skawina beds appear as green and grey marl with rich foraminiferal fauna, sandstone, and siltstone. They are deposited on highly dislocated formations of an older substrate, mainly Upper Jurassic limestone. The thickness of these formations is highly variable and oscillates between 50 m in the western section of the deposit to 350 m towards the east.

The Wieliczka beds contain several layers of rock salt of a variable thickness, shape and NaCl concentration. The rock salt layers are separated by claystone, sandstone and siltstone formations as well as gypsum and anhydrite representing sulphate facies. The boulder deposits are present in the upper part of the Wieliczka beds profile above the bedded section of the salt deposit. The boulder deposit is formed as a conglomerate of marl claystone and salt clays called "zubers" as well as irregularly displaced in their vicinity lumps of laminated green salt and, subordinately, polycrystalline salt lumps, called stained glass window salt.

The Chodenice beds are represented by russet gray argillaceous shale or mudstone and anhydrite claystones containing gypsum and anhydrite nodules as well as limestone and dolomites. It has been confirmed that within the area of the Chodenice beds complex there occur conglomeratic, clastic and sand deposits.

The most recent layer of Quaternary sandstone facies of a very variable thickness and lithology appears above the Miocene evaporites. Clays and silty sediments with interbeds of sand and gravel dominate in the Quaternary profile.

The geological structure of the western section of the Mine traverse had been determined on the basis of reconnaissance and exploitation mining works executed in the years 1950–1964.

Additionally, apart from the reconnaissance corridors test boreholes were drilled in the years 1956–1959 towards the southern and northern boundaries of the salt deposit. Characteristic of the Wieliczka region is its dichotomy of salt deposits.

The western area of operations (chambers Z-25–Z-32) is located in the vicinity of a steep tectonic scale deposited under flysch formations thrust from the south underlain by the barren Skawina beds (Fig. 2). The oldest salt deposit in which chamber Z-32 was excavated dips towards the south at an angle of 45°, resulting in a significant shift of the deposit boundary towards the south.

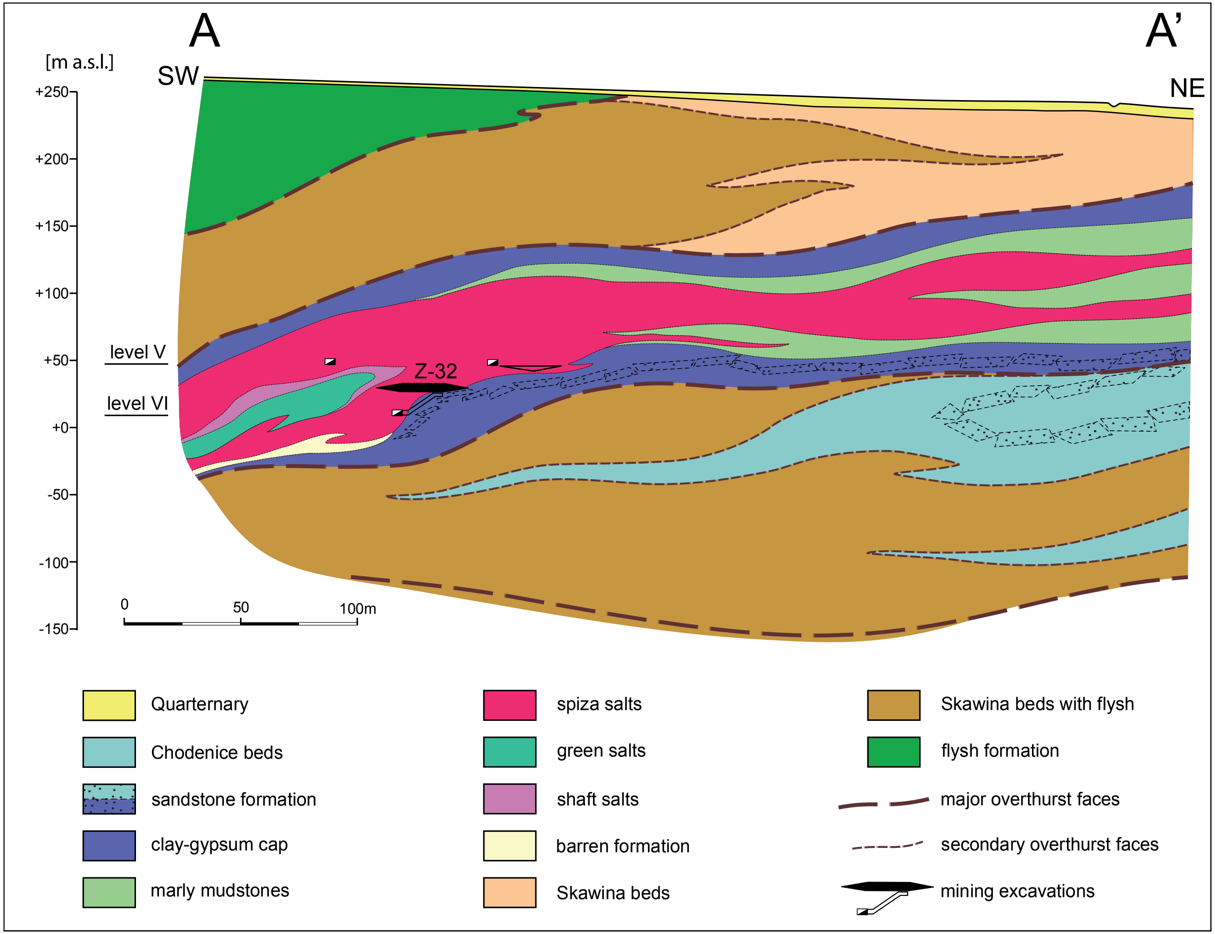

Fig. 2. Geological cross-section SW-NE through western part of Wieliczka salt deposit (after Szybist 2011)

The sulphate series is adjecent to the salt formations from the north. Its thickness measures from a few to several meters, but locally it can even completely disappear (Fig. 1). This series contains marly-sand-clay formations associated with limestone and sulphate with interbeds of sulphate facies. The sulphate series separates salt layers from water-bearing Chodenice beds.

Hydrogeological conditions

Lithology of the Tertiary and Quaternary sediments is essential for hydrogeological conditions in the region of the "Wieliczka" Salt Mine.

The Quaternary aquifer in the region of the "Wieliczka" Salt Mine comprises sands of variable grain size, gravels and rubbles. The water table of the Quaternary sediments occurs at a depth usually not exceeding a few meters.

There are four aquifers separated in the area of the Miocene sediments associated with the layer complexes characteristic for the Wieliczka region:

1) The aquifer within the Grabowiec beds formed as average and fine-grained sands, called Bogucice sands (Skoczylas-Ciszewska & Kolasa 1959), has direct contact with Quaternary sediments occurring on the surface and recharged by atmospheric precipitations. The hydraulic conductivity of the Bogucice sands usually ranges from $2.4\cdot10^{-5}$ m/s to $8.5\cdot10^{-5}$ m/s (Brudnik et al. 2010).
2) The predominat type of lithology in the area of Chodenice, are low permeability formations – claystones and mudstones. Brittle and crumbly sandstone as well as cracked and dislocated claystone below the layer of sandstone were also found here. Distinct dislocation zones are emphasized by the appearance of rocks of a breccia character. The Chodenice complex contains water under pressure measured in the range of about 1.6 MPa. Hydrogeological studies of sandstone have shown hydraulic conductivity ranging from $5.8\cdot10^{-9}$ m/s to $6.4\cdot10^{-6}$ m/s (Brudnik et al. 2010).
3) Waters occuring in the sulphate series formations (mainly in the sandstone interlayers and in the cracks and crevices as well as in the karstic forms developed upon them) are under pressure measured in the range up to 3.0 MPa. The hydraulic conductivity of these rocks is usually of the values from 10^{-8} m/s to 10^{-7} m/s.
4) The oldest level is associated with sandstones and siltstones of the Skawina layers and cracked marly claystones appearing in the area of the same nexus. These formations create a porous-fissure aquifer containing water under pressure in the range of 3.8–4.0 MPa (Brudnik et al. 2010). The hydraulic conductivity of water-bearing rocks of the Skawina layers usually ranges from 10^{-9} m/s to 10^{-7} m/s.

The hydrogeological conditions in the western area of the mine are quite poorly identified. They have been indirectly established as a result of reconnaissance mining works on the basis of which significant water accumulation of geological units situated northward from the boundary of the deposit were defined. Three hydrogeological boreholes, H1, H2 and H6, were drilled from the surface northward from the deposit boundary in the years 1966–1970. Brittle and crumbly sandstone was discovered in borehole H2 in the area of the Chodenice layers reaching the depth in the range from 200.0 m b.s.l to 216.0 m b.s.l. (i.e. 42.9–26.9 m a.s.l.). Distinct dislocation zones whose presence was asserted by the appearance of rocks of a breccia character were encountered below the sandstone. Sandstones contain a confined water table and the level of stabilization level forms at the depth of 20.4 m b.s.l. Test pumping of this borehole showed a hydraulic conductivity $5.4 \cdot 10^{-6}$ m/s.

RESEARCH RESULTS AND DISCUSSION

The chemical composition of waters from investigated inflows

In 2010 waters from the investigated inflows presented pH ranging from 7.27 to 7.46 and TDS values from 63.2 g/dm^3 (Z-28) to 326.0 g/dm^3 (WVI-20). All brines belonged to Cl-Na or Na-Cl type, with Na share 94.2–98.0% amongst cations and Cl share of 94.1–98.3% amongst anions. Concentrations of chlorides varied, from 35.3 g/dm^3 (Z-28) to 192.0 g/dm^3 (WVI-20). Concentrations of sodium in the collected samples ranged from 28.2 g/dm^3 (Z-28) up to 128.0 g/dm^3 (WVI-20).

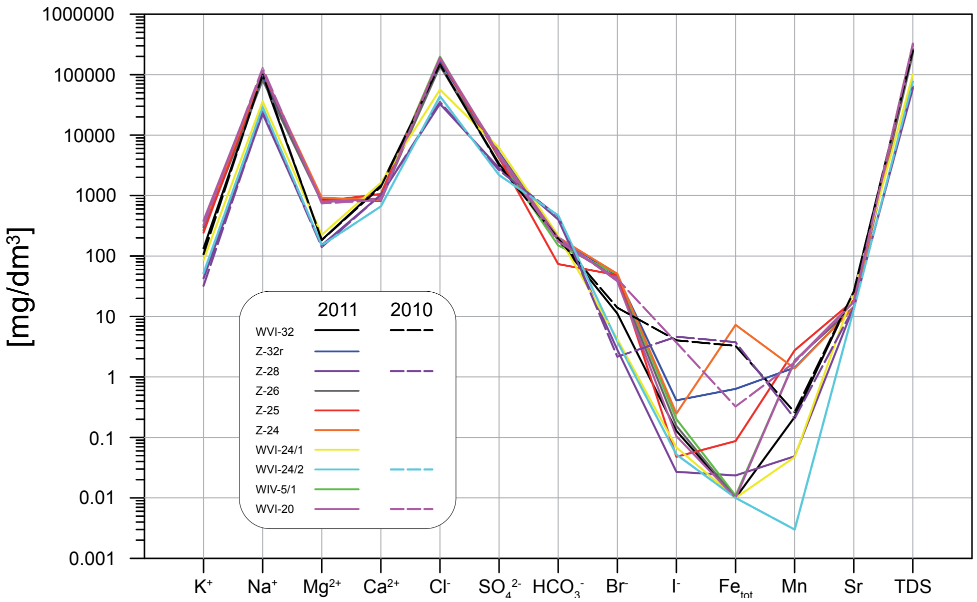

Fig. 3. Chemical composition of samples collected in 2010 and 2011

The samples collected in 2011 showed general chemical composition similar to those in 2010.

TDS values from 59.6 g/dm^3 (Z-28) to 321.0 g/dm^3 (WVI-5/1). All waters belonged to Cl-Na or Na-Cl type, with Na share 93.8–97.8% and Cl share of 92.4–98.5%.

Figure 3 presents summarised the results of 2010 and 2011 sampling campaigns. Significant differences between the two series can be observed in case of bromides, iodides, iron and manganese.

Sodium-chloride ratio

The sodium-chloride ratio $r\mathrm{Na}^+/r\mathrm{Cl}^-$ can be applied for assessing hydrochemical zonation. The value of this ratio does not exceed 0.86 in the dynamic and hydrochemical stagnation zone that is, the accepted value average for ocean water (Macioszczyk 1987). The ratio value drops in synsedimentary (basin-derived) waters and paleoinfiltration waters due to the enrichment of water with Ca^{2+} ions at the expense of Na^+ ions following ion exchange. When mineralization of water is caused by salt deposit leaching then the value of $r\mathrm{Na}^+/r\mathrm{Cl}^-$ ratio assumes values exceeding 1.0.

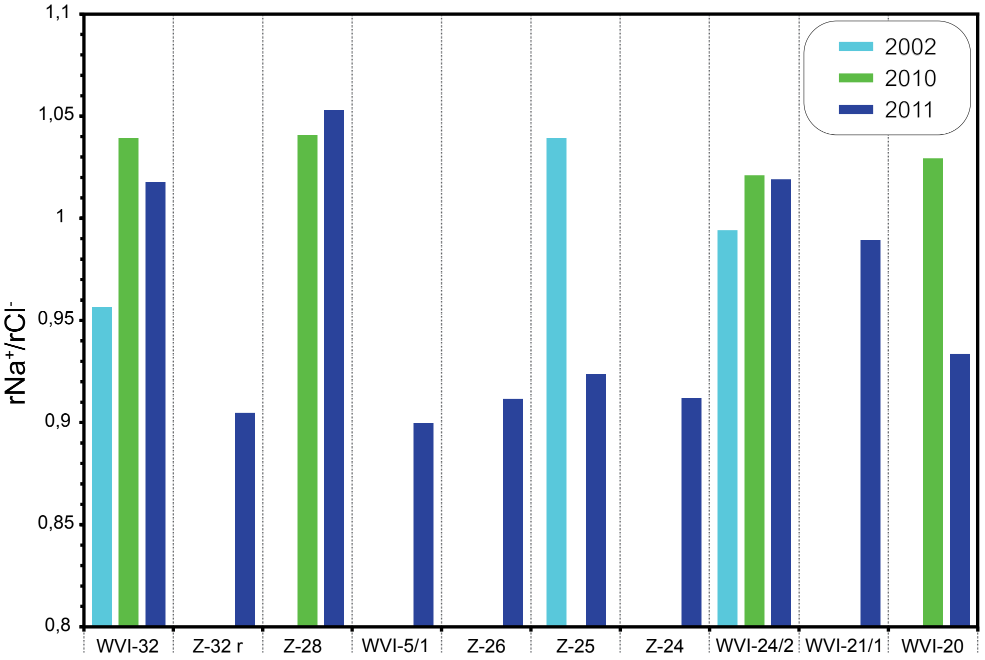

Fig. 4. Sodium-chloride ratios calculated for waters from investigated inflows

The value of the sodium-chloride ratio in all the analysed cases exceeded 0.90. The maximum ratio value (1.05) was noted for a sample take in the year 2011 from inflow WVI-6 in the Z-28 chamber (Fig. 4).

Such values of the discussed ratio are typical for highly mineralized waters whose chemical composition formed, to a large degree, due to rock salt deposit leaching (Macioszczyk 1987, Pazdro & Kozerski 1990). The differentiation of ratio $r\mathrm{Na}^+/r\mathrm{Cl}^-$ values between the particular inflows serves as evidence of the diversity and significant degree of complexity of the inflow boosting routes. This effects the time of contact of water with the formations through which it flows. In effect, the rate of salt dissolution reaction and ion exchange processes is differentiated. The observed changes of ratio value in time (at the same points) do not give grounds to form an unambiguous interpretation.

The calculated ratio $r\mathrm{Na}^+/r\mathrm{Cl}^-$ values are close to 1. They are contained within the range 0.9–1.05.

Generally, a weak trend towards increasing the ratio $r\mathrm{Na}^+/r\mathrm{Cl}^-$ in time is confirmed in most cases of the studied inflows (under the condition, that the same inflows were studied several times). Thus, the water from inflow WVI-32 flowing out from under chamber Z-32 demonstrated, though in 2010, the value of 1.04, whereas in the year 2011 – 1.02. A comparison of these values to the results of the study by Winid & Witczak (2007) gives a clearer image of the situation. This study was conducted in 2000. The value of the coefficient calculated for water from inflow WVI-32 equalled at that time 0.96, hence an increase of value in time is noticeable. This may indicate the existence of contacts with lower mineralized waters of a shorter flow time. A spray method was used for mining during the final stage of exploitation of chamber Z-32 in order to change the triangular shape of the chamber to a trapezoid and increase the coefficient of deposit exploitation. It is quite probable that during this process the layer of salt was removed separating salt formations from the sulphate series and water-bearing formations of a sandstone character present in the area of the Chodenice beds. Following the termination of mining works in 1962 the chamber was excluded from operations and left without backfilling. It was only in1966 that the leakage was discovered in the chamber already partially destroyed (cave in) due to rock mass stress relief. From then on this inflow has been continuously active.

In the case of inflows WVI/Z-28 and WVI-24/2 the rising trend is much less pronounced (Fig. 4). This indicates stable in time conditions of the chemical composition formation of water from this inflow.

Unlike the previous, the value of ratio $\mathrm{rNa}^+/\mathrm{rCl}^-$ dropped in inflows WVI-20 and WVI/Z-25. In the case of inflow WVI-20 the value dropped from 1.03 in 2010 to 0.94 in 2011. Inflow WVI/Z-25 sampled in the years 2000 and 2011 demonstrated a drop from 1.04 to 0.92. Such a phenomenon can be explained by way of the decrease in time contribution of freshwater components in the formation of the chemical composition of this inflow.

Sulphate-chloride ratio

The sulphate-chloride ratio defined as an equivalence ratio $r\mathrm{SO}_4^{2-}\cdot 100/r\mathrm{Cl}^-$ is recognized as a measure of water metamorphosis due to the fact that reduction processes lead to the decrease of the sulphate ions concentration. The ratio in isolated and metamorphosed waters is accepted as below 1 (Pazdro & Kozerski 1990). The value of the sulphate ratio calculated for waters sampled from the inflows are contained within the range from 1.53 to 8.04 (Fig. 5).

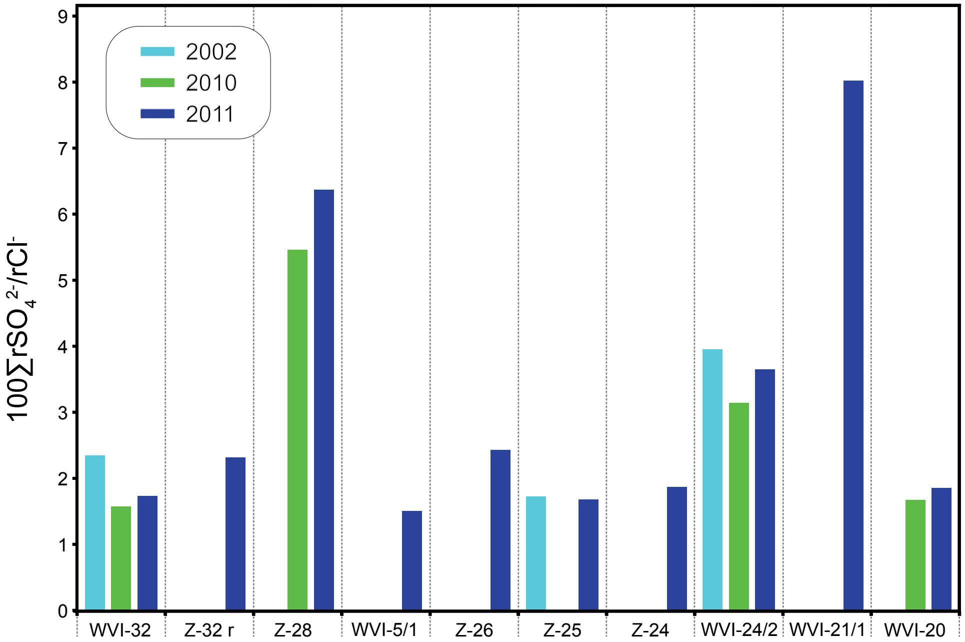

Fig. 5. Sulphate-chloride ratios calculated for waters from investigated inflows

This indicates towards the diversification of the degree of the advancement of the reduction processes and confirms the thesis concerning the high level of diversification and complexity of routes feeding the particular inflows. The fluctuation in the value of this ratio verified in the subsequent years in the same inflows are minor and do not allow for more advanced considerations. However, a downward trend can be noticed in the case of inflows WVI-32 and WVI-24/2. The fluctuation of values of this ratio suggests varying in time conditions of forming the chemical composition of waters from these inflows.

Chloride-iodide ratio

The chloride-iodide ration (Cl^-/I^-) can communicate information about the contacts of fossil water or bitumen deposits. The value of this ratio for ocean waters is $3.8 \cdot 10^5$ (Macioszczyk 1987).

The values of this ratio, calculated on the basis of study results obtained in 2010 and 2011, are contained in the range from $7.6 \cdot 10^3$ to $3.8 \cdot 10^6$. Such a large value difference associated with considerable (in orders of magnitude) value changes in the subsequent years may certify towards the complex and differentiated feeding routes of the particular inflows and the changeability of these conditions in time. On the other hand, one cannot rule out errors made by researchers while taking and transporting samples to the laboratory or at the laboratory itself.

It is highly probable that the observed image result from storing the samples for too long a period prior to the determination of iodide concentration in the 2011 sample series. Under the circumstances more elaborated considerations are not possible.

CONCLUSIONS

The chemical composition of inflows at level VI in the "Wieliczka" Salt Mine is mainly composed by way of dissolution of various kinds of salt with water of a lower mineralization inflowing through a complicated system of routes. This is quite understandable as what we are dealing with here is a complex geological structure additionally disturbed by the mining activaties continuing over centuries. The particular inflows are boosted by various circulation systems resulting in different times of water / rock contact and in effect this presents a complex and difficult to interpret hydrochemical image.

The analysis of hydrochemical ratios combined with the results of other studies, especially isotope tests would permit a better identification of the scale and sources of water hazard in the mine, especially salt mines. However, it is necessary to improve the sampling process on order to guarantee reliability of the future research.

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Streszczenie

Stosunki zawartości jonów głównych i niektórych mikroskładników w wodzie, zwane wskaźnikami hydrochemicznymi, mogą być pomocne w analizie genezy wód podziemnych i interpretacji zmian, jakim wody ulegały w czasie krążenia w górotworze. Skład chemiczny wycieków na poziomie VI Kopalni Soli „Wieliczka” kształtuje się w efekcie rozpuszczania różnych typów soli przez wody krążące w skomplikowanym systemie półprzepuszczalnych skał typu mułowce i spękanych, pokruszonych piaskowców. Dodatkowo sytuację komplikują efekty, trwającej tu od siedmiu stuleci, działalności górniczej. Analizie poddane zostały podstawowe wskaźniki hydrochemiczne: sodowo-chlorkowy $r\mathrm{Na}^{+}/r\mathrm{Cl}^{-}$, siarczanowy $r\mathrm{SO}_4^{2-}\cdot 100/r\mathrm{Cl}^{-}$ oraz chlorkowo-jodkowy $\mathrm{Cl}^{-}/\mathrm{I}^{-}$. Wyniki badań posłużyły jako narzędzia wspomagające ocenę zagrożeń wodnych w zachodnim rejonie kopalni.