

Origin of sulphates in the water inflows to Zn-Pb “Pomorzany” mine (Olkusz Zn-Pb ore district, S Poland)

Czop Mariusz and Motyka Jacek

Faculty of Mining and Geoengineering,
AGH-University of Science and Technology
al. Mickiewicza 30, 30-059 Cracow.
E-mail: mariucz@agh.edu.pl, motyka@agh.edu.pl

Keywords: mine water, sulphide minerals, sulphate, Pomorzany Zn-Pb mine, Zn-Pb Olkusz district

ABSTRACT

Zn - Pb ore - bearing formations, consist of Triassic carbonates, in the Olkusz ore district is also a very productive karst-porous-fissured aquifer. Mining activity in this region has been connected with intensive drainage of different age aquifers, mainly Triassic aquifer. Total amount of water pumped by “Pomorzany” mine is about 230 m³/min. (331 200 m³ per day). Long lasting intensive drainage of the Triassic aquifer has led to significant transformation of hydrodynamic conditions, resulted in changes of flow directions and formation of the extended artificial aeration zone. In the water inflows to the “Pomorzany” mine galleries concentration of the sulphate (SO₄) range from several tens mg/L to over 12 000 mg/L. Different sources of sulphates in mine waters (oxidation of the sulphides, inflows from neighbouring aquifers and seeping from pollution sources) are discussed in this paper.

INTRODUCTION

The Olkusz region is the historical area of the Zn-Pb ore mining in Poland. The first mentions about metallic ore exploitation in the vicinity of Olkusz dates back to 12th century.

Lead and zinc ore bearing minerals are hosted in the Middle and Lower Triassic dolomites, which also form a very productive groundwater aquifer. Karstification of the Triassic carbonates is a main reason that groundwater inflow to the Zn-Pb mines, located in the Olkusz region, are possibly one of the most in all over the world.

Groundwater dewatering in the Olkusz region started in 16th century with the ore exploitation in the zone located below the water table. Initially, horizontal adits were served as a dewatering system main elements. Some fragments of this historical working still exist at present.

Intensive groundwater drainage in the Olkusz Zn-Pb mining region was started in the end of 19th century, in connection with the application of the steam-driven pumps. After II World War “Bolesław” mine, abandoned and flooded in the thirties, was drained and two new mines were built “Olkusz” (in the beginning of sixties) and “Pomorzany” (in mid seventies).

Water environment changes in the Olkusz were formed during last few centuries. The main problem is connected with relatively high depression of the groundwater table within the Triassic aquifer. Hydrochemical processes connected with dewatering and oxidation of the ore-bearing sulphide minerals impact on the groundwater and also surface water chemical composition. It's a common knowledge that consequently and also often increase of the sulphate (SO₄) concentration in the mine water is observed. Other sulphate sources as contaminated precipitation or high-sulphate brine admixture also can cause significant increase in concentration of SO₄ ion. Analysis of the possible sources of sulphate in the groundwater inflowing to the Zn-Pb “Pomorzany” mine has been delineated in this paper.

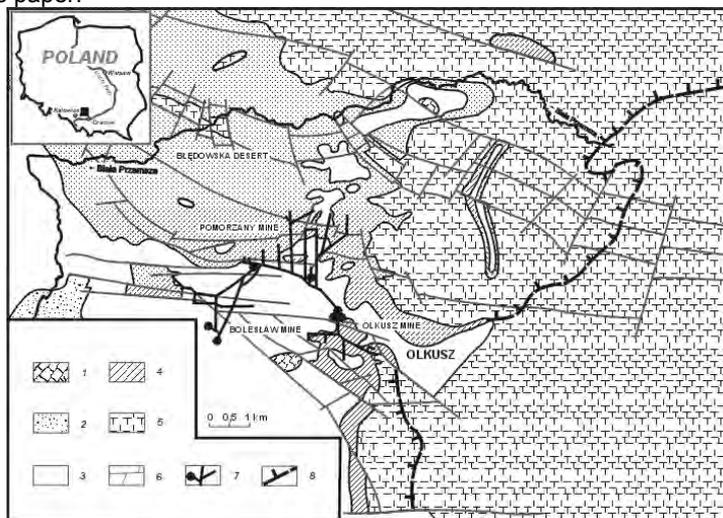


Figure 1. Geological map of the Olkusz Zn-Pb ore district

Legend: 1) D-C₁ carbonates, 2) P-conglomerates, 3) T_{1,2}- carbonates, 4) T₃-clay and claystones, 5) J₃-limestones, 6) Main faults, 7) Main mine galleries, 8) Range of T₃ under J₃.

HYDROGEOLOGICAL BACKGROUND

Four main groundwater aquifers are present in the Olkusz Zn-Pb region. There are: 1) Quaternary, 2) Jurassic, 3) Triassic and 4) Palaeozoic.

The Quaternary aquifer is of porous type, built up of fluvio-glacial sands with gravels, debris or rarely dust, clays or silt clays insertions. Average hydraulic conductivity of water bearing Quaternary rocks is $2,5 \times 10^{-4}$ m/s (Motyka & Wilk, 1976). Jurassic, Triassic and Palaeozoic aquifers are of karst-fissures type, built up of carbonate rocks: dolomites and limestones with thin marl layers. Average hydraulic conductivity of Jurassic water bearing rocks is $1,6 \times 10^{-5}$ m/s, and Triassic aquifer is $6,5 \times 10^{-5}$ m/s (Motyka & Wilk, 1976).

The Quaternary aquifer is recharged mainly by precipitation infiltration, while under mine drainage conditions also by water infiltrating from the Biała Przemsza river, major river in the Olkusz region. The Jurassic aquifer present in the eastern part of the Olkusz area (Fig. 1) is recharged by infiltration of precipitation and discharged by springs, brooks, wells as well as runoff to other aquifers by hydraulic connections. Jurassic aquifer is underlying by semi permeable Middle Jurassic marls and practically impermeable Upper Triassic (Keuper) claystones.

Triassic aquifer, hosted Zn-Pb ores, is recharged directly by infiltration of precipitation in the zone of outcrops, runoff from other aquifers in zones of hydraulic connections (Wilk & Motyka, 1977) and infiltration of water from the Biała Przemsza river. The main source of Triassic aquifer discharge are Zn-Pb mines: "Bolesław" (abandoned), "Olkusz" and "Pomorzany". Total inflow to this mines range around the value of 300 m³/min. (5 m³/s). "Pomorzany" mine is recharged by about 60% of this water amount. The secondary recharge source of this aquifer is water capture.

The Triassic aquifer is underlying by semi-permeable Permian molasses (conglomerates). Hydraulic conductivity of Permian conglomerates is in the order of 10^{-8} m/s but during the mining operations for release of the ore body in the main galleries were observed over 40 water inflows. Outputs of inflows range from a few drops per minute to 15-20 L/min. (Adamczyk A. *et al.*, 1978).

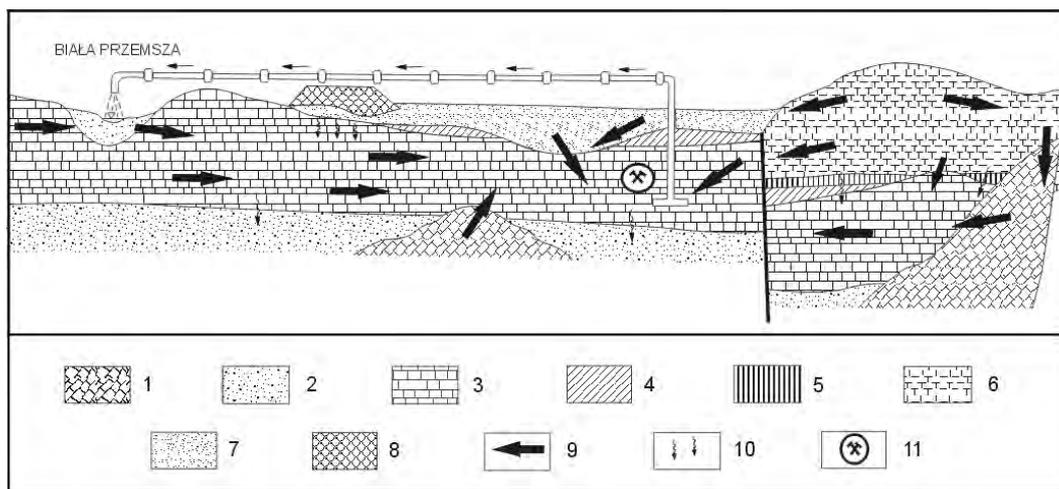


Figure 2. Schematic hydrogeological profile of the Olkusz Zn-Pb ore district

Legend: 1) D-C₁ carbonates, 2) P-conglomerates, 3) T_{1,2}- carbonates, 4) T₃-clay and claystones, 5) J₂-marls, 6) J₃-limestones, 7) Q-sands, 8) Wastes, 9) Direction of the groundwater flow, 10) Direction of water leakage, 11) Mine workings.

The Palaeozoic aquifer built up of limestones and dolomites is located in the eastern part of the Olkusz area under Permian conglomerates, Triassic and Jurassic carbonates (Fig. 2). The Palaeozoic aquifer is recharged by water infiltrating from Jurassic and Triassic aquifers in the zones of direct hydraulic connection with them (Wilk & Motyka, 1977).

SULPHATE CONCENTRATION IN THE WATER INFLOWS TO THE POMORZANY MINE'S GALLERIES

Sulphate concentrations in water inflows to the underground workings of the „Pomorzany” mine strongly depend on the geology of the crosscut rocks. Mining workings in the southern part of the “Pomorzany” mine are made within semi-permeable Permian conglomerates. Zn-Pb ore-bearing formation in Triassic carbonates is laid in the northern part of the mining area. Pomorzany fault with amplitude of about 70 m, separate geological formation depicted above, Permian rocks are in elevated fault-wall while Triassic rocks are in depressed fault-wall. Then on the north from “Pomorzany” fault zone mining workings are executed in dolomites and limestones of the Lower and Middle Triassic age (Fig. 3).

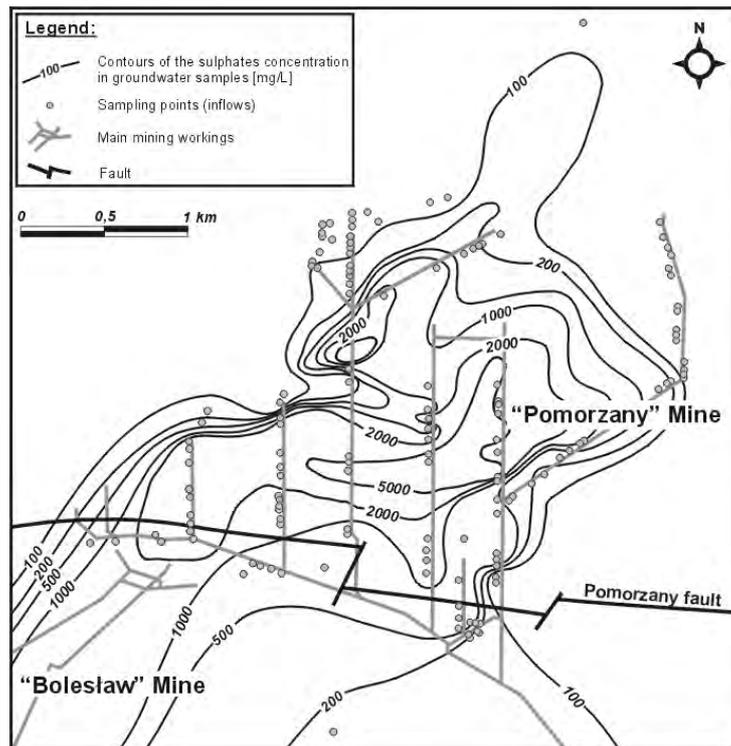


Figure 3. Spatial distribution of the sulphates in waters samples from inflows to the „Pomorzany“ Zn-Pb mine

Main underground workings within Permian conglomerates were executed between 1969 and 1975. Pomorzany fault was crossed in September 1975 and it was a beginning for the opening out of the Zn-Pb ore. Chemical composition of the water inflows from Permian rocks was a very diversified. Dissolved-solids concentrations range from 0,5 g/L to about 21,5 g/L and also increase with the working depth from the Permian rock's roof (Adamczyk A. *et al.*, 1978). It was also observed decrease of the TDS in water samples from inflows located in the fractured zones in the vicinity of the main fault dislocations. Sulphates concentrations in groundwater from Permian conglomerates also has a wide range of values from 39 mg/L, in the western part of mine to about 2750 mg/L, in the eastern part.

Inflows from Permian rocks in the eastern part of the "Pomorzany" mine were dried completely due to water discharge to the mine's dewatering system. In 2001-2002 it was found that in this zone were only 2 active inflows from Permian conglomerates. Sulphate concentrations in water samples from these inflows were very similar - 520 mg/L and 580 mg/L.

Western part of the "Pomorzany" mine's area with workings executed in Permian conglomerates is characterising by relatively high groundwater inflows. Total discharge of all inflows located in this part is in an order of several hundred litres per minute. Sulphate concentrations in water samples from these inflows range from 470 mg/L to 3370 mg/L, while in the beginning of the "Pomorzany" mine activity (1971-75) ranged from 40 mg/L to 320 mg/L.

Sulphate concentrations in first water inflows from Triassic carbonate rocks in the "Pomorzany" fault zone and also in the depressed fault-wall were measured within a period of 1971-73. These constituent values were relatively small and range from 25 mg/L to 60 mg/L. Only two water inflows located in the workings that were made in the middle of seventies (1976-78) has a higher sulphate concentrations 150 mg/L and 335 mg/L.

Water quality measurements carried out within a period of 1997-2002 indicated significant increase of the sulphate concentrations in all inflows from Triassic aquifer, with maximum about 3500 mg/L.

Collected data indicate that in the Triassic carbonate aquifer, within the mining area of the "Pomorzany" mine, three main hydrochemical zones with different sulphate concentrations are present. North-western (i) zone is characterised by relatively low sulphate concentrations that ranged from 61,5 mg/L to 128 mg/L. Similar range of sulphate concentrations from 31 mg/L to 94 mg/L was also observed in the north-eastern (ii) zone. Within the last, central zone (iii) sulphate concentrations were very diversified and ranged from 160 mg/L to 11260 mg/L. It's also observed that sulphate concentrations in water inflows are in inverse correlation with inflow's discharge.

DISCUSSION

According to Adamczyk *et al.*, 1978 and Grabczak *et al.*, 1991 highly mineralised groundwater within Permian conglomerates was formed as a consequence of dissolution of the dispersed evaporates by glacial meteoric waters.

Additionally, Permian groundwater geochemistry depends on the diffusion-convection salt transport from deeper Palaeozoic base and also on the fresh Triassic groundwater admixture in the fault zones and near Permian conglomerates roof (Adamczyk *et al.*, 1978, 1979).

Complicated genesis of the groundwater from Permian rocks is a reason for relatively high diversification of their chemical composition. It's quite depicted on the diagram of the molar indexes mMg/mCa vs. mCl/mSO₄ (Fig. 4).

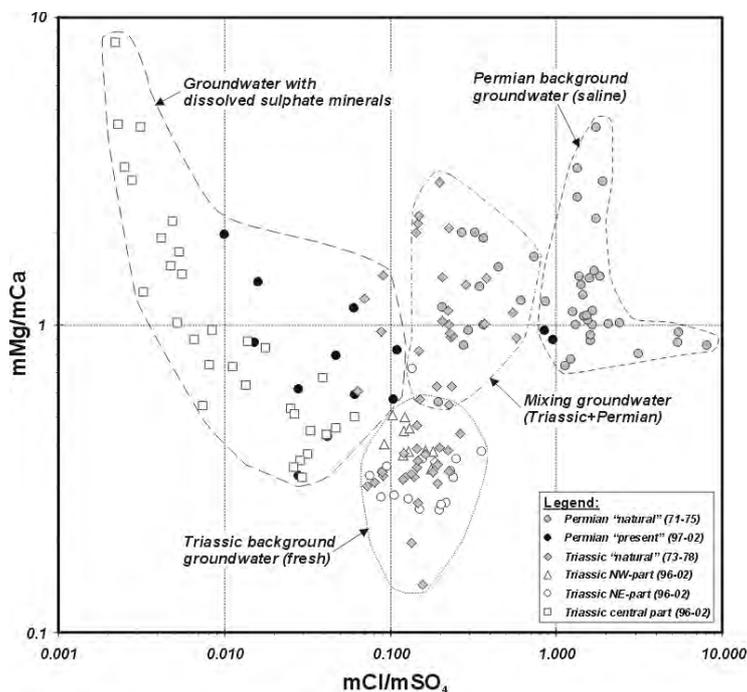


Figure 4. Diagram of the molar ratios mMg/mCa vs mCl/mSO₄ for water samples from inflows to the „Pomorzany“ Zn-Pb mine

First group consists of inflows from Triassic aquifer, which was analysed in seventies at the beginning of “Pomorzany” mine activity. Chemical composition of these water samples complies with background or “natural” groundwater quality. Second group of samples is connected with inflows located within Pomorzany fault zone. Main influence on the genesis of these waters has a mixing of the fresh groundwater from Triassic carbonates and mineralized groundwater from Permian conglomerates.

Long lasting intensive drainage of the “Pomorzany” mine has led to significant transformation of hydrodynamic conditions in the zone located to the north of Pomorzany fault, resulted in changes of flow directions. In the central part of the mining area groundwater level depression reached maximum, about 130 m. Currently major groundwater streams are flowing to the underground mine’s workings. Dewatering of the Triassic massive has led to formation of the modern, deeper and also widespread aeration zone in the central part of the “Pomorzany” mine cone of depression. Unbounded oxygen access to this zone causes perfect redox conditions for oxidation of sulphide minerals (mainly marcasite and sphalerite).

Changes in hydrogeological conditions of the study area were influencing on the chemical composition of the groundwater in Triassic aquifer. At first contaminated water from sources located within a distance of several km had an opportunity to inflow to the mine’s dewatering workings. Inflow of the lignosulfonates - liquid wastewater from paper factory in Klucze, located about a few km on the north, is a good example of this impact scenario (Motyka *et al.*, 1994).

Presently, groundwater contaminated by lignosulfonates are inflowing to the north-western part of the “Pomorzany” mines and have a slightly changed hydrochemistry in comparison to background values. Similarly from the south-western direction it was starting the inflow of contaminants from a few sources (sanitary landfill, industrial waste disposal sites) concentrated in this area (Adamczyk Z. *et al.*, 2000).

Second type of the groundwater geochemistry evolution was induced by natural processes occurred in an artificial aeration zone as a result of the changes in redox conditions of the dewatered rock massive (Singer & Stumm, 1970; Fernandez Rubio *et al.*, 1986).

Oxidation of sulphide minerals, mainly marcasite and pyrite, in carbonate rocks environment has led to formation of readily soluble secondary minerals. These are hydroxysulphate and sulphate evaporite minerals, such as well-known melanterit (heptahydrated ferrous sulfate-FeSO₄·7H₂O), epsomite (heptahydrated magnesium sulfate-MgSO₄·7H₂O), hexahydrate (magnesium hydroxysulphate-MgSO₄·6H₂O), gypsum, copiapite, coquimbite and jarosite. Dissolution of these sulphate salts was a main source of the sulphates, calcium, magnesium, iron and also some microelements in groundwater from inflows to the “Pomorzany” mine.

In “Pomorzany” mine high sulphate groundwater is forming as a result of flushing of the modern aeration zone contained sulphide weathering (oxidation) products. Water percolating within aeration zone and dissolving sulphate minerals originates from direct infiltration of the precipitation and also from upper aquifers by

hydrogeological windows in impermeable Upper Triassic (Keuper) rocks (Fig. 5A). According to these scenario high-sulphate waters are forming in the central part of the “Pomorzany mine” (Fig. 4).

Within the Pomorzany fault zone, where possibly water tables in Triassic and Permian aquifers are break-away, sulphates concentrations increase is observed both in inflows from Triassic carbonates and from Permian conglomerates (Fig. 4). It's as a result of the inflow of contaminated groundwater from south-east and also flushing of artificial, modern aeration zone (Fig. 5B).

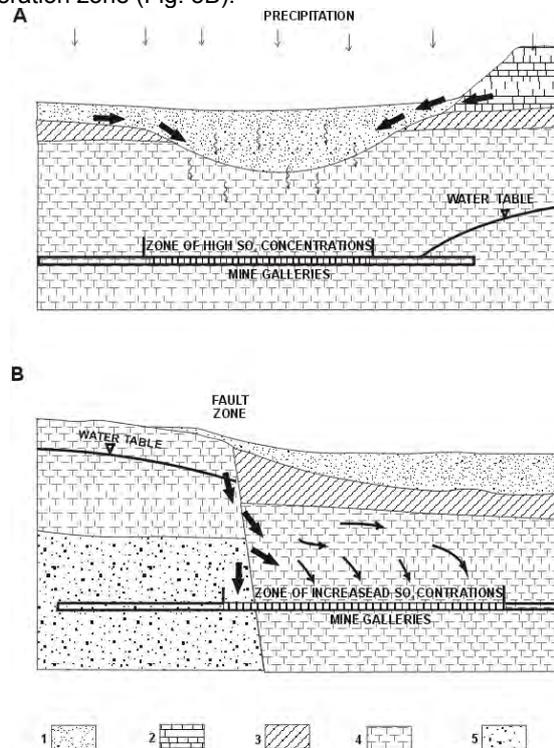


Figure 5. Formation of the high-sulphate groundwater in the vicinity of the Zn-Pb “Pomorzany” mine

Legend: 1) Q-sands, 2) J-limestones, 3) T₃-clay and claystones, 4) T_{1,2}- carbon, 5) P-conglomerates.

CONCLUSION

Sulphates in water inflows to the underground workings of the “Pomorzany” mine have been originating from different sources. At the beginning of the mine’s activity, in a middle of seventies while mining working were executed within Permian conglomerates, main sulphates source was a process of the evaporate minerals dissolution by glacial meteoric waters. Samples of highly mineralised waters have a molar concentration index mCl/mSO_4 that was distinctly higher than 1 (Fig. 4).

In a fault zones mixing of the modern meteoric waters from Triassic carbonates and waters from Permian conglomerates has been proceeding. Mixing process has an impact on the molar concentrations indexes mMg/mCa and mCl/mSO_4 . Currently, they are only two inflows from Permian conglomerates that have been retaining original chemical composition (Fig. 4).

Slightly mineralized inflows with relatively low sulphate concentrations was appeared after crossing of the Pomorzany mine, while mine workings was executed within Triassic carbonates. Chemical composition of these water inflows were fulfilled the Triassic aquifer background. Influence of mixing with water from Permian conglomerates was also noticeable for some of samples (Fig. 4). Intensive drainage of the Triassic aquifer has led to depression of the static water level and changes of the redox condition from reduction to oxidation. Oxidation of the sulphide minerals in the ore body and also dispersed within Triassic carbonates was induced in this way and have been resulting in production of readily soluble magnesium, iron and calcium hydroxysulphates (or sulphates).

Groundwater inflowing currently to the Zn-Pb “Pomorzany” mine is originating from a few different sources. Groundwater with composition similar to hydrochemical background is inflowing from north-east direction. Groundwater from north-western part of the study area is contaminated by containig lignosulfonates, liquid wastewater from Klucze paper factory. Groundwater flux from south-western direction is also contaminated by leachate from sanitary landfill and industrial waste disposal sites. In a central part of the „Pomorzany“ mine prevails the groundwater from infiltration of the modern meteoric waters through hydrogeological windows and also in the Pomorzany fault zone. During percolation in artificial aeration zone these waters has an possibility to dissolve of the sulphide’s weathering products. Dissolution process have been influencing on the increase of groundwater TDS and concentrations of the sulphate, magnesium, calcium, iron and some trace elements. For

these reasons groundwater with dissolved sulphate minerals is characterized by high values of the mMg/mCa ratio and low values of the mCl/mSO₄ index.

The work was with support from the research programme no. KBN 4T12A 02727.

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