Origin of sulphates in waters from Morcinek Coal Mine, Poland

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Abstract: Brines from the Debowiec formation in the Morcinek Coal Mine contain sulphates. Their concentration varies from 60 to 800 mg/dm^3. Sulphates are important because they may remove barium from the other mine waters in the Morcinek Coal Mine. Two different values of the isotopic composition of sulphates were noticed. The values $\delta^{34}S$ from +12.09‰ to +14.27‰ and $\delta^{18}O$ from +12,06‰ to +13,7‰ suggested the dissolution of marine sulphates from the Permian to the Cretaceous ages. Value $\delta^{34}S$=-4.67‰ shows that sulphate originate from hydrogen sulphide which is the product of the reduction of sulphates. The results seem to indicate that is only one source of sulphates. The sulphur from hydrogen sulphide comes to the water by the reaction of the oxidation with calcite.

1 INTRODUCTION

Mine waters in the twelve* coal mines of the southern part in the Upper Silesian Coal Basin (USCB) are saline and practically sulphate-free (Pluta, 1999). In these waters high concentration of the barium and radium isotopes was found (Pluta, Pałys, 1999; Lebecka, Tomza, Pluta, 1986). Mine waters flowing into the Morcinek Coal Mine contain these toxic elements. Barium and radium discharged in waters caused problems with sediments in pipes and pump in coal mine and environmental pollution. Purification of mine waters from barium and radium is therefore necessary. The release of barium and radium can be reduced by treating the waters with addition of sulphates. Gypsum and anhydrite are used in coal mine workings of the Morcinek Coal Mine as components of an isolating mixture for fire containment. Anhydrite was also used for the protection of workings against overpressure of the Carboniferous rocks. Sulphates from these minerals are dissolved in mine waters. Sulphates precipitate barium and radium (Pluta, Ślaski, 1993).

Since 1988 the sulphates in mine water on the level 950 m were found. Concentration of sulphates in this mine water from the Debowiec formation was about 800 mg/dm^3. Analyses the other waters from the Debowiec formation, during last ten years, show that few of them contain sulphates. These ions are important because they may remove barium from the other mine waters.

This paper explains the source of sulphates in the Morcinek mine waters.

* name and number of the coal mine before 1990

2 GEOLOGY AND HYDROGEOLOGY

The Morcinek Coal Mine is situated in the southwestern part of the USCB (Figure 1). The aquifers in the Carboniferous rocks are in sandstone, claystone and interbedded with mudstone and sandstone complexes. The Carboniferous formations are covered by Tertiary formations and Quaternary fluvio-glacial

Figure 1 The coal mine areas in the Upper Silesian Coal Basin (Poland)
(• coal mine which natural mine waters contain the barium)

sediments from few to several tens of meters thick. The Tertiary in the region of the Morcinek Coal Mine is the Miocene sediments: clays and mudstones with thickness from 500 m to 1000 m. This rocks are impermeable. At the floor of the Miocene, permeable Debowiec formation very often occur. It is about 150 m thick. The filtration coefficients in sandstones of the Debowiec formation are between $1x10^{-7}$ to $3x10^{-6}$ m/s.

3 SAMPLING AND ANALYTICAL PROCEDURES

The samples of water were collected from mine workings of the Morcinek Coal Mine in the roof of Carboniferous rocks, close to the Debowiec formation (Figure 2). Waters were flowing from two longwalls: A-4 and C-1 and the inclined drift. The concentrations of Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, SO_4^{2-}, HCO_3^-, Br^- and I^- were determined by common gravimetric and titrimetric methods while concentrations of Na^+, K^+, Ba^{2+}, Fe_{total} and B by emission spectrometry (ICP-AES). The isotopic composition of waters and sulphates were measured by mass spectrometry method at the Department of Environmental Physics Academy of Mining and Metallurgy (Kraków) and at the Mass Spectrometry Laboratory UMCS (Lublin). The isotope data $\delta^{34}S$ are expressed versus CDT, while δD and $\delta^{18}O$ versus SMOW.

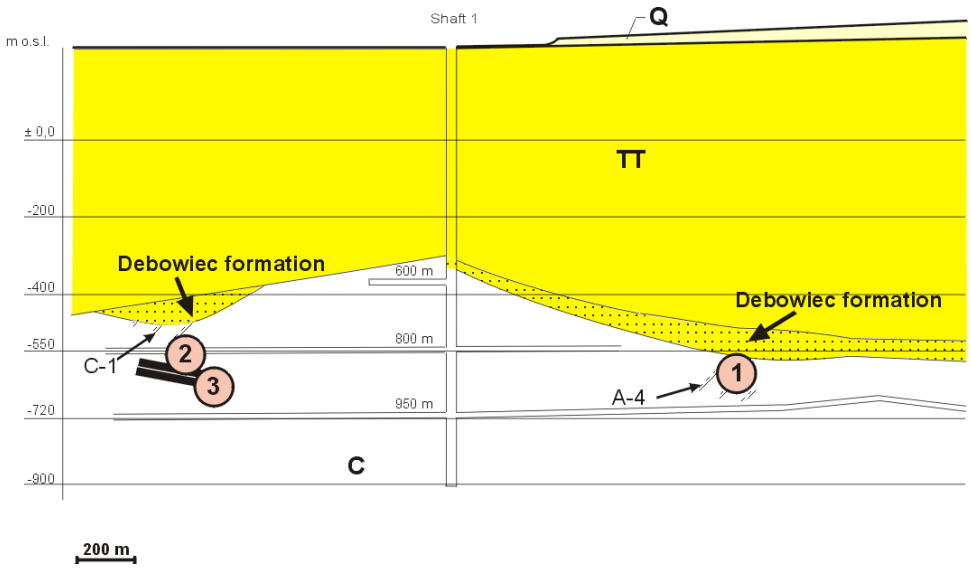

Figure 2 Sampling sites on simplified geological section (N-S) of the Morcinek Coal Mine
Q- Quaternary, TT- Tertiary, C- Carboniferous formation

4 RESULTS AND DISCUSSION

The Debowiec formation is isolated from surface by Miocene sediments about 500 m thick. In such conditions the waters from this formation are brines. Studies of chemical and isotope data of brines were performed from 1989 (Pluta, Zuber, Grabczak, Ślaski, Bebek, 1993). All results show that isotopic and chemical composition of waters from the Debowiec formation in the Morcinek Coal Mine differ from typical waters in the Carboniferous formations. These are brines with the concentration of Cl^- ranging from 18 to 21 g/dm^3. They are rich in NH_4^+ (up

to 35 mg/dm^3) and B (up to 9 mg/dm^3). The isotopic analyses of brines show that $\delta^{18}O$ varies from –3.4‰ to –4.4‰ while δD from –31‰ to –36‰. Concentration of Ca^{2+} is from 800 to 1250 mg/dm^3, while Mg^{2+} from 350 to 550 mg/dm^3.

Changes in concentrations of Ba^{2+} and sulphates in brines from Debowiec formation were found. Some of brines have concentration of Ba^{2+} up to 90 mg/dm^3. These brines are practically sulphate-free. The other brines contain sulphates. Concentration of these ions riches up to 800 mg/dm^3. The Ba^{2+} content did not exceed 10 mg/dm^3.

In order to explain the content of sulphates in waters from three sample of waters taken from the longwalls: A-4, C-1 (1 and 2) and the inclined drift in section C (3) were analysed. The results of chemical composition of these waters are given in Table 1. They show that chemical composition of waters from the longwalls: A-1 and C-1 differs from the inclined drift. Chemical data in brines from longwalls are typical for waters from the Debowiec formation, while in water from the inclined drift have higher concentration of Ca^{2+} (1895 mg/dm^3) and HCO_3^- (370 mg/dm^3). The increase of Ca^{2+} and HCO_3^- concentrations informs that that reaction with calcium carbonate took place. In the order to validate this suggestion calculation of ion ratios (Razowska 1999) and chemical equilibrium were performed using WATEQ4F. The values of ion ratios: $Ca^{2+}/(Ca^{2+}+SO_4^{2-})$, $Mg^{2+}/(Ca^{2+}+Mg^{2+})$ and calculations indicate that the dissolution of calcite in waters took place.

Table 1 Chemical composition of the waters in the Morcinek Coal Mine (in mg/dm^3)

Chemical component	Water from the longwall A-4	Water from longwall C-1	Water from the inclined drift in section C
pH	6.6	6.3	6.7
δD [‰]	- 32	- 34	- 32
$\delta^{18}O$ [‰]	- 3.7	- 3.4	- 3.1
Na^+	10390	10000	11495
K^+	116	112	205
Ca^{2+}	935	955	1895
Mg^{2+}	425	365	470
NH_4^+	27.5	32.0	0.9
Fe_{total}	1.4	4.5	1.2
Ba^{2+}	1.8	1.3	0.8
B	7.7	8.6	5.0
Cl^-	17900	17250	20010
SO_4^{2-}	320	160	330
HCO_3^-	180	115	370
J^-	14.2	15.5	7.6
Br^-	65.8	62..3	76..5

The results of the isotopic composition: $\delta^{34}S$ and $\delta^{18}O$ of sulphates in waters from the longwalls and inclined drift are presented in Table 2. The isotope data of sulphur and oxygen have two different values.
Sulphate with $\delta^{34}S$=+12.09‰ and +14.27‰ and $\delta^{18}O$=+12.06‰ and +13.7‰ were in waters from the longwalls A-1 and C-1 may be identified as the dissolved marine sulphates from the Permian to the Cretaceous ages (Claypool, Holser, Kaplan, Sakai, Zak, 1980).

The $\delta^{34}S$= -4.67‰ in sulphates of the brine from the inclined drift suggests that the sulphur isotopes originate from sulphide (for example Krouse, Gould, McCreardy, Rajan, 1991). The oxidized material may come from sulphide minerals in Carboniferous rocks or hydrogen sulphide. In the brine from the Debowiec formation probably the reactions of sulphates reduction and of hydrogen sulphide oxidation are as follows:

$$SO_4^{2-} + 2C + 2H_2O = H_2S + 2HCO_3^-,$$

$$H_2S + 2CaCO_3 + 2O_2(\text{or } CO_2) = 2Ca^{2+} + SO_4^{2-} + 2HCO_3^-.$$

The difference in $\delta^{34}S$ between sulphates from the Debowiec formation is about 20‰ (Table 2). This is in accord with the value designated by Thode (1991) for the reaction of the reduction of sulphates (20-25‰). The sulphur from hydrogen sulphide comes to the water by the reaction of the oxidation with calcite.

Table 2 $\delta^{34}S$ and $\delta^{18}O$ in sulphates from the waters in the Morcinek Coal Mine

Isotope data	Water from the longwall A-4	Water from the longwall C-1	Water from the inclined drift in section C
$\delta^{34}S_{CDT}$ [‰]	+ 14.27	+ 12.09	- 4.67
$\delta^{18}O_{SMOW}$[‰]	+ 12.06	+ 13.7	+ 1.41

Chemical and isotope data lead to the conclusion that probably is only one source of sulphates in waters of the Morcinek Coal Mine, which have $\delta^{34}S$ from +12.09‰ to +14.27‰. and $\delta^{18}O$ from+12,06‰ to +13,7‰.

5 CONCLUSION

Brines from the Debowiec formation in the Morcinek Coal Mine contain sulphates. Sulphates are important because they may remove barium from the other waters. The chemical and isotope data seem to indicate that is only one source of sulphates.

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Pochodzenie siarczanów w kopalni węgla kamiennego Morcinek, Polska

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Streszczenie: Solanki utworów warstw dębowieckich drenowane wyrobiskami górniczymi w kopalni węgla kamiennego Morcinek zawierają siarczany. Ich koncentracje wahają się od 60 do 800 mg/dm³. Skład izotopowy i chemiczny tych wód różni się od wód występujących w utworach karbonu. Stwierdzono dwie różne wartości składu izotopowego siarczanów. Wartości $\delta^{34}S$ = +12,09‰ do +14,27‰ sugerowały rozpuszczanie morskich siarczanów wieku od Permu do Kredy. Wartości $\delta^{34}S$ – 4,67‰ wskazują na pochodzenie siarczanów z siarkowodoru, który jest produktem redukcji siarczanów. W celu sprawdzenia tych sugestii przeprowadzono kalkulacje równowagi chemicznej używając programu WATEQ4F. Wyniki wydają się wskazywać, że siarczany pojawiły się w solance w wyniku rozpuszczenia produktów reakcji minerałów siarczkowych (pirytu lub markasytu).