## Technical Article

# Hydrogeological and Hydrochemical Characteristics of the Partially Flooded Piaseczno Opencast Sulphur Mine in Southeastern Poland

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**Abstract.** The basic chemical properties of Tertiary (T) and Quaternary (Q) aquifers near the Piaseczno opencast sulphur mine and the water in the open pit, along with the stratigraphy and hydrogeology of the area, were characterized to assess the feasibility of inundating the mine with ground water. Ground water quality varied markedly in the opencast area. A distinct stratification was noted in the pit water; total dissolved solids, calcium, chloride, hardness, and hydrogen sulphide increased from the top water level to the bottom of the pit lake. The concentrations of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> in the opencast water were very high, especially in the hypolimnion zone. Based on our preliminary analysis, it appears that an artificial lake formed in the Piaseczno open pit could be used in the future as a fish and wildlife habitat as well as for recreational purposes.

**Key words:** Geology; hydrochemistry; meromictic lake; pit lake; Poland; water quality

## Introduction

Rich native sulphur deposits were deposited in the Carpathian foredeep (in southeastern Poland). This foredeep was formed during the Tertiary period as a result of orogenic movements, and stretches along the northern Carpathian Mountains across southern Poland to Ukraine. Polish and Ukrainian sulphur deposits are associated with gypsum and anhydrite of Lower Badenian (Miocene) age, which have been transformed into sulphur-bearing limestone as a result of biochemical processes. The richest sulphur deposits (Piaseczno, Machów, and Jeziórko-Grębów) in Poland are in the vicinity of Tarnobrzeg (Figure 1).

The Piaseczno and Machów sulphur deposits were mined from 1956 to 1992 by the open-pit method; mining ceased for economic reasons. The Machów opencast mine is being transformed into a 500 ha water reservoir with a maximum depth of 40 m. Pumps were used to remove the highly mineralised water, and the source of this water, the Tertiary horizon, was sealed with a 25 m thick clay layer. The open pit is now being filled with water from the Vistula River. The new artificial lake, together with the surrounding reclaimed area, will be transformed in the future into a recreational site.

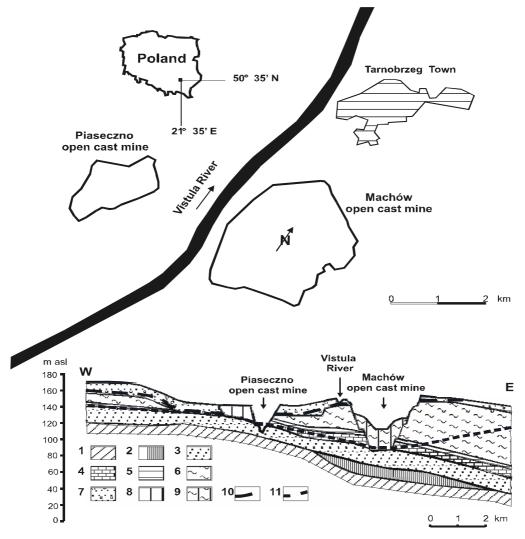
The Piaseczno opencast mine has partially filled with ground water. Presently, the water level is maintained by a forced drainage system at 122 m above sea level (ASL). Surplus water (up to 12,000 m³ d⁻¹) is pumped to the Vistula River. The initial plan was to fill the partially flooded pit with ash from the neighbouring electric power station. This concept was abandoned because of opposition by the local community and

concerns that unexpected ecological consequences might develop. The pit will now be filled (to 146 m ASL) with ground water from two aquifers, and the future lake will be used for recreation.

There have been many studies published on water quality in metal ore and lignite pit lakes (e.g. Castro and Moore 2000; Friese et al. 1998a, b; Kohfahl and Pekdeger 2004), but literature on the formation of artificial lakes in open pits left by sulphur ore exploitation, and the hydrochemical processes in these specific geological mining conditions, is limited (Gaydin and Zozula 2002). There are also few studies published on the use of pit lakes for recreation purposes or aquaculture, or the results of long-term monitoring studies conducted to explain the hydrochemical changes in this kind of artificial lake (cf. Parshley and Bowell 2003), though a very good, concise review of such issues was presented by Bowell (2003). The aim of this study was to determine the chemical composition of the Piaseczno pit water and influent ground water. Predicting the long term geochemical behaviour of the pit water is important in assessing potential environmental effects and lake ecology. It also establishes a baseline that can be used in the future as a reference point for detailed monitoring programmes and prognosis of water quality evolution.

## Geology and Hydrology

The Piaseczno opencast mine is situated on the eastern bank of the Vistula River, south of Tarnobrzeg, in southeastern Poland (50° 33.08'N, 21° 36.01'E, Figure 1). The geological structure of the mine region is composed of Cambrian (represented by shale),



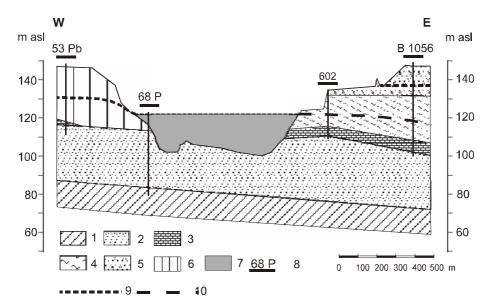
**Figure 1.** Location and geological cross-section of the Piaseczno and Machów opencast mines: 1. shale (Cambrian); 2. sandy siltstones (Lower Badenian); 3. sands and sandstones (Lower Badenian); 4. sulphur-bearing limestone (Lower Badenian); 5. marls (Upper Badenian); 6. Cracowian clays (Sarmatian); 7. sand and gravels (Quaternary); 8. inner waste bank; 9. clay layer; 10. Quaternary aquifer; 11. the potentiometric surface of the Tertiary aquifer

Lower Badenian (Miocene), and Sarmatian formations (Miocene). The Badenian formations are fine-grained sands overlain by native sulphur-bearing limestone, barren limestone, and gypsum. The Sarmatian formations consist of clays and claystone (Cracovian clays). The clay strata are overlain by Quaternary riverine sands and gravels. The geological structure of the area is presented in Figures 1 and 2.

In the vicinity of the Piaseczno opencast mine, there are two aquifers separated by a stratum of Sarmatian clay. The Quaternary unconfined aquifer is recharged by surface water. Before sulphur exploitation, the water table in this aquifer was at 146 m ASL. Presently, this water table ranges between 122 and 136 m ASL. The Tertiary aquifer includes the sulphur-bearing limestone and underlying sands,

and is confined by a thick clay formation in the vicinity of the Piaseczno and Machow pits. Before exploitation, the potentiometric surface in this aquifer was stabilised at 147-150 m ASL but pumping lowered it to 118-125 m ASL. The two aquifers interconnect 3.5 to 4 km northeast of the Piaseczno open pit, due to a gradual pinching out of the intervening clay layer.

Two cones of depression, separated by the Vistula valley, were formed in the Quaternary aquifer when the Piaseczno and Machów mines were being dewatered. The Piaseczno pit lies within reach of the depression cone formed in the Tertiary aquifer around the Machów mine area, which causes a constant flow of water towards the Machów mine (Figure 1). Pumping has ceased at Machów, so this flow of water will be progressively reduced.



**Figure 2.** Geological cross-section of the Piaseczno opencast mine: 1. Cambrian shale; 2. Tortonian, sands and sandstones; 3. Torton, chemical series, sulphur-bearing limestone, barren limestone and gypsum; 4. Sarmatian, Cracovian clays; 5. Quaternary, sand and gravels; 6. inner waste bank - sands, gravels, clays, silts; 7. present water level of Piaseczno reservoir; 8. documented geological exploratory bore-holes; 9. water table of Quaternary aquifer; 10. potentiometric surface of Tertiary aquifer

#### Methods

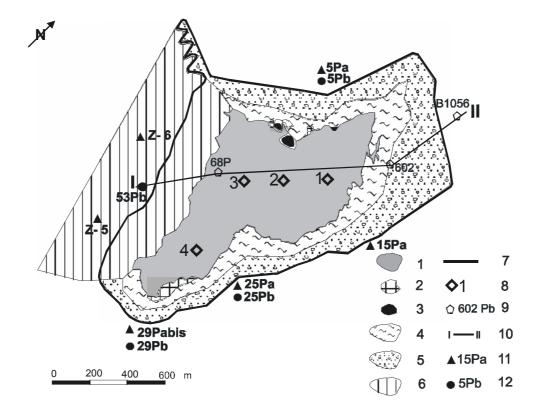
Preliminary chemical analyses of waters in the partially flooded Piaseczno pit and in underground waters of the adjacent area were carried out in 1994, 1996, and 2000 within the framework of environmental monitoring. The water samples from the reservoir were collected at four points; their location was intended to provide a profile at different depths in the reservoir (Figure 3). At each sampling point, a number of water samples were collected at different depths, using a water sampler that works similarly to a 5 L Ruttner bathometer. In the following years of the study, two series of tests (in spring and autumn) were carried out. To determine the variability of chemical composition within a horizontal profile and to eliminate the influence of external factors (in the form of water inflows), the results of analyses were averaged for water samples taken from depths of 5, 10, and 15 m. Water samples were analysed in a laboratory within four hours.

Ground water was sampled in the spring and autumn of 2000 and the data were averaged. The samples were collected from six piezometers for the Quaternary aquifer and four piezometers for the Tertiary aquifer, located near the shoreline of the Piaseczno pit (Figure 3). A deep-well pump (Grundfos, type MP-1) and an Eijkelkamp filtration unit with a 0.45  $\mu$ m membrane filter (Gelman Sciences) were used for water sampling. Before each sampling event, water was bailed until electrical conductivity, pH, and temperature were stable.

Sampling and sample stabilisation procedures were consistent with the Polish Standards PN-88/C-04632/03 and 04, International Standard ISO/DIS 5667/3, and the recommendations of Adams (1991), Macioszczyk (1987), and Nielsen (1991).

Water samples from the reservoir and the piezometers were collected in 1 L borosilicate glass-stoppered bottles, except for samples being analysed for  $H_2S$ , which were collected in 100 cm³ bottles. The water samples (excluding samples analysed for alkalinity, chloride, and hydrogen sulphide) were preserved with 5 ml/L nitric acid and stored at 4°C. Samples being analysed for total dissolved solids (TDS) were preserved with 2 ml/L of chloroform. Samples from the Piaseczno pit lake were filtered through 0.45  $\mu$ m filter paper in the laboratory before analysis.

Chemical analyses were carried out according to Polish and commonly used standard methods for the analysis of waters and waste waters (Adams 1991; Greenberg et al. 1992; Hermanowicz et al. 1999). The chemical oxygen demand (COD) value was determined by warming the sample, adding potassium permanganate and sulfuric acid, then reducing it with sodium oxalate, and titrating with potassium permanganate. Alkalinity was determined by titrating the sample (to pH 4.5) with hydrochloric acid, using methyl orange as an indicator. Total iron was determined colorimetrically with 1,10-phenathroline. TDS was determined gravimetrically. Total hardness was estimated by compleximetric titration of calcium and magnesium (pH 10) with 0.01 M Na<sub>2</sub>-EDTA in the



**Figure 3.** Geological map of the Piaseczno opencast mine: 1. contemporary water table of the Piaseczno reservoir; 2. sulphur-bearing limestone; 3. gypsum; 4. horizontal extent of Tertiary formations (Cracovian clays); 5. horizontal extent of Quaternary formations; 6. horizontal extent of inner waste bank; 7. designed final water table in the opencast; 8. sampling points; 9. location of geological exploratory bore-holes; 10. line of geological cross-section; 11. piezometer in the Quaternary aquifer; 12. piezometer in Tertiary aquifer

the presence of Eriochrom Black T. Sulphate was determined gravimetrically (with the addition of barium chloride) with ignition of the residue, according to Hermanowicz et al. (1999). Chloride ion was determined by argentometry. Low concentrations of H<sub>2</sub>S were calculated from the total dissolved sulphide concentration (H<sub>2</sub>S and HS<sup>-</sup>), determined using a Hach spectrophotometer, Model Drell 2000, taking into account the sample pH and practical ionization constant of H<sub>2</sub>S. The HS<sup>-</sup> ion concentrations were calculated based on the H<sub>2</sub>S concentrations.

A modified iodometric method was used to determine higher (above 0.8 mg L<sup>-1</sup>) concentrations of H<sub>2</sub>S. The sample of 100 cm<sup>3</sup> of water was preserved (in the field) by adding 1g of cadmium acetate and storing the sample at 4°C. The yellowish colour of cadmium acetate precipitate indicated the presence (and rough concentration) of the hydrogen sulphide. In the laboratory, the sample was filtered through the medium filter paper. The filter together with its content was moved to a 500 cm<sup>3</sup> flask containing 10 or 20 cm<sup>3</sup> (depending on expected H<sub>2</sub>S concentration) of 0.1M iodine solution and acidified with 10 cm<sup>3</sup> of

diluted (1:1) hydrochloric acid. The sample was titrated by 0.1 M sodium thiosulfate using starch as a colour indicator. Na, K, Mg, Ca, and Mn were determined by atomic absorption spectrometry.

#### Results

The Water Chemistry of the Quaternary Aquifer

The water in the Quaternary aquifer piezometers located near the Piaseczno pit had a surprisingly wide range of chemical composition (Figure 3). The water in piezometers 5Pa and 15Pa were generally characterised by the lowest values of determined chemical parameters (except for the highest concentrations of potassium in 5Pa and sodium and chloride in 15Pa) whereas water in piezometers Z-5 and Z-6 had the highest concentrations (Table 1). The main differences involved the sulphate, calcium, and chloride concentrations. The water had generally high TDS, near-neutral pH, and elevated Fe and Mn. Based on the mean values of the characteristic parameters, the waters in the Quaternary aquifer were of the sulphate-calcium (SO<sub>4</sub>-Ca) type, according to the Altovski-Svec classification (Macioszczyk 1987).

**Table 1.** The water chemistry of the Quaternary aquifer in the area of Piaseczno reservoir

| Parameter              | Unit                                 | J 1  | Piezometer |      |         |            |            | Mean |
|------------------------|--------------------------------------|------|------------|------|---------|------------|------------|------|
|                        |                                      | 5Pa  | 15Pa       | 25Pa | 29Pabis | <b>Z-5</b> | <b>Z-6</b> |      |
| Temperature            | °C                                   | 11.1 | 11.3       | 11.4 | 11.8    | 11.8       | 12.3       | 11.6 |
| рН                     |                                      | 6.8  | 7.2        | 6.7  | 6.9     | 6.6        | 6.9        | 6.9  |
| Conductivity           | μS cm <sup>-1</sup>                  | 1470 | 1600       | 2350 | 2720    | 3510       | 3600       | 2540 |
| COD-permanganate value | $mg O_2 L^{-1}$                      | 4.5  | 3.9        | 19.6 | 8.6     | 27.6       | 43.3       | 17.9 |
| Alkalinity             | mg CaCO <sub>3</sub> L <sup>-1</sup> | 270  | 220        | 230  | 200     | 490        | 210        | 270  |
| Total dissolved solids | mg L <sup>-1</sup>                   | 1040 | 910        | 1820 | 2210    | 3310       | 3850       | 2190 |
| Total hardness         | mg CaCO <sub>3</sub> L <sup>-1</sup> | 660  | 290        | 910  | 1250    | 1900       | 1790       | 1130 |
| Sodium                 | mg L <sup>-1</sup>                   | 38   | 179        | 111  | 147     | 127        | 111        | 119  |
| Potassium              | mg L <sup>-1</sup>                   | 36.0 | 5.90       | 5.70 | 8.10    | 4.90       | 4.30       | 10.8 |
| Magnesium              | mg L <sup>-1</sup>                   | 22   | 14         | 43   | 47      | 79         | 145        | 59   |
| Calcium                | mg L <sup>-1</sup>                   | 238  | 96         | 312  | 419     | 629        | 480        | 362  |
| Total iron             | mg L <sup>-1</sup>                   | 8.6  | 3.5        | 86.5 | 14.7    | 120        | 250        | 80.5 |
| Manganese              | mg L <sup>-1</sup>                   | 3.9  | 1.1        | 14.0 | 2.3     | 14.7       | 12.3       | 8.1  |
| Chloride               | mg L <sup>-1</sup>                   | 41   | 255        | 180  | 184     | 122        | 81         | 143  |
| Sulphate               | mg L <sup>-1</sup>                   | 470  | 140        | 880  | 1130    | 1770       | 2230       | 1100 |
| Bicarbonate            | mg L <sup>-1</sup>                   | 287  | 271        | 287  | 250     | 594        | 253        | 324  |
| Silica                 | mg L <sup>-1</sup>                   | 6.1  | 6.1        | 3.0  | 6.4     | 11.0       | 3.2        | 6.0  |

The Water Chemistry of the Tertiary Aquifer

The water from the Tertiary aquifer in the piezometers located near the Piaseczno pit (Figure 3) was similarly analyzed. The water quality was distinctly different in piezometer 53Pb piezometers 5Pb and 25Pb (Table 2). The differences in concentration concerned mainly sodium, calcium, and chloride as well as magnesium, manganese, and iron. Based on the mean values (Table 2), the water in the Tertiary aquifer near the Piaseczno opencast was determined to be of the sulphate-chloride-sodiumcalcium (SO<sub>4</sub>-Cl-Na-Ca) type according to the Altovski-Švec classification (Macioszczyk 1987). of Characteristically, water some **Teritiary** piezometers (5Pb, 25Pb) had high concentrations of H<sub>2</sub>S. The inverse association between dissolved iron and H<sub>2</sub>S could be expected as a result of probable precipitation of FeS<sub>x</sub> compounds (Table 2).

The Chemistry of the Waters in the Partially Filled Pit

The mean values for the chemical properties of the waters in Piaseczno reservoir are shown in Table 3. During three years of tests, a distinct stratification of the chemical composition in the vertical profile of this reservoir was observed. The TDS, calcium, chloride, and the total hardness values increased from the top level of the water column to the bottom of the reservoir. Both chloride and H<sub>2</sub>S were highest at the bottom of the water column, and have decreased over time. Sulphate increased slightly with depth but (contrary to chloride), decreased significantly at the bottom of the reservoir (below 18 m). The pH was highest at the surface (to about 5 m) and at the bottom

(below 15 m) (Table 3). There was no visible variation in the mean chemical composition of the water from four sampling points in the pit (Figure 3, Table 4). The above data shows that the lake is horizontally well-mixed, although vertically it is clearly stratified (Table 4).

#### Discussion

The differences in the chemical composition of the waters from the Quaternary aquifer are attributed to the mineralogy in the external waste bank of the former open pit mine. Higher concentrations of sulphate, calcium, iron, and manganese in the water from piezometers Z-5 and Z-6 (Table 1, Figures 3) presumably resulted from natural leaching of these chemical components from the overburden formations (Szarek-Gwiazda et al. 2006).

A mixture of gravels, sands, and Cracovian clays, which were stripped as overburden from the ore deposit and dumped, formed the external waste bank. A relatively high concentration of sulphur and calcium in clay deposits and sulphur-bearing limestone has been determined by Szarek-Gwiazda et al. (2006). A higher chloride and sodium level (Table 1), especially in piezometer 15 Pa but in piezometers 25 Pa and 29 Pabis as well, is evidence of the flow of the waters from the Vistula River towards the Piaseczno reservoir. This flow results from the drainage effect of the Piaseczno pit in the Quaternary horizon of the studied area (Figures 2, 3). The waters of the Vistula River have been characterised for many years by a relatively high concentration of chloride (200 –500 mg L<sup>-1</sup> Cl). The

Table 2. The water chemistry of the Tertiary aquifer in the area of Piaseczno reservoir

| Parameter              | Unit  |      | Mean |      |      |      |
|------------------------|---|------|------|------|------|------|
|                        |   | 5 Pb | 53Pb | 25Pb | 29Pb |      |
| Temperature            | $^{0}$ C                                      | 12.3 | 13.2 | 11.8 | 12.7 | 12.5 |
| pН                     |   | 6.9  | 6.5  | 7.5  | 7.0  | 7.0  |
| Conductivity           | μS cm <sup>-1</sup>                           | 2830 | 2320 | 4100 | 2480 | 2930 |
| COD-permanganate value | $mg O_2 L^{-1}$                               | 23.6 | 11.5 | 34.7 | 14.1 | 20.9 |
| Alkalinity             | mg CaCO <sub>3</sub> L <sup>-1</sup>          | 270  | 370  | 440  | 210  | 320  |
| Total dissolved solids | mg L <sup>-1</sup>                            | 1870 | 1930 | 2570 | 1930 | 2080 |
| Total hardness         | mg CaCO <sub>3</sub> L <sup>-1</sup>          | 730  | 1310 | 360  | 1050 | 860  |
| Sodium                 | ${\sf mg}\ { m L}^{	ext{-}1}$                 | 230  | 60   | 800  | 220  | 330  |
| Potassium              | ${\sf mg}\ { m L}^{	ext{-}1}$                 | 22.0 | 5.4  | 12.5 | 6.2  | 11.5 |
| Magnesium              | ${\sf mg}\ { m L}^{	ext{-}1}$                 | 22   | 50   | 20   | 43   | 34   |
| Calcium                | ${\sf mg}\ { m L}^{	ext{-}1}$                 | 250  | 419  | 112  | 350  | 280  |
| Total iron             | ${\sf mg}\ { m L}^{	ext{-}1}$                 | 5.6  | 19.0 | 0.2  | 48.0 | 18.2 |
| Manganese              | ${\sf mg}\ { m L}^{	ext{-}1}$                 | 2.0  | 9.0  | 0.2  | 5.2  | 4.1  |
| Chloride               | ${\sf mg}\ { m L}^{	ext{-}1}$                 | 530  | 55   | 680  | 216  | 370  |
| Sulphate               | ${\sf mg}\ { m L}^{	ext{-}1}$                 | 450  | 990  | 720  | 940  | 770  |
| Bicarbonate            | mg L <sup>-1</sup>                            | 270  | 460  | 510  | 260  | 370  |
| Silica                 | ${\sf mg~L^{-1}}$                             | 7.1  | 7.9  | 5.1  | 4.4  | 6.1  |
| Hydrogen sulphide      | ${\sf mg}\ {\sf L}^{{\scriptscriptstyle -1}}$ | 7.6  | 0.0  | 16.0 | 0.0  | 6.1  |
| HS <sup>-</sup>        | $mg L^{-1}$                                   | 4.3  | -    | 10.0 | -    | 7.2  |

**Table 3.** Averaged values of determined chemical parameters in a vertical profile of the Piaseczno reservoir for four sampling points

| Tour sair |       |              |                            |                       | _                  |                    |                    |                    |
|-----------|-------|--------------|----------------------------|-----------------------|--------------------|--------------------|--------------------|--------------------|
| Year      | Depth | n pH         | Total dissolved            | Total hardness,       | Ca,                | Cl,                | $SO_{4,}$          | $H_2S$ ,           |
|           | m     |              | solids, mg L <sup>-1</sup> | mval dm <sup>-3</sup> | mg L <sup>-1</sup> | mg L <sup>-1</sup> | mg L <sup>-1</sup> | mg L <sup>-1</sup> |
| 1994      | 2     | 7.8          | 1770                       | 21.9                  | -                  | 300                | 930                | 0.00               |
|           | 5     | 7.2          | 1870                       | 22.6                  | -                  | 350                | 930                | 0.05               |
|           | 8     | 7.1          | 2350                       | 24.0                  | -                  | 430                | 950                | 8.60               |
|           | 11    | 7.1          | 4390                       | 26.3                  | -                  | 1570               | 850                | 1.20               |
|           | 13    | 7.3          | 9320                       | 34.2                  | -                  | 4500               | 470                | 180                |
| 1996      | 0     | 7.9          | 1860                       | 20.4                  | 340                | 180                | 790                | 0.00               |
|           | 8     | 7.3          | 1980                       | 21.5                  | 360                | 190                | 820                | 0.02               |
|           | 13    | 7.1          | 2240                       | 23.3                  | 380                | 260                | 920                | 0.04               |
|           | 17    | 7.1          | 2540                       | 25.4                  | 380                | 340                | 950                | 0.02               |
|           | 22    | 7.3          | 4900                       | 24.9                  | 380                | 1870               | 730                | 0.03               |
| 2000      | 0     | 7.6          | 1840                       | 20.5                  | 330                | 180                | 920                | 0.00               |
|           | 5     | 7.7          | 1880                       | 20.5                  | 330                | 180                | 920                | 0.01               |
|           | 10    | 6.8          | 2140                       | 24.2                  | 390                | 200                | 1020               | 0.02               |
|           | 15    | 6.9          | 2530                       | 25.6                  | 400                | 320                | 1060               | 0.19               |
|           | 17    | 7.0          | 2640                       | 26.1                  | 410                | 370                | 1060               | 0.20               |
|           | 21    | 7.3          | 6830                       | 29.5                  | 420                | 2900               | 630                | 0.19               |
|           |       |              |                            | Reference values      |                    |                    |                    |                    |
| Class I   | water | 6.5-8.5      | 300                        | -                     | 50                 | 100                | 100                | -                  |
| Class V   | water | <5.5 or >9.0 | >1200                      | -                     | >400               | >400               | >300               | -                  |

<sup># -</sup> according to the regulations of the Polish Ministry of the Environment with regard to surface freshwater quality

relatively low concentration of chloride in piezometer 5 Pa, which is located on the other side of the water inflow into the Piaseczno mine pit (Figure 3), provides indirect evidence of the influence of the Vistula River on the water quality in the Quaternary aquifer.

The differences in the chemical composition of the water from the Tertiary aquifer similarly reflect the location of particular piezometers within the different geological formations. The high concentrations of sulfate, calcium, magnesium, and manganese in the piezometer 53 Pb water of the Tertiary aquifer

**Table 4**. The water chemistry (horizontal profile) of the Piaseczno reservoir (year 2000); the mean values (n = 3) are shown for water depths of 5, 10, and 15 m at four sampling points.

| Parameter              | Unit                 | Sampling point |      |      |      |  |  |
|------------------------|----------------------|----------------|------|------|------|--|--|
|                        |                      | 1              | 2    | 3    | 4    |  |  |
| рН                     |                      | 7.2            | 7.2  | 7.2  | 7.1  |  |  |
| Total dissolved solids | mg L <sup>-1</sup>   | 2140           | 2110 | 2210 | 2290 |  |  |
| Total hardness         | mval L <sup>-1</sup> | 23.3           | 23.5 | 23.3 | 23.5 |  |  |
| Calcium                | mg L <sup>-1</sup>   | 370            | 370  | 370  | 370  |  |  |
| Chloride               | mg L <sup>-1</sup>   | 240            | 240  | 230  | 240  |  |  |
| Sulphate               | mg L <sup>-1</sup>   | 1020           | 990  | 980  | 1010 |  |  |
| Hydrogen sulphide      | $mg L^{-1}$          | 0.06           | 0.08 | 0.06 | 0.08 |  |  |

correspond to the high concentrations of these constituents in piezometers Z5 and Z6, situated in the Quaternary aquifer. This results from interconnection of the two aguifers in the area of the internal waste bank, and is also confirmed by the low concentrations of chloride in piezometer 53 Pb and piezometers Z5 and Z6 (Quaternary aguifer) (Tables 1 and 2). The low chloride level and electrical conductivity index in piezometer 53 Pb result from the inflow of water from the Quaternary horizon from the area beyond the outer waste bank, in which Quaternary sands and gravels overlie the sands of the Tertiary formation (Figure 3). Higher values of electrical conductivity, TDS, and concentrations of chloride and sodium in the Tertiary aguifer from piezometers 5 Pb and 25 Pb relative to the water from the Quaternary horizon in piezometers 5 Pa and 25 Pa results from the separation of these aquifers (Tables 1 and 2; Figure 3). These parameters can be recognised as characteristics of the different water chemistry in this particular area.

The distinct stratification of the waters in the Piaseczno reservoir is caused by the different water quality in the water from the Quaternary and Tertiary aquifer and the surface water that flows into the pit, by density differences due to the concentration gradient, and by reactions that take place at depth. The high TDS levels in the bottom layer are due to the high chloride concentrations in the water from the Tertiary aquifer and from the Vistula River.

The rapid decrease in the sulphate concentrations in the bottom layer is probably due to bacterial reductive processes in the anaerobic and aphotic hypolimnion zone (lower stratum) and corresponds well with an increase in H<sub>2</sub>S in 1994 (Table 3).

Sulphate can be reduced to H<sub>2</sub>S in the presence of organic matter (Gammons et al. 2003; Matsujama 1973). Moreover, if iron is present and is reduced to the ferrous state as well, ferrous iron and HS- could precipitate as FeS and can be transformed to FeS<sub>2</sub>. Redissolution of the iron minerals probably occurs in

the reduced zone, causing iron concentrations to peak there (Haładus and Kulma 2001). Szarek-Gwiazda et al. (2006) also found relatively high concentrations of iron in the bottom sediments and a high correlation coefficient (r = 0.9) between total iron and sulphur concentrations. Zurek (2006) also found the highest concentrations of total iron in the bottom layer of the lake on the level of 15 m and 25 m (27 and 28 mg L<sup>-1</sup> respectively), as well as a rapid increase in free CO<sub>2</sub> levels at reservoir depths below 15 m (200-250 mg L<sup>-1</sup>). Moreover, the concentration of sulphur-reducing bacteria in the hypolimnion zone in the Piaseczno pit lake was estimated by Zurek (2002) as 10<sup>5</sup> cells·cm<sup>-3</sup> of water sample. The above mentioned data appears to confirm the important role of reduction processes in the biochemical sulphate transformations.

The high concentration of  $H_2S$  in 1994 in the bottom zone of the reservoir is probably a result of bacterial sulphate reduction but could also reflect the effect of the Tertiary aquifer influent, as can be seen from the  $H_2S$  concentration of piezometers 5Pb and 25Pb (Table 2).

Additional investigations are needed to assess the isotopic composition of the coexisting aqueous sulfide and sulphate to confirm the origin of the H<sub>2</sub>S, as Gammons et al. (2003) did, for it is essential for the future biological life of the lake to know whether the H<sub>2</sub>S originates from bacterial processes (sulphate transformation) or from the Tertiary aquifer water inflow. It is also possible that some of the hydrogen sulphide could originate from bacterial reduction of the elemental sulphur remaining in the sulphur ore deposit (Figure 2, chemical series) but this would seem to be of little importance. The possibility for H<sub>2</sub>S migration into the epilimnion is limited, considering the chemical stratification, difference in water density (Zurek 2006), and the meromictic character of the Piaseczno pit lake.

The dramatic decrease in concentrations of  $H_2S$ , chloride, and TDS during 1996 - 2000 was caused by increased inflow from the Quaternary aquifer to the

reservoir, which in turn was the result of an experimental cessation of pumping and discharge to the Vistula River. The effect of this step was a rise in the water level in the reservoir from 114 to 122 m ASL, and an increase of the fraction of waters from the Quaternary aquifer relative to that from the Tertiary aquifer (from  $\approx 65$  to 80%). Moreover, it is possible that a very dramatic drop in  $H_2S$  in the deep pit lake between 1994 and 1996 was due to increased influx of F-rich ground water from the alluvial aquifer. Iron could have reacted with the  $H_2S$ , forming insoluble  $FeS_x$  precipitates.

A very important aspect of the inundation of the Piaseczno mine is predicting future water chemistry. The chemical nature of the future reservoir will be a major control on biological development and will determine the ecology in the new aquatic ecosystem. Haładus and Kulma (2001) carried out preliminary simulations on two parameters, chloride and sulphate, for the area of the Machów and Piaseczno opencasts, using a mathematical model and the MODFLOW programme. The volumes of the inflow from the Quaternary and Tertiary aguifers and from surface run-off into the Piaseczno reservoir as well as the outflow from it were calculated. In the hydrochemical prognosis, the authors used the influent values of chloride and sulphate ions determined by ground water monitoring for the inflow to the Piaseczno reservoir. This prognosis allowed us to calculate the mean concentrations of chloride and sulphate in the Piaseczno reservoir at the final water level of 146.0 m ASL with the simultaneous exclusion of Tertiary aguifer inflow into the Machów opencast; the model suggests that a general improvement in the Piaseczno reservoir water quality can be expected. However, Haładus and Kulma (2001) suggested that a 20% increase in chloride levels, to 213 mg L<sup>-1</sup> Cl, with a simultaneous 33.8% decrease in SO<sub>4</sub> concentration to about 530 mg L<sup>-1</sup> SO<sub>4</sub>, is possible. They calculated initial concentrations of 177 mg L<sup>-1</sup> Cl and 801 mg L<sup>-1</sup> SO<sub>4</sub> for the whole reservoir, which are similar to their levels in the surface layer of the reservoir, down to 5 m (Table 3). This may suggest that the water chemistry prognosis by Haładus and Kulma (2001) will only pertain to the surface layer of epilimnion waters in their mixing zone but not the entire reservoir. In addition, the extent to which the experimental rise in the water level in the reservoir in 1996 altered the water chemistry, especially with respect to chloride and TDS (Table 3), suggests that a new hydrochemical equilibrium and new reservoir stratification will develop. Confirmation of this hypothesis requires further monitoring and modelling.

According to the regulations of the Polish Ministry of the Environment for surface freshwater quality, water in the Piaseczno pit in years 1994 – 2000 was of poor quality (Table 3), especially with respect to TDS and calcium, chloride, and sulphate ion concentrations. The high TDS exceeded the standard value for the worst class (V) of freshwater. Its maximum value in 1994 amounted to 9320 mg/L in the pit's bottom zone. The calcium and chloride concentrations similarly exceeded the threshold levels for the class V water quality in the bottom layer; concentrations in the epi- and metalimnion were respectively class IV, II and III. Regardless of the water profile depth, the sulphate concentrations were 1.5 to 3.5 times the standard values for class V water.

Assuming that the meromictic character of the lake will remain the same and that the seasonal water mixing in the whole water profile will not occur, sharp deterioration of the water quality should not be expected in the future. Higher salinity in the main water body should not restrict the recreational character of the future artificial lake. Because of the relatively high resistance of fish species to salinity, the Piaseczno lake could even be stocked with fish (cf. Forsberg and Neill 1997; Le Breton and Beamish 1998; Ložys L. 2004; Todolí and Oltra 2000; Watanabe et al. 1997). Moreover, research by Szarek-Gwiazda et al. (2006) and Zurek (2006) indicates that the water and sediments from the Piaseczno pit lake do not have toxic concentrations of heavy metals nor excess levels of biogenic compounds. The water quality should not negatively influence the lake's biocenosis or the ecosystem's trophic chain. Summer and autumn dissolved oxygen concentrations in the photic water layer (to the level of 10 m) reached 10 – 5 mg  $O_2$  L<sup>-1</sup> for the 0 – 10 m layer, respectively (Żurek 2006). As Żurek (2006) estimated, the oxygenated layer was the thickest in winter and could achieve the 15 m level. Below this part of the hypolimnion and beyond the reach of light, the water is free of oxygen. These data suggest that the oxygen level will not constrain biological life (including fish) in the Piaseczno pit lake, especially in the epilimnion zone. Fish, such as crucian, roach, perch, and pike, have been present in the lake for several years.

The current prognosis is that inundation of the Piaseczno opencast to 146 m ASL will take 6-7 years (Kulma and Haładus 2001). The proportion of the Quaternary to the Tertiary waters is estimated to be 93% to 7%, respectively. It is possible to supply water from the Vistula River by a siphon system to inundate the pit more quickly. This kind of operation could cause a significant change in the water chemistry over a short period of time (about four years). Either way, when the reservoir is full and the water table stabilised, the volume of the lake will be  $30 \cdot 10^6$  m³. In order to maintain a constant water

table, an average volume of 6000 m<sup>3</sup> d<sup>-1</sup> of the water will have to be discharged to the river, though the reservoir will not be a lake of constant flow. Kulma and Haładus (2001) predict that the period of water exchange will be about 13 years.

A very important consideration during the inundation process will be the removal of the abundant vegetative cover (originating from natural succession) from the slopes of the opencast scarps. At present, about 60% (ca. 57 ha) of the slope surface is covered with clumps of trees that are more than 20 years old. It is unfortunately impossible to reconcile the technical requirements of the post-mining inundation with preservation of the present landscape, and the semi-natural flora and fauna habitats. The trees, shrubs, and grasses must be successively removed, together with the surface layer of soil, to protect the reservoir waters against eutrophication caused by a sudden enrichment in carbon, nitrogen, and phosphorous. Excessive enrichment in organic matter could also increase the bacterial process of sulphate reduction. However, in the transitional phase of the inundation, while the water table in the reservoir is rising, it will be necessary to plant bands of grasses as biological barriers to minimize erosion and leaching of soil contaminants (especially sulphate and chloride) to the reservoir (Szarek-Gwiazda et al. 2006).

### Conclusion

Our preliminary research suggests that the artificial lake in the Piaseczno mine pit could be used in the future as a fish and wildlife habitat as well as for recreational purposes. Relatively high concentrations of sulphate and chloride ions will probably determine the physical, chemical, and biological transformation processes and the future hydro-chemical balance of the reservoir. Additional detailed monitoring and modelling is needed to accurately characterise the hydrochemical processes in the particular water zones in the reservoir. This should include determining the extent of bacterial sulphate reduction and H<sub>2</sub>S formation, as this will be very important for the biological life of the whole lake ecosystem.

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