Barium discharged in waters from the closed Żory Coal Mine in the Upper Silesian Coal Basin, Poland

Irena Pluta

Central Mining Institute, Plac Gwarków 1, 40-166 Katowice, Poland;
e-mail: snxip@boruta.gig.katowice.pl

Abstract: Mine waters from the closed Żory Coal mine in the south-western part of the Upper Silesian Coal Basin contain toxic barium. The discharge of this element into the neighbouring Borynia Coal Mine causes contamination of pipelines and sediments. The studies of the mine waters discharged from the Żory Coal Mine during more than two years after its closure were performed. The changes of concentrations of barium and iron ions, sulphates, chlorides were analysed. Barium was removed from waters by precipitation of sulphates. Isotopic data of sulphates ($\delta^{34}S$ and $\delta^{18}O$) showed that these sulphates come from the oxidation of sulphides (pyrite, markasite or hydrogen sulphide). The process, which reduce the content of barium in the mine waters from the closed Żory Coal Mine, keeps the hazardous substances in the underground mine workings.

1 INTRODUCTION

Waters discharged from coal mines in the Upper Silesian Coal Basin (USCB) in Poland contaminate rivers and their sediments. Mine waters of the twelve* coal mines in the southern region contain elevated barium concentration (Pluta & Palys, 1999). High concentration of this element in waters causes environmental pollution and problems in transportation of waters in pipes and pumps. Specific situation is in the Olza Collector (Pluta, 1998). In this pipeline mine waters discharged from most coal mines of the southwestern part of USCB flowing into the Odra by the Olza river create deposits, which contain mainly barium sulphate (Figure 1) (Pluta, 1998; Pustelnik, Pluta, Andrejewicz, 1999). Purification of mine waters from barium is therefore necessary.

Some coal mines in the USCB must be closed. The first mine closed in the southwestern part of the USCB was the Żory Coal Mine. The mine waters of the Żory Coal Mine contain the barium. The discharge of this element into neighbouring Borynia Coal Mine causes contamination of pipelines and sediments. The release of barium can be reduced by treating sulphates.

The studies of the discharged mine waters from the Żory Coal Mine into the neighbouring Borynia Coal Mine was performed. The observations show that sometimes in mine waters the sulphates are generated. The paper explains this treatment process that reduce barium in mine waters.

*name and the number of coal mine before 1990

Figure 1 The deposit made in pipe of the Olza Collector

2 GEOLOGY AND HYDROGEOLOGY

The Żory Coal Mine area is located in the south-western part of the USCB (Figure 2). In geological structure there are Quaternary, Tertiary and Carboniferous formation. The Quaternary formation contains Pleistocene and Holocene rocks. The aquifers in Carboniferous rocks are sandstone, clays and interbeddings with mudstone and sandstone complexes. The Carboniferous formation occurs beneath by impervious Tertiary formation of Miocene sediments: clays and mudstones. There are 100 meters beneath on north and 300 meters on the south region of the Żory Coal Mine area. The Carboniferous water-bearing horizon is related to permeable sandstone of the Cracow Sandstone Serious. The filtration coefficients of sandston's are between $1.0x10^{-8}$ and $3.5x10^{-6}$ m/s.

3 SAMPLING AND ANALYTICAL PROCEDURES

The investigations were performed in mine workings of the Borynia Coal Mine, where discharged saline waters from the Żory Coal Mine were sampling. Samples of water were collected once a month at three points (Figure 3):

- Świerklański Drift on 588 m level (point 1),
- Świerklański Drift on 713 m level (point 2),
- Main Drive A on 713 m level (point 3).

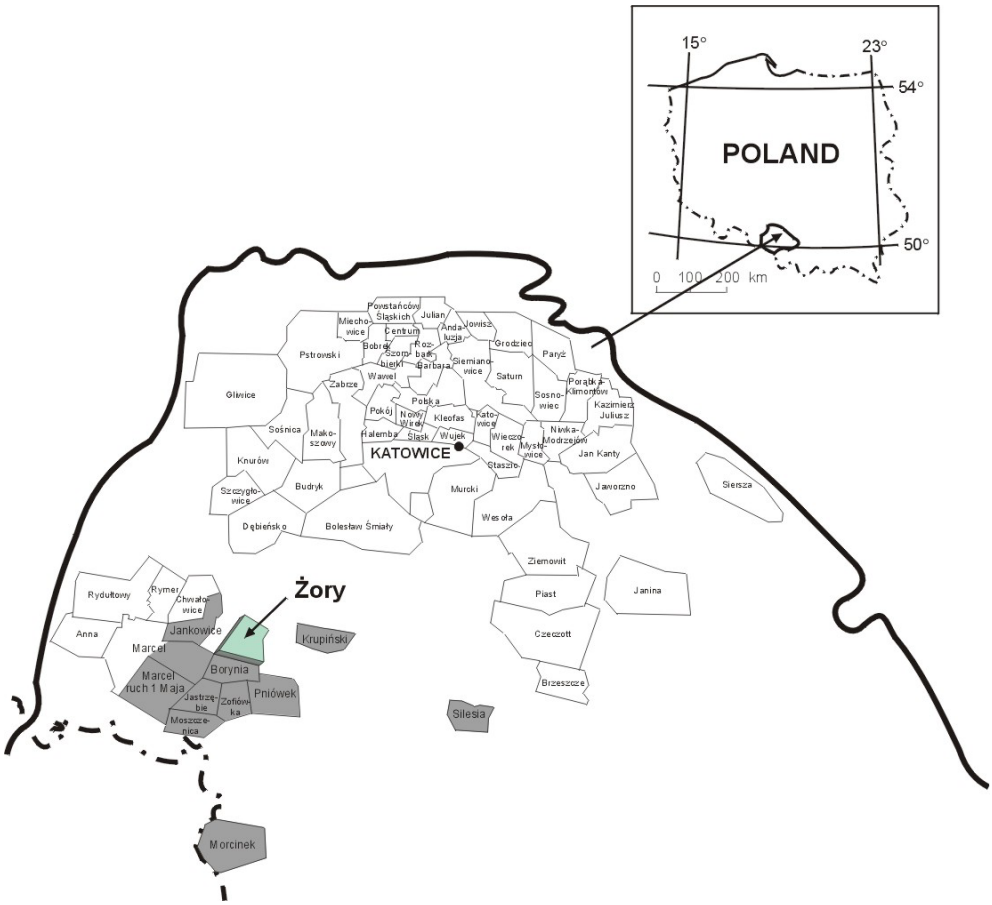

Figure 2 The coal mine areas in the Upper Silesian Coal Basin (Poland)
(• coal mine which natural mine waters contain the barium)

The concentrations of barium and iron ions were determined by emission spectrometry (ICP-AES). Chlorides were measured by the titration method and sulphates by the gravimetric method, according to Polish Analytical Norm. Isotopic composition of sulphates were determined by mass spectrometry at the Mass Spectrometry Laboratory, UMCS Lublin (Hałas, Wołącewicz, 1981). The measurements of $\delta^{34}S$ values were expressed versus CDT standard while $\delta^{18}O$ expressed versus SMOW.

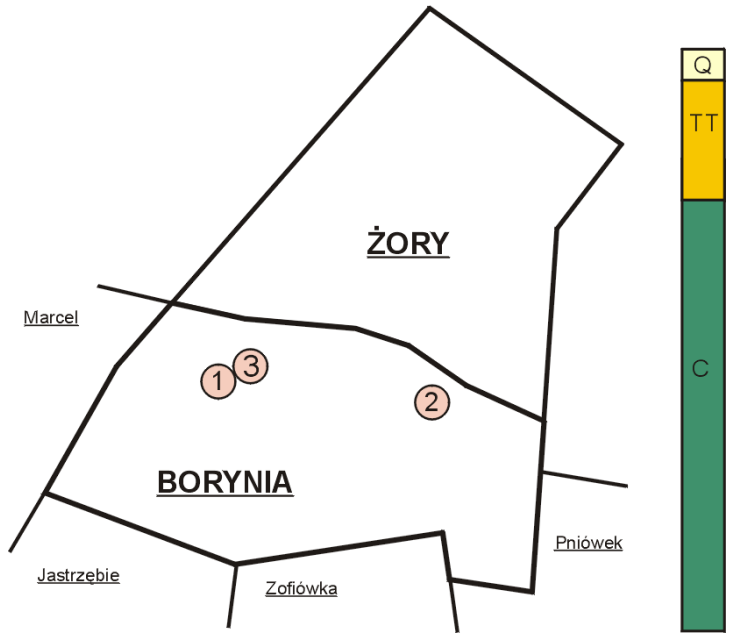

Figure 3 Sampling sites on the Żory and Borynia areas with simplified stratygrafy
Q-Quaternary, TT-Tertiary, C-Carboniferous formation

4 CHEMICAL COMPOSITION OF MINE WATERS OF THE ŻORY COAL MINE

The Żory Coal Mine, as was noted, is situated in the southwestern part of the USCB. The Carboniferous rocks are underlying the Tertiary clays and mudstones. In such conditions the Carboniferous formation is isolated from surface waters. The waters flowing into the mine workings are mostly brines. Concentration of chlorides can reach 70 g/dm^3. The increase of the concentration of chlorides with the depths is observed. These brines are practically sulphate-free. Concentration of barium is up to 1400 mg/dm^3 and iron ions (Fe^{3+}+Fe^{2+}) up to 20 mg/dm^3. Concentrations of sulphates, chlorides, barium and iron ions in five brines from the Żory Coal Mine are presented in Table 1.

Table 1 Concentrations of sulphates, chlorides, barium and iron ions in mine waters from the Żory Coal Mine

Sampling point	SO_4^{2-} [mg/dm^3]	Cl^- [mg/dm^3]	Ba^{2+} [mg/dm^3]	Fe^{3+}+Fe^{2+} [mg/dm^3]
Drift N level 400 m	< 10	24530	190	1.2
Drift W level 580 m	< 10	27300	250	1.5

5 CHEMICAL COMPOSITION OF DISCHARGED MINE WATERS FROM THE CLOSED ŻORY COAL MINE

Systematic investigations of chlorides, sulphates, barium and iron ions once a month from September 1997 to December 1999 were performed. The chemical composition of the discharged waters flowing into the Borynia Coal Mine primarily reflects the composition of mine waters in the closed Żory Coal Mine. These are brines with concentration of chlorides from about 27 to about 58 g/dm^3. Analyses show that concentration of barium is up to 430 mg/dm^3. Sulphates and iron ions show the opposite trend in discharged waters from the Żory Coal Mine after its closure. The concentration of sulphates reaches up to 320 mg/dm^3 while iron ions up to 100 mg/dm^3.

Changes in concentrations of barium, sulphates, iron ions particularly were observed in three brines (points 1-3) flowing into the neighbouring Borynia Coal Mine on the levels: 588 and 713 m. The results are shown in Figures 4-6.

The barium content did not exceed 10 mg/dm^3 in the brine flowing from the closed Żory Coal Mine into the Borynia Coal Mine on 588 m level (point 1) (Figure 4). In this brine, with concentration of chlorides from about 27 to about 32 g/dm^3, sulphates were observed. Concentration of sulphates varies from 175 to 320 mg/dm^3. The brine flowed into the Borynia Coal Mine until July 1998 when the dam was made.

Analyses of brine from Świerklański Drift on 713 m level (point 2) show that concentration of barium ion and sulphates varies in two periods (Figure 5). From

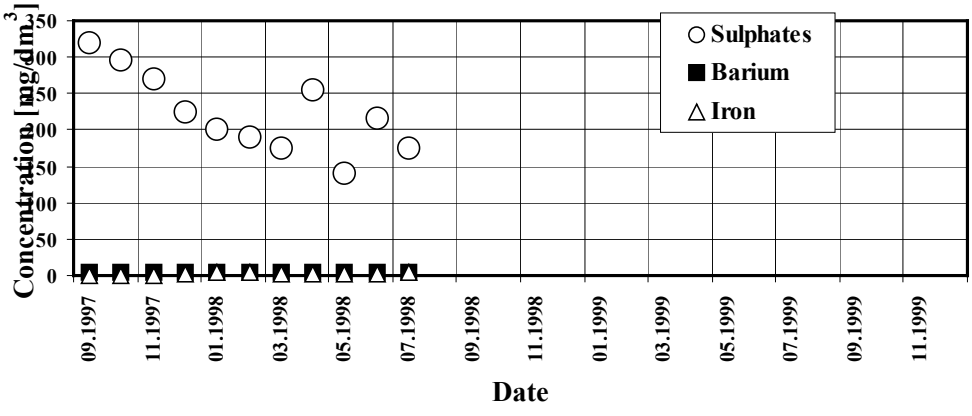

Figure 4 Concentration of sulphates, barium and iron ions in the water from Świerklański Drift on 588 m level

September 1977 to March 1999 the concentration of barium ion averaged ca. 400 mg/dm^3, while in the period from April to December 1999 was less than 10 mg/dm^3. The concentration of sulphates showed the opposite trend. This brine in the first period was practically sulphate-free, while in the second period contents of the sulphates ranged from 85 to 285 mg/dm^3. From April to

December 1999 the concentration of iron ions reached up to 100 mg/dm^3 and chlorides up to about 53 g/dm^3.

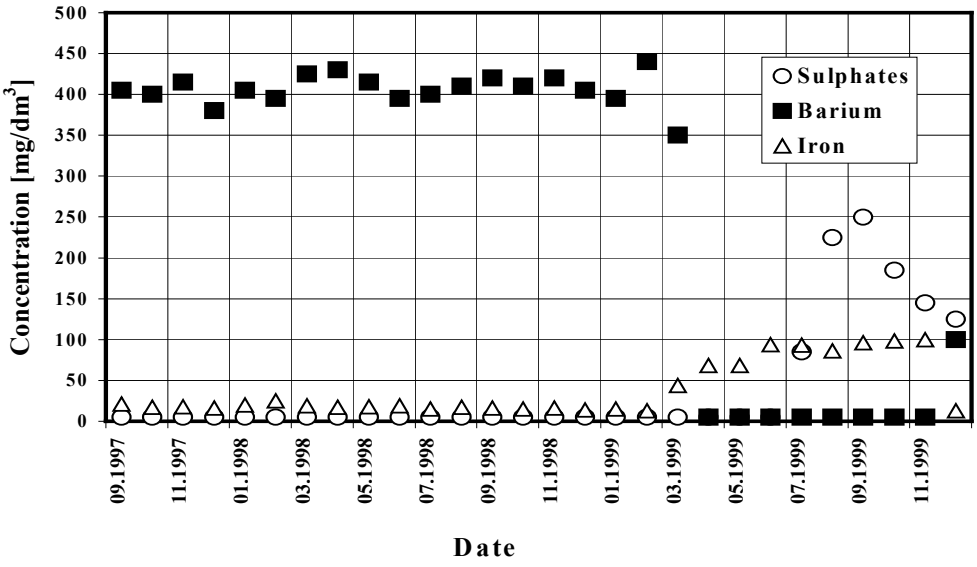

Figure 5 Concentration of sulphates, barium and iron ions in the water from Świerklański Drift on the 713 m level

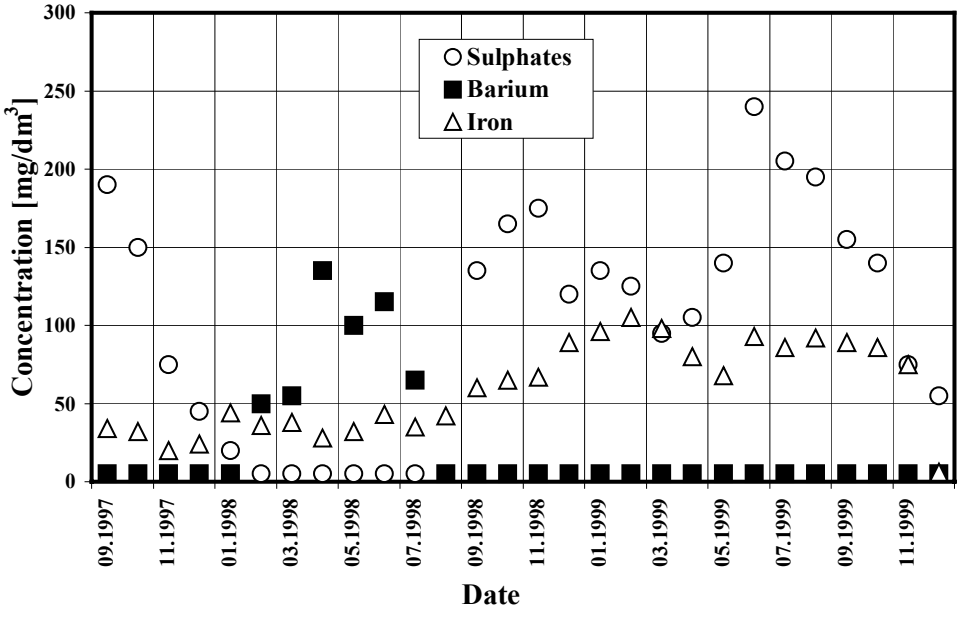

Figure 6 Concentration of sulphates, barium and iron ions in the water from Main Drive A on 713 m level

Differences in barium and iron, sulphates, chlorides ions concentration in brine from Main Drive A on 713 m level (point 3) of the Borynia Coal Mine were observed, too (Figure 6). Concentrations of sulphates and barium ion had three variations. Sulphates in brine from September 1997 to January 1998 and from August 1998 to December 1999 were observed. The brine in this period was practically barium-free. Concentration of barium varies from less than 10 to 135 mg/dm^3 but of sulphates from less than 10 to 240 mg/dm^3. The brine discharged from the Żory Coal Mine into Main Drive A on 713 m level was the richest in chlorides and iron ions. Concentration of chlorides was from about 45 to about 57 g/dm^3 while iron ions from about 25 to 100 mg/dm^3.

Changes in chemical composition of brines from Świerklański Drift and Main Drive A on 713 m level can be explained by filling the cavities and contacting the drainage roads in the Żory Coal Mine after its closure. Under these conditions sulphates were dissolved into waters and barium was precipitated from waters.

6 PRECIPITATION OF BARIUM FROM MINE WATERS OF THE ŻORY COAL MINE

Mine waters in the Żory Coal Mine are practically sulphate-free while the same waters discharged into the neighbouring Borynia Coal Mine sometimes contain sulphates. Sulphates precipitate barium from mine waters in the mine workings after the closure of the Żory Coal Mine. This process reduced the impact of toxic element into the Borynia Coal Mine and the Olza Collector.

Purification of barium in two periods was observed. The first period was after the closure. The second was from August 1998 to December 1999. In this period the increased concentration of sulphates and iron ions in brines discharged on 713 m level of the Borynia Coal Mine was noticed. This process can be explained by oxidation process of iron sulphides (pyrite or markasite). The source of sulphates could have been sulphides containing minerals from the Carboniferous rocks or sulphides from the wastes flowed into mine workings the Żory Coal Mine through T/112 borehole. The flotation tailings of coal from the Borynia Coal Mine injection into T/112 borehole from September 1998 to November 1999.

7 SOURCES OF SULPHATES IN MINE WATERS

In order to explain the mechanism of introducing of sulphate in the brines the Żory Coal Mine by the isotopic composition of $\delta^{34}S$ and $\delta^{18}O$ was determined. Sulphates were precipitated from discharged water samples. The results are presented in Table 2. Isotopic data of sulphur and oxygen in sulphates are typical for the sulphide oxidation processes (for example: Krouse, Gould, McCreardy, Rajan, 1991). The oxidized material may come from sulphide minerals: pyrite,

markasite or hydrogen sulphide. These sulphide minerals occur in Carboniferous rocks.

Sulphates flowing into 713 m level in 1999 had the $\delta^{34}S$=+5.21‰. The positive values: $\delta^{34}S$ from +4,85 to +6,40‰ in sulphates from the flotation tailings of coal in the southern part of USCB were noticed (Pluta, 2000).

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

Sampling point	Data	$\delta^{34}S$ [‰]	$\delta^{18}O$ [‰]
Świerklański Drift 588 m level	15.03.1998	- 5.24	+1.25
Świerklański Drift l 713 m level	10.08.1999	+ 5.21	+ 6.14
Main Drive A 713 m level	10.09.1997	- 5.84	+ 0.75

8 CONCLUCIONS

The mine waters in the closed Żory Coal Mine are brines, which contain the toxic barium. The release of this element into neighbouring Borynia Coal Mine causes contamination of pipelines and sediments. Studies of brines discharged from the Żory
Coal Mine after its closure, from September 1997 to December 1999, show that they contain sometimes the sulphates. In this case, the release of barium reduced by treating sulphates. Isotopic data of sulphates ($\delta^{34}S$ and $\delta^{18}O$) showed that they come from the oxidation process of sulphides (pyrite, markasite, hydrogen sulphide).

The removal of barium from mine waters the closure Żory Coal Mine keeps the hazardous substance in the mine workings. This process of reducing the impact of the toxic element into neighbouring Borynia Coal Mine should be monitored.

ACKNOWLEDGEMENTS

The author is grateful to Professor S. Hałas from UMCS in Lublin, for fruitful discussions about the origin of sulphates. Studies was financed from CSS in Project No. 2561/C.T12-9/99.

REFERENCES

Hałas S.& Wołącowicz W., 1981. Direct extraction of sulphur dioxide from sulphatesfor isotopic analysis. Anal. Chem., 53, 685-689

Krouse H.R., Gould W.D., McCreardy R.G.I.& Rajan S., 1991. A incorporation intosulphate during the bacterial oxidation of sulphide minerals and the potential for oxygen isotope exchange between O_2, H_2O and oxidized sulphur intermediates, Earth and Planetary Science Letters, 107, 90-94

Pluta I., 1998. Past and future of the Collector Olza from the chemical data of mine waters in the south-western part USCB (in Polish). *Przegląd Górniczy*, No 1, 29-32

Pluta I.& Pałys J., 1999: Barium from mine waters of the Upper Silesian Coal Basin (in Polish), *Przegląd Górniczy*, No 4, 16-22

Pluta I., 2000: Possibility of identification of mine waters in the southwester Upper Silesian Coal Basin by $\delta^{18}O$ and $\delta^{34}S$ in sulphates, In: *Proceeding V Isotope Workshop*. Kraków 2000

Pustelnik J., Pluta I.& Andrejewicz M., 1999. Condition of the Olza collecting pipe and evaluation of its further exploitation (in Polish). *Przegląd Górniczy*, No 1, 24-28.

Bar w wodach podziemnych z zamkniętej kopalni węgla kamiennego w Żorach w Górnośląskim Zagłębiu Węglowym, Polska

Irena Pluta

Streszczenie: Wody kopalniane z zamkniętej kopalni węgla kamiennego w Żorach w południowo-zachodniej części Górnośląskiego Zagłębia Węglowego zawierają toksyczny bar. Przenikanie tego pierwiastka do sąsiadującej kopalni węgla kamiennego Borynia powoduje zanieczyszczenie rurociągów i osadów. Prowadzono badania wód kopalnianych odprowadzanych z kopalni węgla kamiennego w Żorach przez okres dwóch lat po jej zamknięciu. Analizowano zmiany stężenia jonów żelaza i baru, siarczanów i chlorków. Bar został usunięty z wód przez wytrącanie się siarczanów. Dane izotopowe siarczanów ($\delta^{34}S$ i $\delta^{18}S$) wykazały, iż są one produktem utleniania siarczków metali i H_2S . Procesy wytrącania się baru z wód redukują jego zawartość w wodach kopalnianych dopływających z zamkniętej kopalni węgla kamiennego w Żorach. Strącone niebezpieczne substancje w postaci osadu pozostają w podziemnych wyrobiskach.