Original Research

Physical-Chemical Properties of Coal Mine Waters of Old Adits and Spring Waters

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Abstract

Two water adits that drain the old, closed excavation tanks of a coal mine were characterized in terms of the physical-chemical properties of their waters and compared them with the waters of two springs. These adits are "Krystyna" and "318," and the springs are Maria and Mniszek, which are situated in the Upper Silesian Region (sothern Poland). The results that were obtained permitted us to infer that acid drainage can occur within the pits. Thus, the waters of the adits are acid and typified by a high concentration of sulphates and iron ions. A distinguishing feature of the "318" adit is its high thermal stability. The variation in temperature during the year does not exceed 1°C. The springs flow from Carbon sandstone and therefore, they functioned as reference samples for the adits that were investigated. A high synchronicity of changes in the selected physical-chemical parameters of adit waters and natural springs was observed.

Keywords: mining waters, acid mine drainage, springs, hydrochemistry, tunnels

Introduction

One effect of underground mining exploitation is the formation of many pits, including adits, that have varying characteristics. According to [1], an adit is a horizontal tunnel with a slope ranging from 1 to 5% toward a vent that terminates above the surface of the ground. Adits can have different functions. They are used most frequently for the gravitational drainage of pits and they are also water grooves. Such objects are only built in areas with a diversified land relief where all mining works are performed above the level of the adit. Water grooves usually have a discharge canal that transports the waters to the closest water course. There are many examples of such objects [2]. In Upper Silesia, the largest number of these objects is associated with the mining of silver and lead ores. There are also several adits that are associated with coal mining.

Many water grooves still function as drainage elements of a formation today despite the cessation of mining activities. The outflow of waters is possible due to gravity. There is an enormous body of literature that reports the presence of these objects, including [2-6].

In the present study two old adits that were associated with coal mines are characterized in terms of their hydrographic-hydrochemical characteristics. They are old adits "Krystyna" and "318," which are situated in the Upper Silesian Industrial Region (Fig. 1). The coal that was exploited was in Upper Carbon layers. Additionally, the physical-chemical properties of two springs that drained the water-bearing Carbon layer were analyzed. These objects served as reference sites for the adits that were studied. The characteristics of the physical-chemical properties of the spring waters have been the subject of many studies [7-10].

Location of Investigated Objects

The Krystyna adit is located in Gwóźdź near Krzeszowice (Fig. 2). The beginning of this groove was situated in the shaft of the same name at a depth of 43 m

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below the surface, i.e., 260 m a.s.l. (Fig. 3). It is almost two kilometers long and its outlet was finished with a tunnel vault made of bricks. At present, it is buried under a rocky rubble of limes. Concrete tubes, which in the past transported waters directly to the Krzeszówka River, were used to transport the waters from the coal mine outside [6]. Over time they were destroyed and the waters that flowed through the adit infiltrated the alluvium of the Krzeszówka supplying Quaternary water-bearing level. Only a small amount of coal mine waters is transported by the new sewage system that was constructed in 2008. The outflow of the waters is described by the geographic coordinates (50º7' 35.64" N; 19º38' 36.31" E). The amount of these waters is small and varies between 0.1 to 0.5 $dm^3 \cdot s^{-1}$ [2]. However, there are periods when there is no water outflow (autumn, winter). The periodicity of the outflow may be linked to the partial drainage of coal mine waters by the new sewers.

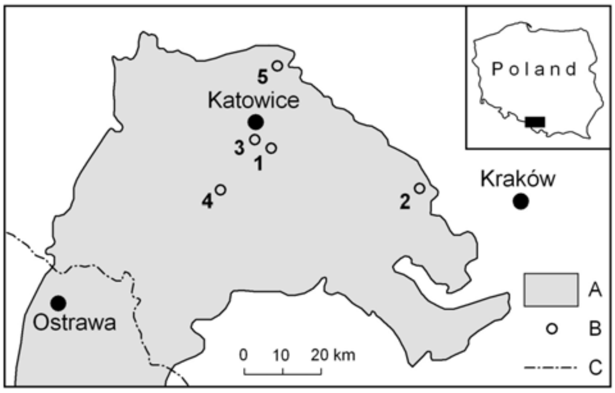

Fig. 1. Location of the investigated objects. A – territory of the Upper Silesian Industrial Region, B – objects: 1. adit 318, 2 – adit Krystyna, 3 – Maria Spring, 4 – Mniszek Spring; 5 – Pradło Spring, C – border of state.

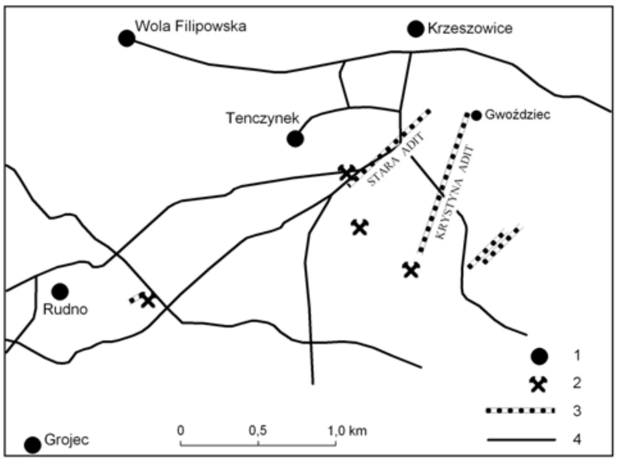

Fig. 2. Location of the adit Krystyna.
1. town, 2. former coal mines, 3. former shafts, 4. water adits

Adit "318" is located in the area of the "Murcki" coal mine (Fig. 4) (50º10' 41.65" N; 19º1' 16.35" E). The history of building adits in this area dates back to 1808. The focal groove was probably built in 1824, and in 1930 a partial reconstruction took place. Nowadays, the adit has a concrete cover along nearly its entire length and at sites where it crosses excavation tunnels, the cover is made of concrete and steel. The length is estimated to be 1,643 meters. The entry of the groove is at a depth of 264.67 m a.s.l. and the exit is at 262.8 m a.s.l. Thus, the difference in the levels amounts to 1.87 m (1.2%). The adit ditches unexploited the excavation of level 318. The exit of the adit is a short 10 m channel that flows into Rów Murckowski River. Its efficiency ranges from 2.1 to 3.6 $dm^3 \cdot s^{-1}$ [2]. Mine waters affect changes in the water chemistry of the Rów Murckowski River. Their discharge increases the concentration of sulphates and iron in the watercourse. Both the "Krystyna" and "318" adits are the local basis for the drainage of old mining excavations. The maximum depth of the cut of the formation in the "Krystyna" adit is 55 m under the surface and it is 45 m in the case of "318."

Three natural objects, which are also situated in the Upper Silesian Industrial Region (Fig. 1), were selected as the reference objects. It was assumed that these springs must ditch the carbon water-bearing level. Only Maria Spring in Katowice (50º11' 18.11" N; 18º59' 48.04" E) Mniszek Spring in Łaziska (50º8' 4.47" N; 18º51' 55.97" E), and Pradło in Psary (50º22' 45.87" N; 19º7' 7.26"E) met the criteria.

Methods

Hydrographic mapping that was designed to estimate the water courses in the area of the adits were carried out according to methods by [11]. The measurements of the chosen parameters of the adits and the establishment of their courses were made based on archived cartographic materials (old mining maps). Measurements of pH, temper-

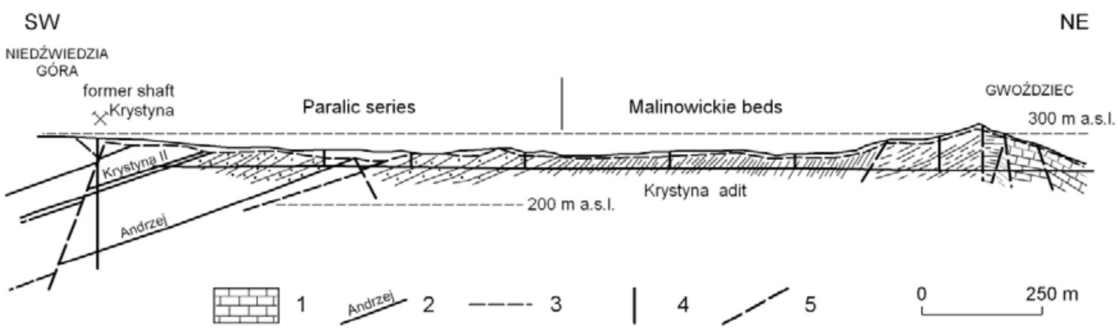

Fig. 3. Horizontal section of the adit Krystyna (according to Bednorz 1959, modified).
1. limestones (Upper Jura), 2. coal seam, 3. border of the occurrence of Quaternary deposits, 4. shafts, 5. downcast.

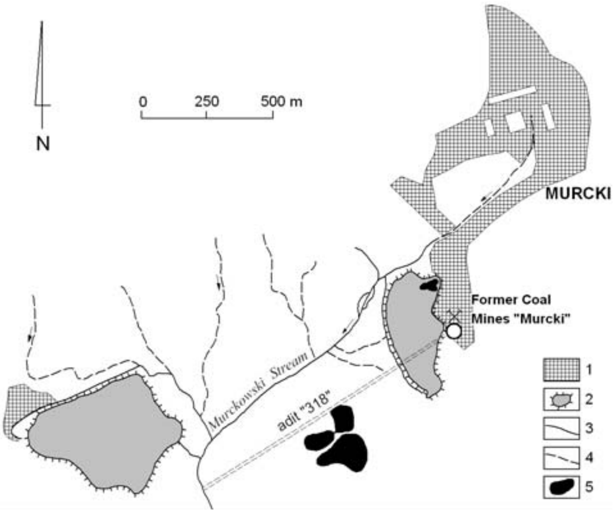

Fig. 4. Location of adit 318.
1. urbanized area, 2. colliery waste tips, 3. permanent water courses, 4. ephemeral water courses, 5. water bodies.

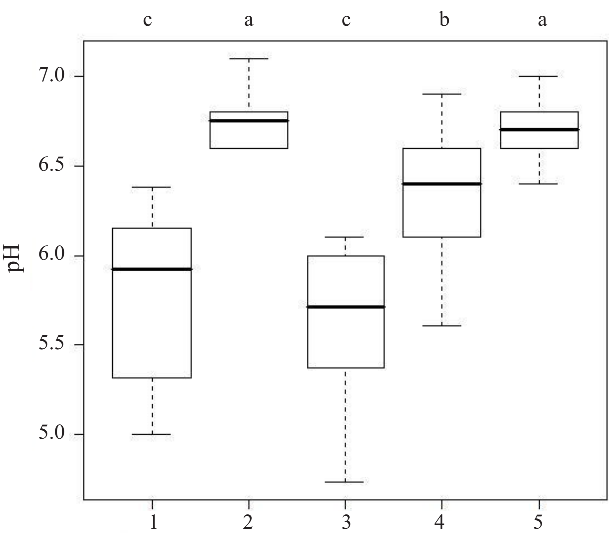

Fig. 5. Reaction pH of the adits and the springs.
1. adit 318, 2. adit Krystyna, 3. Maria Spring, 4. Mniszek Spring, 5. Pradło Spring.

ature, redox potential and electric conductivity (PEW) were made in the field using a Multiline PR gauge or Professional Plus. Twenty-four measurement series were performed for each of the sites in 2004 to 2009. Two series of measurements were conducted in each calendar month. The number of measurements performed on the synthetic box plots was the same (n = 24).

Water samples for chemical analyses were sampled in bottles. Transport of waters to the laboratory took place at 4ºC. Before the analyses, the samples were filtered (0.45 µm Millipore). The lab analyses included the determination of main cations and anions in water: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, NO_3^{-}, PO_4^{2-}, and NH_4^{+}. The chemical analyses of waters were performed according to Polish Standards (PN 1971-2002). The hydrochemical type of the waters was described after [12].

The data that were obtained were subjected to statistical analyses based on [13, 14]. In order to determine any significant differences between the objects, the non-parametric ANOVA Kruskal-Wallis test was applied and for a pairwise comparison, the Conover test was used. In order to test the relationship between natural objects (springs) and anthropogenic objects (adits), the Spearman rank correlation test was used for the data gathered at the same time. Adit 318 and Maria Spring were chosen for the correlation test. This choice was determined by the smallest distance between the objects – 2 km. This is important because the physical-chemical properties of the waters are mainly dependent on climate-meteorological factors [15]. The different lower case letters above a box and whisker plots in the figures mean that the medians differ significantly at $p<0.05$.

Results and Discussion

The most characteristic feature of the waters of adit "318" is low pH (Fig. 5). The source of acid substances is the process of the oxygenation of pyrite. This mineral decreases according to chemical reaction [16] in the presence of oxygen and water:

$$FeS_2 + 3.5\ O_2\ H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2H^{+} \qquad (1)$$

If water is not present with pyrite, then dissolved iron (VI) sulphate (II) undergoes oxygenation (2) and the newly formed sulphate (VI) iron (III) is hydrolyzed and iron (III) oxide-hydroxide (3)

$$Fe^{2+} + \tfrac{1}{4}\ O_2 + H^{+} \rightarrow Fe^{3+} + \tfrac{1}{2}\ H_2O \qquad (2)$$

$$Fe^{3+}\ 3H_2O \rightarrow Fe\ (OH_3)\downarrow + 3H^{+} \qquad (3)$$

Thus, the adit that was studied is an example of the "acid drainage of a coal mine" (Fig. 6). This phenomenon has been described in many mining areas [17-20]. The formation of sulphuric acid under the conditions of a lack of calcium carbonates is not buffered and the waters show high aggressivity.

Fig. 6. Inflow of mining waters from the adit No 318 to Murckowski Ditch (phot. T. Molenda)

The waters of the "Krystyna" adit, which also drains old coal mine excavations, are characterized by a slightly acid range (Fig. 5). This situation is both an effect of the buffering impact of the carbonate rocks themselves, in which the last section of the adit is cored (Fig. 3), and the inflow of alkaline waters from the drainage of this fragment of the massif [2]. The processes in the final section of the adit can be described by the following reactions:

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2O + CO_2 \quad (4)$$

$$CaCO_3 + 2H+ \rightarrow Ca^{2+} + CO_2 + H_2O \quad (5)$$

The signals of an active reaction are precipitated calcium sulphates, which was confirmed by x-ray analyses of the deposits that were sampled from the adit [2]. In the case of Maria Spring, the median of pH was 5.6 but minimum

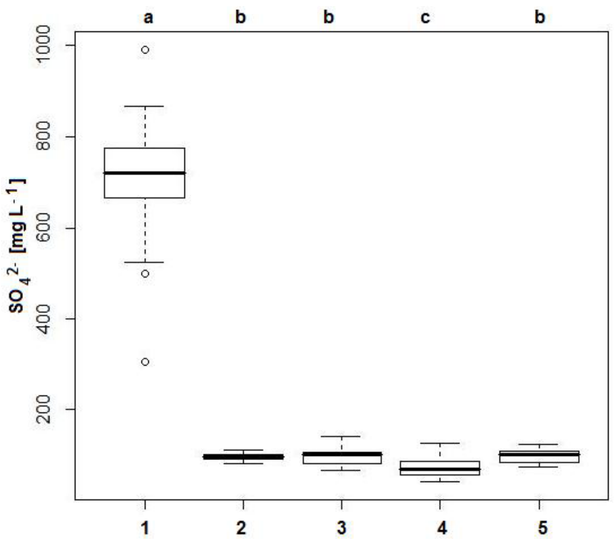

Fig. 7. Sulphate concentrations of the adits and springs.
1. adit 318, 2. adit Krystyna, 3. Maria Spring, 4. Mniszek Spring, 5. Pradło Spring.

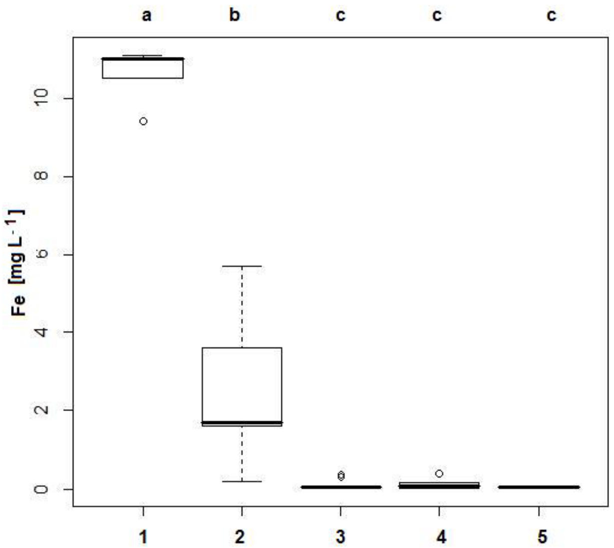

Fig. 8. Concentrations of iron in the adits and springs.
1. adit 318, 2. adit Krystyna, 3. Maria Spring, 4. Mniszek Spring, 5. Pradło Spring.

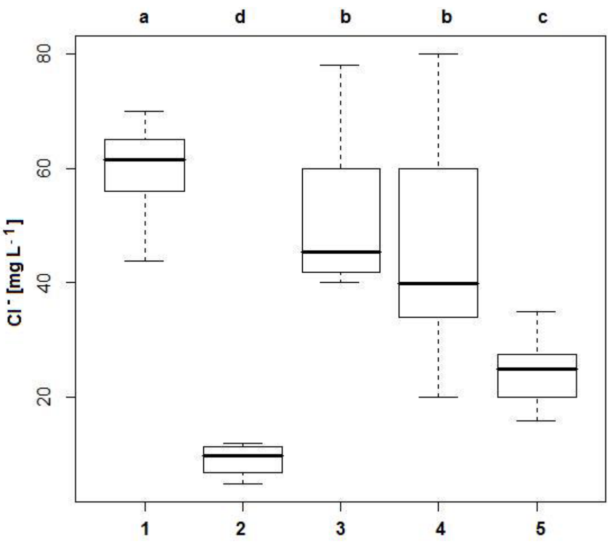

Fig. 9. Concentrations of chloride ion in waters of the adits and springs.
1. adit 318, 2. adit Krystyna, 3. Maria Spring, 4. Mniszek Spring, 5. Pradło Spring.

value was 4.7 pH. Moreover, another spring in the Upper Silesia Region that flows from the Carbon reservoir is characterized by acid waters [21]. The reactions of both the adits and natural springs showed a low variability – $C_v <$ 8%.

Acid coal mine waters are typified by a high concentration of sulphates. This was particularly visible in the waters of adit 318, where the content of these ions was 682 mg·dm^{-3} (Fig. 7). A surprisingly low content of sulphates was found in the waters of the Krystyna adit. The mean concentration of this ion was estimated at 97 mg·dm^{-3}, which is comparable to the concentration in the natural springs (Fig. 7). A low concentration of sulphates, in spite of the occurrence of the reaction of the decay of pyrites, should be attributed to their removal during the above-mentioned reaction (4). This reaction does not occur in the case of adits that were cored only in Carbon rocks, and therefore sulphates are more abundant [2]. The value of cv for sulphates varied from 9% (Krystyna) to 30% (Mniszek Spring).

The process of the decay of pyrites also releases high amounts of iron ions into water (1), which then undergoes oxygenation (2). Therefore, the waters of the adits are characterized by an orange color. This is partially an effect of the presence of suspension in the shape of fillies of iron hydroxides. A much lower concentration of iron was observed in the waters of the springs; however, there were no significant differences (Fig. 8). Among the ions that were analyzed, the content of iron undergoes the biggest changes. In the Maria and Mniszek springs the coefficient of variation exceeded 100%. One of the ions that was analyzed was chloride. The biggest concentration of this ion was recorded in the adit 318 waters and was 60.5 mg·dm^{-3} (Fig. 9).

The lowest concentration of this anion – 9 mg·dm^{-3} – was reported in the waters of the Krystyna adit. Both the

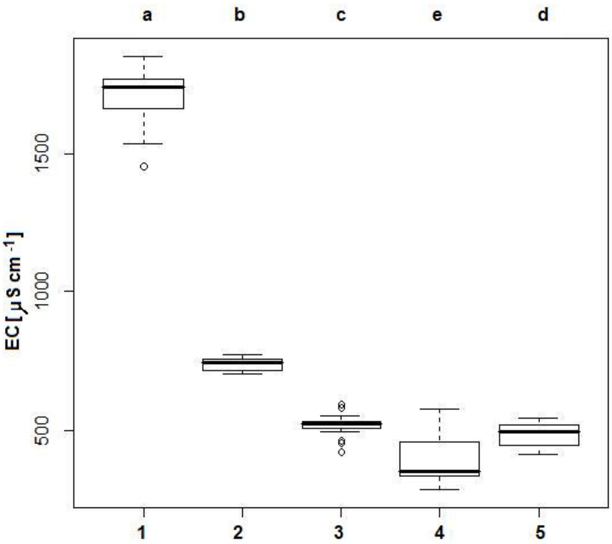

Fig. 10. Electric conductivity of adit and spring water.
1. adit 318, 2. adit Krystyna, 3. Maria Spring, 4. Mniszek Spring, 5. Pradło Spring.

content of chlorides in the waters of the Krystyna adit and adit 318 differed significantly from the content of chlorides in the waters of the carbon springs (Fig. 9). The coefficient of variation for chlorides varied between 10.6% (adit 318) and 42.5% (Mniszek spring). Such a high variation of chloride ions in Mniszek Spring may be the result of the inflow of pollution together with infiltration waters. The area around the supply spring is highly urbanized. In this case, one anthropogenic source of chlorides could be the salt that is used for thawing the road surface. The negative influence of winter treatments for the removal of ice from roads on the quality of waters was mentioned by [22, 23].

The diversified concentration of the dominating ions is reflected in the hydro-chemical parameters of the waters that were studied. The waters of adit 318 and all of the

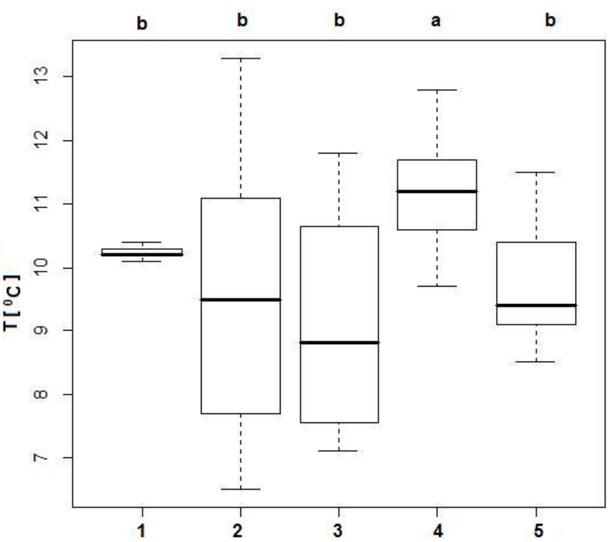

Fig. 11. Water temperatures in the adits and springs.
1. adit 318, 2. adit Krystyna, 3. Maria Spring, 4. Mniszek Spring, 5. Pradło Spring.

Table 1. The values of Spearman ran correlation (rs) test between selected properties of waters in 318 and Maria Spring ($p<0.05$).

Variable	rs
Electrical conductivity	0.76
Temperature	0.73
Chlorides	0.78
Sulphates	0.73
pH	- 0.58

Carbon springs that were studied represent a sulphate-calcium type (SO_4-Ca). Only the waters from the Krystyna adit represent a bicarbonate-calcium type (HCO_3-Ca). This is connected with the geological structure of the final section of the adit. The drainage of this limestone fragment of the adit provides waters with bicarbonate ions, which determines this hydrochemical type of water.

High concentrations of particular ions have an impact on the electrical conductivity of the waters of the adit (Fig. 10). The highest mean value of electrical conductivity was observed in the adit 318 waters. A much lower mean conductivity was recorded in the waters of the Krystyna adit and was 741 $\mu S \cdot cm^{-1}$. However, this was significantly higher than the waters of the natural carbon springs (Fig. 10). The value of the coefficient of variation of the waters of the adits did not exceed 10%. Such values have also been reported in natural springs [24]. This coefficient was estimated at 21% only in the case of the Mniszek spring. Such a high variability is the result of human impact. The area around the spring supply is also strongly urbanized. A higher variation of electrical conductivity also is found in other urban-industrialized areas [23].

Among the physical properties, the high thermal stability of adit 318 is worth mentioning (Fig. 11). This high stability is determined by the specific atmosphere of the underground excavations. Both within natural caves and the post-coal mine excavations, changes in air temperature, especially in the deepest parts, are relatively low [25, 26]. Thus, waters flowing from underground pits are characterized by a low variation in temperature. Nevertheless, the highest variability in temperature was noted in the "Krystyna" adit, which contradicts this statement. Such high variations in temperature are caused by the release of waters through the tubes of a drainage system that is situated at a great depth and that are under the influence of meteorological conditions. There were no significant differences in temperature between the waters of the adits and the springs. The only exception was the Mniszek, for which the mean temperature of the waters was higher than in the remaining inflows (Fig. 11).

The positive and significant values of the correlation coefficients were calculated for all of the variables that were studied (Table 1). This indicates that the high concentration of ions in the Maria spring corresponds with the high concentration in the adit. Therefore, changes in the concentration of ions in the focal objects are synchronized. The same situation is observed in the physical properties such as temperature and electrical conductivity, which was revealed by a high correlation rs > 0.7. The high synchronicity of temperature changes proves a similar response to changes of weather of these anthropogenic objects as the natural ones. There was a medium negative correlation (rs = -0.58) only for pH. A lower pH of the waters in Maria spring was noted than in the adit. An explanation of this phenomenon could be as follows: a low water reaction is associated with the intense inflow of thaw and precipitation waters. These are acid waters, especially thaw waters, from which the load of the acid substances that are collected during the winter is released. The increase of the inflow of waters into the adit partially sinks the excavations and limits the reaction of the decay of pyrites, which are the source of acid substances. When acid drainage occurs, the amount of buffering substances is enough for the neutralization of acid infiltration waters and this results in an increase in the pH of the waters in the adits.

Conclusions

The obtained data indicate that:

- acid drainage phenomenon occur in old coal mine excavations
- the waters of the adits are characterized by a different hydrochemical type determined by the distinct geological structure of the adit
- the waters of adit 318 and the springs that were studied represent the same hydrochemical type SO_4-Ca
- the concentrations of sulphates and iron in the waters of adit 318 are higher than in the waters of the Carbon spring, which should be attributed to oxygen inflow and the phenomenon of acid drainage
- adit 318 is typified by the lowest changes in temperature; this inflow can be treated as thermally stable
- changes in ions Cl^- and SO_4^{2-} as well as temperature and electrical conductivity in the waters of adit 318 and Maria Spring show high synchronicity.

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