Water quality of the abandoned aquifer in the area of the abandoned iron mines (in southern Poland)

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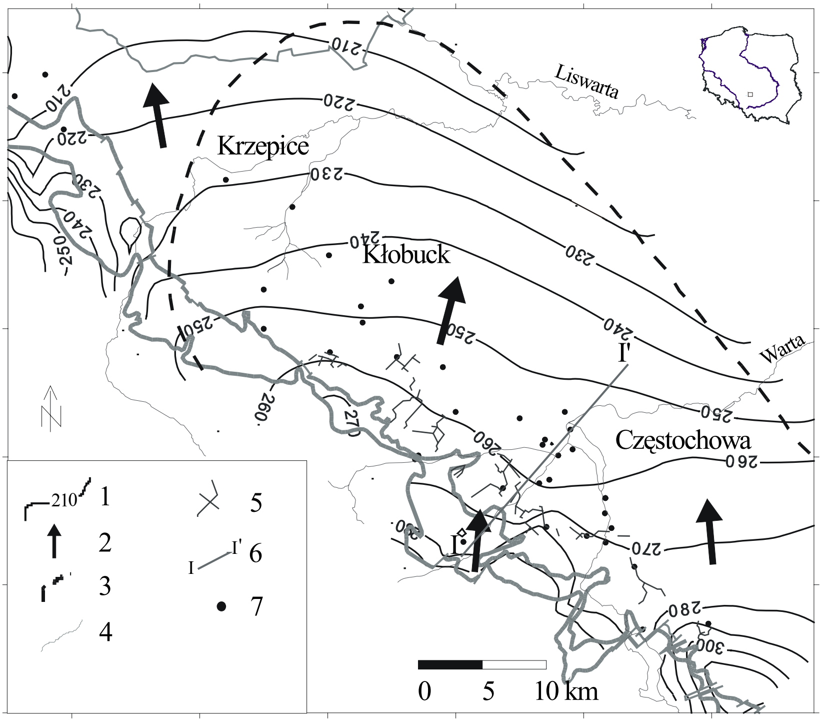
Abstract: Deep iron mines were operating in the Czestochowa region (southern Poland) until early the 1980s. The hydrogeological environment of the Middle Jurassic aquifer has been strongly altered due to the groundwater drainage by the mines. Water was pumped from these mines for over 50 years causing the lowering of the water table. After 1970 the government decided to close the iron mines; dewatering ceased and all the mines were allowed to flood. As the Czestochowa region has an alternative source of groundwater which is a highly productive Upper Jurassic aquifer, the Middle Jurassic aquifer has been abandoned after the flooding, and a big changes of chemistry have occurred there due to the dissolution and flushing of the oxidation products and mine waters. The objectives of this study were to identify the dominant hydrogeochemical processes operating in the disturbed and neglected aquifer and attempt to predict any quality changes of groundwaters that might be anticipated in the region as the result of groundwater rebound. Two models have been developed: a hydrological model of water flow and a hydrochemical speciation model. The results indicate that the changes in groundwater chemistry within the flooded iron mines area are significant. Maximum SO_4^{2-} contents reach 1103.0 mg/l, Mn^{2+} contents reach 6.61 mg/l and Fe_{tot} reach 271.4 mgl. The results of the hydrochemical studies suggest that twenty years after the flooding, waters stored in the mine workings may be defined as quasi-stagnant. The predicted contamination of waters will last for centuries.

1 INTRODUCTION

The Czestochowa region, which covers approximately 1500 square kilometres, is a part of the Krakow-Czestochowa Upland located between Zarki and Praszka in the Silesian district (Figure 1). This region is a part of a large Mesozoic sedimentary basin and the main stratigraphy consists of the Upper and Middle Jurassic sediments which overlay Triassic deposits. Iron ores occur in the Middle Jurassic Clay Formation. There are three significant aquifers in the area: Quaternary deposits composed of the glacial and fluvial materials, Upper Jurassic limestones, and Middle Jurassic sandstones. The Middle Jurassic aquifer consists of fissured-porous, semiconsolidated sandstones and sands. Its thickness ranges from 15 to 60 m and the average hydraulic conductivity is 6×10^{-5} m s^{-1} (Hermanski, 1984). This formation extends from the south to the north, and dips to the north-east direction at the angle of 3°. The major town in this region is Czestochowa, with a population about 250 000. The public water supplies had been derived from the Upper and Middle Jurassic aquifers before dewatering of the mines began. The hydrogeological environment is always strongly altered due to the groundwater drainage by the mines (Dudgeon, 1999 and Rubio, Lorca, 1993) and their flooding (Ammou et. al., 1982, and Rosner, 1998) . Water was pumped from the iron mines in the Czestochowa region for over 50 years causing the lowering of the water table of the Middle Jurassic aquifer. After 1970 the government decided to close the iron mines; dewatering ceased and all the mines were allowed to flood. After theflooding a big changes of groundwater quality have occurred there due to the dissolution and flushing of the oxidation products and mine waters.

Figure 1 Hydrogeological map of the Middle Jurassic aquifer in the Czestochowa region



1- water table countours in metres above sea level (1996), 2- direction of groundwater flow (1996), 3- maximum extent of the cone of depression caused by the iron mining (1967), 4- rivers, 5- water galleries of iron mines, 6- line of the hydrogeological cross-section, 7- wells and mine shafts.

2 METHODS

This study was carried out in the Department of Hydrogeology, Polish Geological Institute, Upper Silesian Branch in Sosnowiec and was financed by the Polish National Environmental and Water Management Foundation.

Water samples have been collected since 1991 from the Polish Geological Institute observation wells, water supply wells and flooded mine shafts (Figure 1). A total of 215 water samples were taken (Razowska et al., 1997), pH and Eh (redox potential) were measured in the field along with EC (specific electric conductance) and temperature, total alkalinity was also measured in the field by acid titration from unfiltered water samples. Water samples were analysed for major and minor dissolved chemical constituents. Water from selected wells and mine shafts were analysed for bacteria and gas composition. In addition, the results of historic water analyses performed by the Czestochowa Geological Works when the iron mines were working and during flooding, have been taken into account in this study.

3 MODELLING OF GROUNDWATER FLOW AND CHEMISTRY

A computer model of groundwater flow in the Middle Jurassic aquifer has been developed. The *SP2H HYDRYLIB* model was chosen as the basis for the numerical modelling (Razowska et al., 1997). The model implemented the finite - difference method. The piezometric contours in the figures 1 and 2 depict the results of the simulations. The patterns of contours indicate that water flow directions under the current hydrologic conditions are close to those which prevailed prior the pumping.The hydraulic gradients in this aquifer, obtained from the modelling are low and range from 0.002 to 0.009.

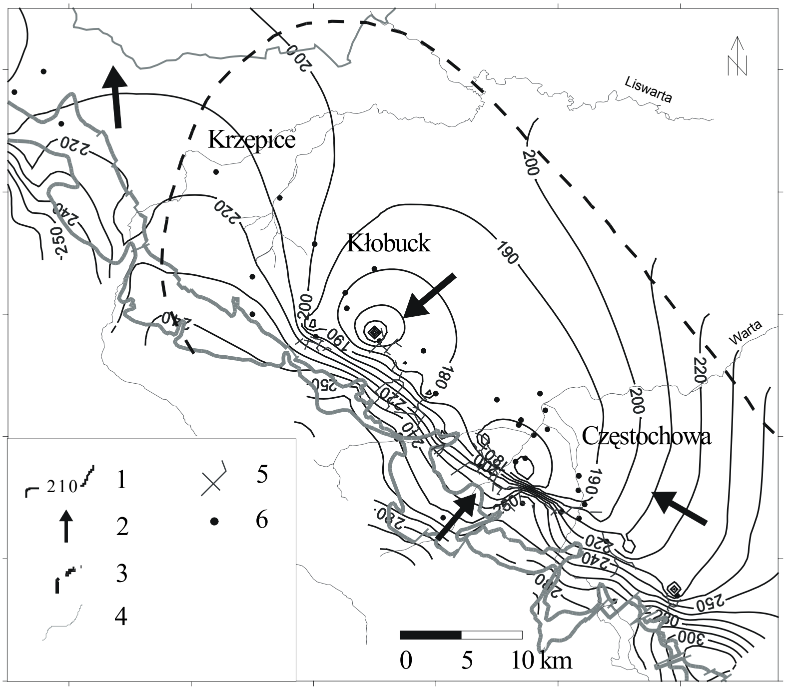


Figure 2 Water table countours of the Middle Jurassic aquifer during the maximum pumping rates of the iron mines

1- water table countours in metres above sea level (1967), 2- direction of groundwater flow (1967), 3- maximum extent of the cone of depression caused by the iron mining (1967), 4- rivers, 5- water galleries of iron mines, 6- wells and mine shafts.

In order to study the processes governing the water chemistry in this area, the author performed the calculations using *WATEQ4F* speciation model (Appello and Postma, 1994). The model was based on the data from the field measurements of pH, Eh, temperature and EC and the results of chemical analyses. Principal aqueous species of Ca, Mg, Na, K, Fe, Mn and Zn were predicted for the waters as well as the saturation indices (SI).

The verified analytical and field data for every sample site have been input to the Polish Geological Institute hydrogeochemical spatial database (based on the ARC/INFO GIS) for permanent storage, retrieval and analysis. All the data is kept in 16 information layers. For the modelled data spatial distribution and interpolation SURFER was used, and the Linear Regression analysis and correlations between anions and cations were also performed.

4 GROUNDWATER QUALITY

Ion concentrations in groundwaters from the Middle Jurassic aquifer in the area which has been impacted by mining are much higher than in the natural waters (Table 1). Average sulphate concentration in the flooded mines is about 700 mg/l and the concentration of bicarbonate is about 200 mg/l. Among cations the highest is calcium content - about 160 mg/l. Average magnesium content is 50 mg/l, iron 105 mg/l and manganese 3.5 mg/l. Sulphate, iron and manganese

Table 1 Average and extremal values of the concentration of the selected ions, pH and electrical conductivity (EC) of waters in the mine waters and background in the Middle Jurassic aquifer (1996)

	pH	**Ion concentrations in mg/l**									**EC**
		HCO_3^-	**SO_4^{2-}**	**Cl^-**	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**Mn^{2+}**	**Fe_{og}**	**µ S/ cm**
Mine waters											
Average	6.60	179.5	688.5	6.6	162.3	52.4	6.1	5.8	3.6	106.3	1316.4
Minimum	5.94	135.371	37.20	3.15	48.20	5.50	2.50	2.07	0.603	8.89	330.0
Maximum	6.89	264.60	1103.00	13.20	245.90	82.02	9.40	13.50	6.612	271.37	1950.0
Mixed waters											
Average	6.64	193.9	204.5	8.0	86.3	20.0	4.7	3.4	0.87	22.6	606.8
Minimum	5.98	72.44	4.98	1.47	18.00	3.07	1.60	1.20	0.067	6.14	135.0
Maximum	6.97	393.90	779.00	29.50	261.60	72.98	11.10	7.61	2.576	56.62	1640.0
Background											
Average	6.95	126.8	9.7	3.9	34.7	4.6	3.0	2.5	0.16	3.4	217.2
Minimum	6.20	72.99	2.64	0.00	13.40	1.03	1.20	1.10	0.002	0.03	114.0
Maximum	7.80	239.81	42.40	37.90	81.50	12.02	10.70	8.10	1.000	10.04	466.0

contents exceed the acceptable limits for drinking water in Poland, which are: 200 mg/l, 0.5 mg/l and 0.1 mg/l respectively. Although the high concentration of heavy metals were expected in this zone, only nickel content (1.62 mg/l) exceeds the drinking water limit of 0.03 mg/l. The concentrations of Zn, B, Co and Li are higher than background values but do not exceed limits for drinking water. Waters have TDS values ranging from 1000 mg/l to 2000 mg/l and values of pH ranging from 5.9 to 6.9 which indicate weak-acidic conditions. Redox potential of the waters (Eh) range from -0,20 to -0,06 V indicating the weak-reducing conditions. Waters from 5 wells are determined as mixed waters with hybrid chemistry. These wells are located along the water flow direction. The ion concentrations are lower than in the flooded workings but much higher than in the „background".

The preliminary analyses of bacteria presence show that these waters are rich in iron reducing bacteria. These bacteria are involved in the microbial reduction of Fe in anoxic conditions.

The preliminary isotopic analyses of gas show that CO_2 may be connected either with organic (microbial) processes or with chemical processes such as dissolution and diffusion.

5 HYDROCHEMICAL PROCESSES

The Figure 3 shows very well known proccess of the formation of the acid mine waters and neutral mine waters.

The deep iron mining in the Czestochowa region disrupted groundwater flow patterns and exposed rocks containing iron sulphides such as pyrite, marcasite to the oxygenated environment. As a result of the pumping, surface waters infiltrated to the dewatered zone of the Middle Jurassic strata and the mine workings. The oxidation products such as: gypsum, melanterite, epsomite, jarosite, calcite precipitated in the dewatered zone. As flooding occurred, highly soluble minerals dissolved, and this resulted in the production of acid mine waters rich in sulphate, iron, manganese, calcium and magnesium contents (Barnes, Clarke, 1964). Acidity was neutralised then by the interaction with the carbonate rocks and pH values increased to 6 -7. Despite the neutralisation, ion contents in groundwater within the zone of the flooded mines remain high. These are neutral polluted mine waters with high sulphate, iron and manganese concentrations compared to the background contents in this aquifer (Razowska, 1998). The bacteria role in these processes were also comfirmed.

WATEQ was used for the calculation of the saturation indices (SI) for these minerals which are significant for the chemistry of waters in this area (Table 2). SI values of gypsum are close to zero and water is saturated with respect to this mineral, implying that gypsum is one of the mineral phases controlling groundwaters chemistry in this zone. Carbonate is most likely controlled by the siderite ($FeCO_3$). Predicted SI of siderite is approximately equal to zero, which indicates the saturation of these water with respect to this mineral phase. Besides siderite, iron concentrations are correlated with iron oxides and hydroxides with the tendency to precipitation (e.g. goethite).

Figure 3 Diagram showing the generation of the acid and neutral mine waters

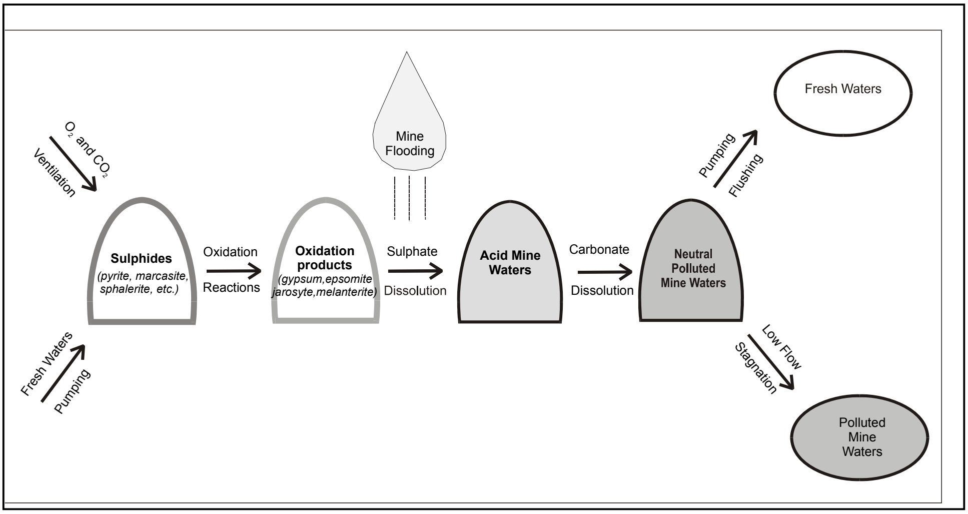


Table 2 Saturation Indices (SI) of waters with respect to selected minerals

Minerals	Chemical	Saturation Indices (SI)		
		Flooded	Mixed	Background
Barite	Ba SO_4	-0.1 ÷ 0.5	0.3 ÷ 0.4	-0.32 ÷ -0.89
Calcite	$CaCO_3$	-0.5 ÷ -1.0	-0.004 ÷ -2.2	-1.5 ÷ -2.0
Dolomite	$CaMg(CO_3)_2$	-1.0 ÷ -3.0	-1.0 ÷ -6.0	-3.9 ÷-5.3
Epsomite	Mg $SO_4 \cdot 7H_2O$	-2.0 ÷ -5.0	-3.0 ÷ -6.0	-6.8 ÷ -6.2
Goethite	FeOOH	8.5 ÷ 10.0	1.0 ÷ 9.5	8.4 ÷ 8.9
Gipsum	Ca $SO_4 \cdot 2H_2O$	-0.4 ÷ -2.0	-0.5 ÷ -3.2	-3.1 ÷ -3.3
Jarosite	$KCaOHSO_4$	3.5 ÷ 6.0	0.2 ÷4.0	-0.8 ÷ -2.4
Magnesite	Mg CO_3	-1.5 ÷ -2.5	-1.0 ÷ -3.3	-2.4 ÷ -3.2
Manganite	Mn O_3	-11.5 ÷ -14.0	-5.5 ÷ -13.6	-6.0 ÷ -14.0
Rodochrosite	Mn CO_3	-0.5 ÷ -1.5	-0.2 ÷ -2.6	-1,8 ÷ -2.7
Siderite	Fe CO_3	0.1 ÷ 0.6	-0.03 ÷ -1.2	-0.2 ÷ -0.8
Strontianite	Sr CO_3	-2.5 ÷ -3.5	-1.2 ÷ -4.4	-3.2 ÷ -4.0

6 SPATIAL-TEMPORAL ANALYSIS OF GROUNDWATER CHEMISTRY

Hydrochemical studies showed that after the flooding, when the equilibrium was approached in mine waters, changes of ion concentrations should not have been controlled by the oxidation products solubility factors, but by the rate of release of ions from the oxidation sites and by the dilution factors (Cairney, Frost, 1975). Now, fifteen years after the flooding the iron content is still very high as well as sulphate content (Figure 4). The flowing rates of the polluted waters from the flooded mines, estimated by the modelling, are low and range from 3 to 6 m/y. Hence, the flushing process is insignificant here and therefore the self-cleaning process of the polluted mine waters will develop slowly.

This has been confirmed by the spatial-temporal analysis of the selected ion concentrations (Razowska, 1998). The observations of the ion contents have been conducted for the last eight years in groundwaters from wells and mine shafts. The results obtained from the statistical analysis have shown that the variations of the ion concentrations are not significant and no trends of increase or decrease have been observed.

7 CONCLUSIONS

The results indicate that the changes of groundwater chemistry in the Middle Jurassic aquifer within the flooded mine workings are significant. Twenty years after the flooding of mines, the ion concentrations in the polluted mine waters are much higher than in the background. Maximum SO_4^{2-} contents are 6 times higher than the acceptable levels for human consumption of water (Polish Drinking-Water Limits), maximum Mn contents are 70 times higher, and maximum Fe_{tot} are 500 times higher.

The results of the hydrochemical studies suggest that waters stored in the mine workings may be defined as quasi-stagnant. If the remediation of the Middle Jurassic aquifer is not provided here the contamination of waters may last for at least 300 years. The formation of the polluted acid and neutral waters, in such mined sedimentary ores as in the Czestochowa region should be prevented prior the flooding.

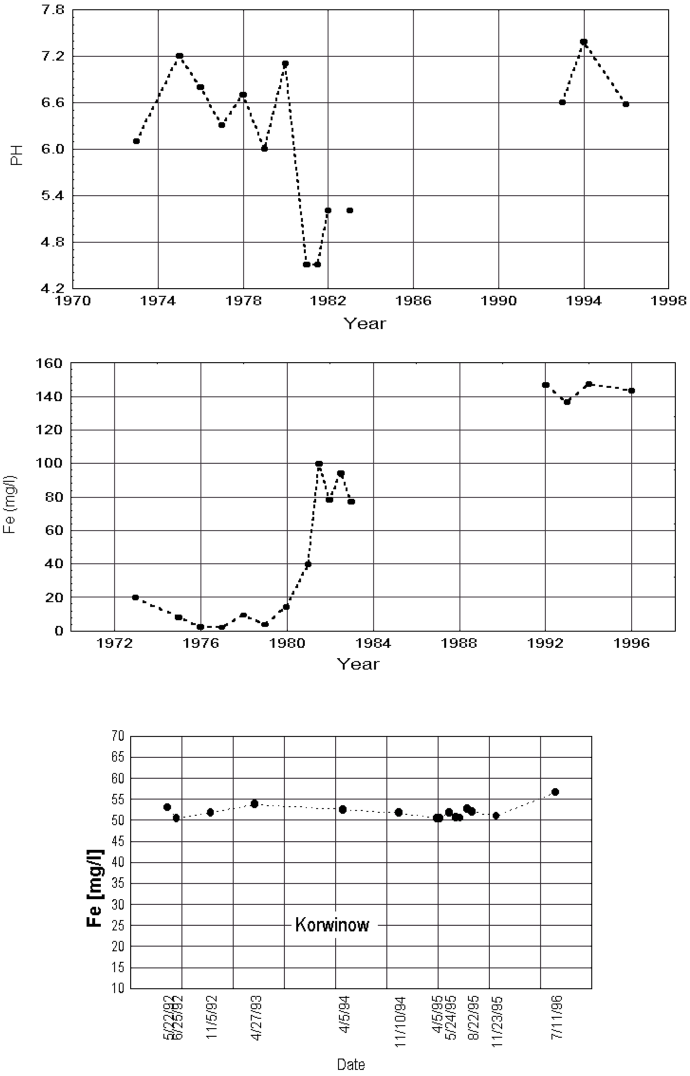


Figure 4 Variations of pH and Fe_{total} concentrations over the time in waters from Szczekaczka iron mine shaft and Korwinów well

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Jakość wód zbiornika na terenie opuszczonych kopalń żelaza (południowa Polska)

Lidia Razowska

Streszczenie: Kopalnie żelaza prowadziły eksploatację rud przez okres ponad 50 lat w rejonie Częstochowy (południowa Polska) do wczesnych lat 80-tych. Środowisko hydrogeologiczne zbiornika środkowojurajskiego zostało znacznie zmienione w wyniku drenażu wód podziemnych przez kopalnie. Celem przeprowadzonych badań było zidentyfikowanie procesów hydrogeochemicznych zachodzących w środkowojurajskim kompleksie wodonośnym oraz próba prognozowania zmian jakości wód podziemnych, które zaszły w wyniku odbudowy zasobów wód podziemnych. Opracowano dlatego dwa modele: hydrogeologiczny model przepływu wody i hydrochemiczny model specjacji. Wyniki wskazują na znaczne zmiany w składzie chemicznym wód podziemnych w obszarze zalanych kopalń. Maksymalne stężenie SO_4^{2-} osiąga

1103,0 mg/l, stężenie Mn^{2}+ osiąga 6,61 mg/l, a stężenie Fe_{og} osiąga 271,4 mg/l. Wyniki badań hydrochemicznych sugerują, że po dwudziestu latach od zalania wody gromadzone w wyrobiskach kopalniach mogą być określone jako quasi-stagnujące. Skażenie wód będzie się utrzymywać przez setki lat.