

ENVIRONMENTAL IMPACT OF THE AMD BUFFERING PROCESS ON THE GROUNDWATER QUALITY IN THE TRZEBIONKA ZINC-LEAD MINE VICINITY (SOUTH POLAND)

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Abstract

The Chrzanow ore district is one of the most important areas of Zn-Pb ore mining in Poland. Long-lasting drainage of the Triassic carbonate aquifer has caused changes in hydrodynamic and also hydrogeochemical conditions of the study area. Collected hydrochemical data indicate that in the Triassic carbonate aquifer, within the mining area of the Trzebionka Zn-Pb mine, high-sulphate groundwater is present. Important geochemical processes that can affect sulphate and some trace elements concentrations in this system include oxidation of the sulphides (mainly pyrite and marcasite), sulphuric acid buffering and dissolution of the calcium, magnesium and iron sulphate minerals.

Introduction

The Chrzanow district, located between Cracow and Katowice, is a part of the Cracow-Silesian Triassic formation, the only area of Zn-Pb ore mining in Poland (Fig. 1).

The Chrzanow district has a long history of metal ores mining. The first mentions about exploitation of silver and lead in this area dates back to the 14th century. Mining activity in the Chrzanow region started considerably earlier, since the Iron Age at Halstatt culture in 6th century BC (Szuwarzyński, 2003).

During the 20th century exploitation of the Zn-Pb ores was carried out in three mines: Galmany, Matylida and Trzebionka. In seventies the exploitation of the ores in Galmany and Matylida mines stopped and their underground workings were flooded. These mines at the present time are used as drinking water intakes. The Trzebionka mine started with production in 1962 and after 46 years of the continuous operation is planning for closure at the end of 2008.



Figure 1. Location of the Zn-Pb ores within Cracow – Silesian region. Legend: 1 – border of the Upper Silesian Coal Basin, 2 – range of the Triassic rocks occurrence, 3 - areas of the Carboniferous coal exploitation, 4 – Zn-Pb ores, 5 – closed Zn-Pb mines, 6 – operating Zn-Pb mines.

Hydrogeology

Zinc and lead mining in the Chrzanów area is based on the ore deposit of the Mississippi Valley type located within the Chrzanów Trough. These are stratabound tabular orebodies with very complex internal structure hosted by the Triassic dolomites (Szuwarzyński, 1993, 1996).

The Zn-Pb ore-bearing formation in the Chrzanow district is a very productive aquifer, called Chrzanow Main Groundwater Basin (MGWB No. 452). Groundwater is present within karst-fissured-porous dolomite, limestone and marls of Triassic age.

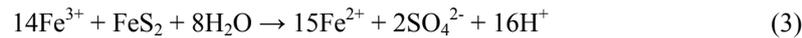
Total thickness of Triassic formation is about 20-150 m, permeability of the carbonate rocks varies from 1.4×10^{-6} m/s to 3.3×10^{-4} m/s, with average value of 5.2×10^{-5} m/s (Rózkowski and Wilk, 1980). High transmissivity of the Triassic formation is a reason why inflow to the Trzebionka mine dewatering system is relatively high and reached about 40 m³/min. (57600 m³/day).

The carbonate rock aquifer is generally confined. The essential recharge of Triassic aquifer occurs mainly by infiltration of precipitation from the outcrops, located along margins of the structural Triassic basin (Chrzanów Trough) (Kowalczyk et al., 2000).

Groundwater chemistry within the Triassic aquifer in natural conditions is controlled by mineralogy of the aquifer material. The dissolution of calcite and dolomite is responsible for the presence of the Ca-Mg-HCO₃ water. Dissolved solids concentrations in the water from carbonate rocks range from 200 mg/L to about 600 mg/L. Sulphates concentrations in non-polluted groundwater were very low, and range from 30 mg/L to about 90 mg/L. Chlorides concentration in this water samples range from 5 mg/L to about 30 mg/L. Composition of the natural and non-polluted groundwater was obtained from literature, generally reports and publications and also analysis of the water samples located on the periphery of the Trzebionka mine cone of depression (springs, wells and underground inflows). Groundwater from Triassic aquifer, because of good quality, is used as a main drinking water source in Chrzanów region (Czop et al., 2003, 2005).

Consequences of the AMD generation and buffering

Dewatering of the Trzebionka mine has been connected with formation of extensive depression cone. In the central part of the mining area groundwater level depression reached maximum values (over 250 m). Availability of the oxygen within this “modern” aeration zone was a main factor for oxidation of the sulphide minerals, mainly iron sulphides such as pyrite and marcasite. This process has led to the formation of acid mine drainage (AMD). The coupling reactions of the iron sulphide oxidation probably are the best known and most cited in the scientific literature (Singer and Stumm, 1970):



The most environmentally important secondary phases associated with marcasite and pyrite oxidation are ferrous

□

or/and ferric hydroxysulphate minerals, such as melanterite (heptahydrated ferrous sulphate – FeSO₄ · 7H₂O), copiapite, coquimbite and jarosite.

Occurrence of the ore bodies within carbonate rocks (limestone and dolomite) is a reason why generated acidity can be buffered (Fernandez–Rubio et al., 1986; Smith et al., 1993). Groundwater in the vicinity of the dewatered Trzebionka mine has a near neutral or slightly alkaline pH, typically ranging from 6.5 to 8.9.



Sulphuric acid buffering by carbonate rock dissolution is a source of secondary phases, including gypsum and

□

hexahydrate (magnesium hydroxysulphate - $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), which often form by water evaporation. Melanterite and hexahydrate are readily soluble in water in large quantities, 295 and 357 g/L respectively (Lide, 2001). The leaching tests for Triassic rocks from Trzebionka mine underground workings indicate that secondary sulphate minerals are present in relatively high quantities from a few to about 50 g/kg. Dissolution of these phases and possibly also other sulphate salts was a main source of sulphate, magnesium, iron and also some microelements in groundwater inflowing to the underground workings of the Trzebionka mine (Motyka et al., 1999; Czop et al., 2007).

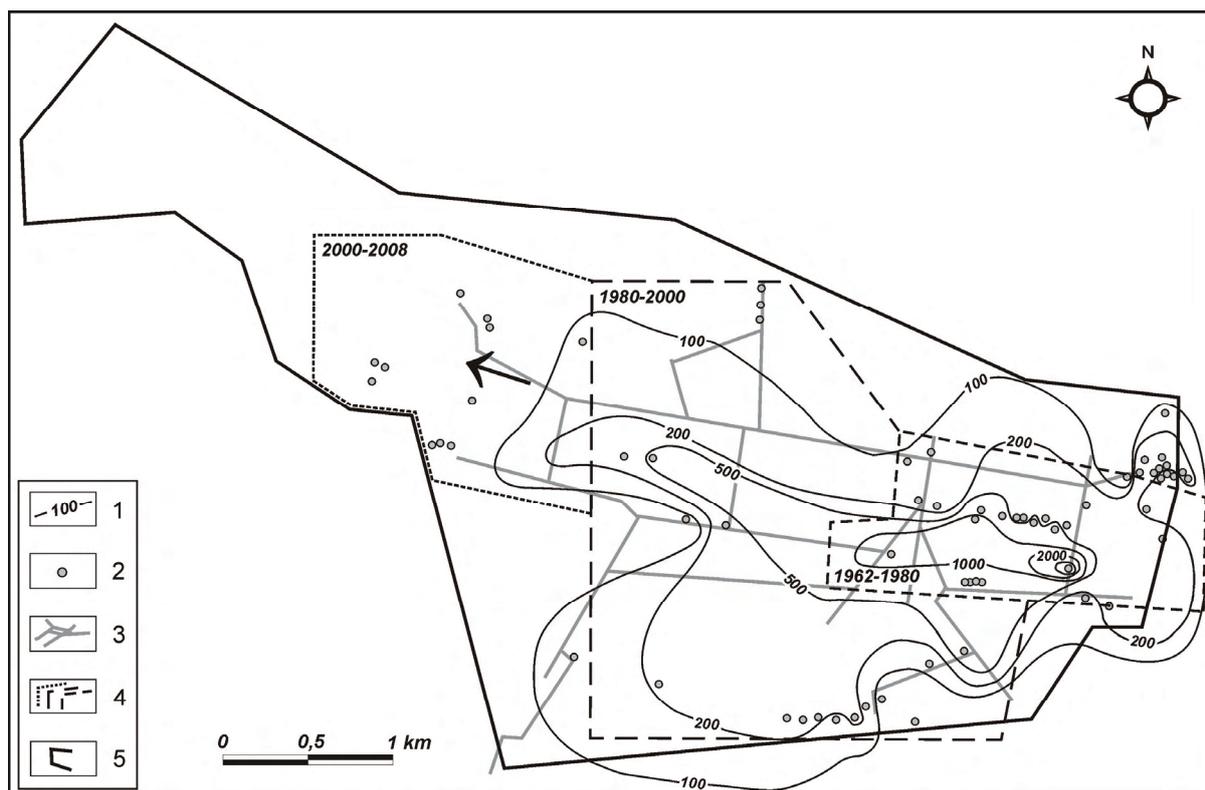


Figure 2. Spatial distribution of sulphate in groundwater samples from inflows to the Trzebieńka mine workings (Czop et al., 2001). Legend: 1-sulphate concentration contours (in mg/L), 2-groundwater sampling points (inflows), 3-main workings, 4-areas of the mining activity in specified years, 5-mining area of the Trzebieńka mine.

Sulphate concentrations in the outer zone of the Trzebieńka mine mining area are relatively low, only about 100 mg/L; this value is close to natural background for Triassic groundwater in Chrzanów region. The lowest concentrations of the SO_4 ion are also observing in the zone of the latest mining activity within the period of 2000 – 2008 (Fig. 2).

Inner zone of the mining area, with exploitation from sixties to eighties (20th century), is characterised by high sulphate groundwater with SO_4 concentrations ranging from 200 mg/L to about 3500 mg/L (Fig. 2).

The general evolutionary sequence of the groundwater chemistry in the vicinity of the Trzebieńka mine is given by the increase of SO_4 associated with the decrease of HCO_3 . Natural groundwater from the Triassic aquifer of the Ca-Mg- HCO_3 type after flushing of the weathering zone, rich in secondary sulphate minerals, evolves towards the following sequence of multi-ion hydrochemical facies: Ca-Mg- HCO_3 - SO_4 , Mg-Ca- SO_4 - HCO_3 and finally Mg-Ca- SO_4 . Evolution sequence of the groundwater type is presented in the Piper diagram (Fig. 3).

Evolution of the groundwater chemical facies from Ca-Mg- HCO_3 to Mg-Ca- SO_4 is strictly correlated with increasing distance along groundwater flow path within the Trzebieńka mine cone of depression. Groundwater from the central part of the mine simply has a longer contact time with secondary sulphate minerals.

The inflows with elevated concentrations of sulphate (in comparison with background groundwater) contain also elevated quantities of iron and manganese (Table 1). Concentrations of these metals in high sulphate groundwater commonly exceed the Polish drinking water standards. Inflows of the polluted groundwater to the underground workings are also connected with precipitation of calcite and iron and manganese oxides as well.

Neutral pH of groundwater within the Triassic aquifer has influence on the relatively low concentration of trace elements such as nickel, selenium and thallium. Concentrations of these constituents in groundwater samples are independent on the sulphate amounts. So it is possible that background groundwater can contain quantities of trace elements which exceeds Polish standards for drinking water (Table 1).

Within the Trzebieńka mine underground workings were found a few zones with anomalous concentrations of the selected trace elements. Samples of the background groundwater, presented in Table 1, are located within one of them and typically contain high concentration of selenium. The possible source of the selenium for this groundwater is connected with occurrence of the Keuper evaporites in the Triassic aquifer overburden.

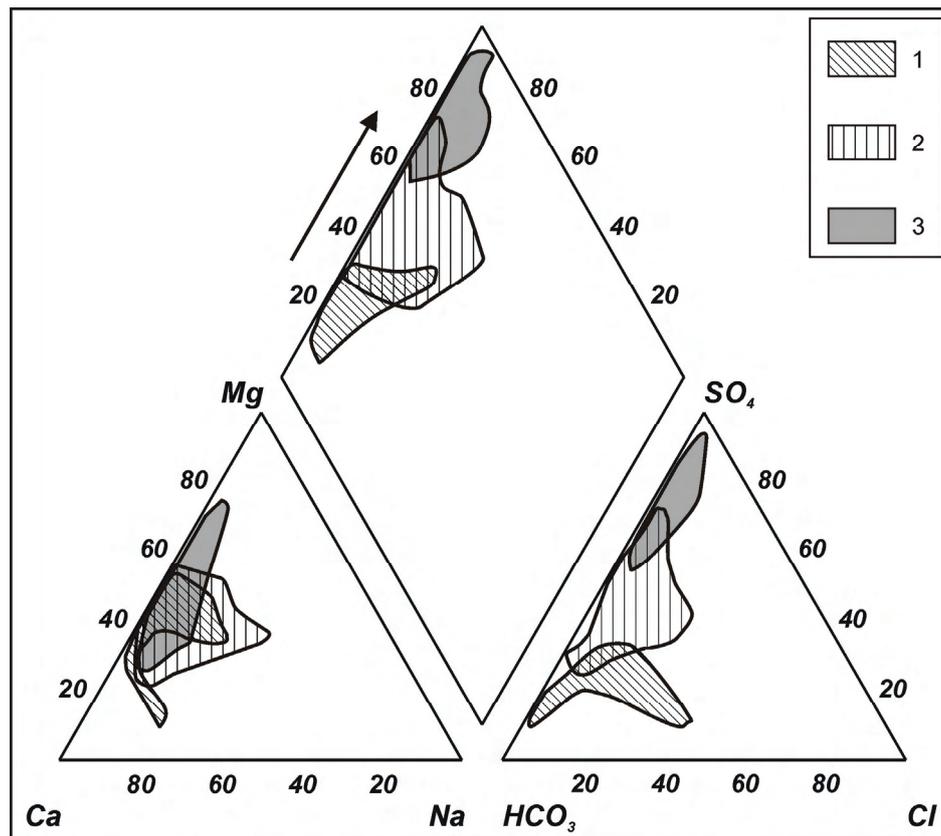


Figure 3. Piper diagrams for Triassic groundwater samples from inflows to Trzebionka mine workings. Legend: 1-“natural” background groundwater, 2-“mixed” groundwater, 3-high-sulphate groundwater.

Table 1. Concentrations of selected constituents in groundwater inflows to the Trzebionka mine.

Sample ID	Date	EC μS/cm	SO ₄	Fe	Mn	Ni	Se	Tl
			mg/L					
<u>Polish drinking water standards</u>								
-	-	2500	250.0	0.20	50.0	20.0	10.0	2.0*
<u>High sulphate groundwater >500 mg/L SO₄</u>								
TR57	2001-10-23	4120	3348.8	0.89	154.0	29.3	5.0	1.0
TR28	2001-10-23	2090	784.2	0.21	0.3	2.7	4.0	0.1
TR22	2001-10-23	1949	756.9	0.44	0.7	3.1	9.0	0.3
TR65	2001-10-23	1342	520.9	0.28	17.9	9.2	2.0	0.7
<u>Mixed groundwater 100 – 500 mg/L SO₄</u>								
TR25	2001-10-23	1158	369.2	0.31	58.4	6.0	3.0	0.3
TR63	2001-10-23	1198	360.8	0.33	59.1	6.8	1.0	0.2
TR68	2001-10-23	1044	283.7	0.21	15.8	5.4	1.0	0.3
TR67	2001-10-23	933	221.5	0.26	24.7	3.7	0.5	0.4
<u>Background groundwater < 100 mg/L SO₄</u>								
TR98	2002-10-15	516	55.0	0.63	64.2	6.1	27.0	0.2
TR93	2001-10-10	658	54.7	0.11	0.4	1.5	7.0	0.3
TR94	2001-10-10	725	43.6	0.07	0.05	0.4	1.0	0.2
TR95	2001-10-10	608	47.5	0.11	2.4	1.3	81.0	0.7
TR96	2001-10-10	537	31.1	0.13	0.2	0.6	12.0	0.1
TR97	2001-10-10	498	31.1	0.06	0.1	0.2	14.0	0.1

* adopted from US drinking water standards

Conclusion

Chrzanów ore district is subjected to serious risk of groundwater contamination. Long-lasting drainage of the Triassic aquifer has caused changes in redox condition of the Triassic massif containing the sulphide minerals. It was a reason for the activation of the coupling processes of the AMD generation and buffering of the produced acidity by carbonate rocks (limestone and dolomite). As a result significant quantities of secondary sulphate minerals (mainly hexahydrite and melanterite) are accumulated within dewatered Triassic ore-bearing rocks.

Flushing of the extended unsaturated zone, rich in weathering products, gives rise to high-sulphate groundwater. Additionally groundwater also contains elevated quantities of metals such as iron, manganese and others.

Presented examples of the groundwater quality deterioration in the vicinity of the Trzebionka mine are closely connected with flooding of mine workings, scheduled at the end of 2008. In consequence of this operation groundwater will come in contact with the products of sulphide minerals oxidation. The preliminary results of the hydrochemical studies suggest that, after complete flooding of the Trzebionka mine, groundwater contamination in the Triassic aquifer will last for decades or centuries.

Acknowledgements

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