

## **SOME ASPECTS OF CHEMICAL COMPOSITION OF GEOLOGICAL STRUCTURE OF „ANTROPOGENIC LAKE DISTRICT”**

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The research results of some aspects of soil chemical composition in the surroundings of the biggest pit, acid reservoir located on Łuk Mużakowski (SW Poland) are presented. Samples were taken every 1m depth, from three 25m deep, boreholes and content of TOC, iron, calcium and aluminium was analyzed. Boreholes were located in the closest neighbourhood of the reservoir, one on side of groundwater inflow, two others on the opposite site. Watertable in each places was confined and groundwater had the chemical composition typical for AMD. Geological structure consisted mainly from sand and clay with sand and brown coal layers. Concentrations of TOC varied from trace amounts to 22,65% dry mass dependently on geology. Soils under research contained high amounts of iron and were poor in calcium. Aluminium concentrations were imperceptibly lower than iron ones and varied from 0,27 to 7,45% dry mass. The following conclusions were formulated: chemical composition of soils stayed under influence of interactions with AMD, the content of iron and calcium may be the result of secondary minerals precipitation form AMD, lack of calcium created conditions favourable water and soil acidification.

Keywords: AMD, soil acidification, soil chemical composition

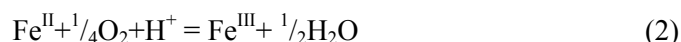
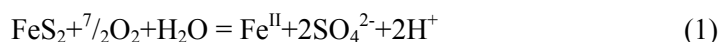
### **1. INTRODUCTION**

Antropogenic lake district is located along the polish-german border between Trzebiel and Łęknica. It comprises about 100 reservoirs of different size and chemical properties. The reservoirs were generated due to lignite mining which started in the second half of the 19-th century and was lasting till seventies of the 20-th century. The research presented below, were focused on the biggest lake, numbered 54 (Jędrzak 1992). From the previous study it is known, that the lake is extremely acidic with high concentration of iron and sulphur. The reservoir is classified to the meromictic type with relatively deep monimolimnion (more than 10 m) (Solski, Jędrzak 1991a). The chemical

composition of its waters was previously presented (Solski, Jędrzak 1990; Solski, Jędrzak 1991b; Jędrzak, Jachimko, Najbar 1998). Geological conditions were presented by Gontaszewska et al. (2007). The aim of the research was to recognize the chemical composition of the geological structure of the lake surroundings and interactions of soil with ground and lake waters.

## 2. THEORETICAL BACKGROUND

Mining wastes containing sulphides are the most common sources of acidity (Dubikova et al., 2002). If groundwater was protected before oxygen from the atmosphere, the acidification processes caused by pyrite weathering were blocked. Resulting mining activity aquiferous layer was air opened and brought into contact with oxygen. It started sulphides, especially pyrite weathering processes due to the following reactions (Evangelou 1995):



The process are accelerated by high contamination of ferric compounds. Nordstrom (1982) pointed, that in the pH values below 4,5 pyrite is oxidized by Fe III more rapidly than by oxygen. Under pH below 3 the conversion of ferrous to ferric (reaction 2) is the limiting step of pyrite oxidation. Wisotzky (1996) calculated, that the pH of water in equilibrium with pyrite is about 1. In the pH range the aluminum silicate begin to weather. The silicate weathering increase water pH to above 3. Further acidity neutralization may be caused by base components such as calcium or magnesium salts. The processes described above produce extremely acid, sulphate and iron rich waters named acid mine drainage (AMD). The chemistry of AMD influence on soil composition on different ways. The weathering of clay minerals by AMD is affected by its composition. AMD contains cations which suppress the release of alkali and alkali-earth ions from the soil and cause the precipitation of amorphous material and secondary minerals. The stability of clay minerals under aggressive weathering conditions depends on their chemical composition and organic matter concentration. The weathering processes are followed by the precipitation of secondary minerals, such as iron and aluminum hydroxides and hydroxysulfates and calcium sulfates, mainly gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) (Blodau, 2006). Interactions of AMD with soils affect surface exchange properties, coating with oxyhydroxides,  $\text{SO}_4$  retention on Fe and Al oxides, formation a new minerals in soils.

## 3. AREA OF STUDY

The area under study is located about 2 km far on the east, from Łęknica, 2.3 km on the west from Przewoźniki and 2 km on the south from Nowe Czaple (fig. 1.). The reservoir is surrounded by strongly eroded heap of excavation. The surrounding area is covered by forest. The morphometry of the reservoir is presented in Table 1.

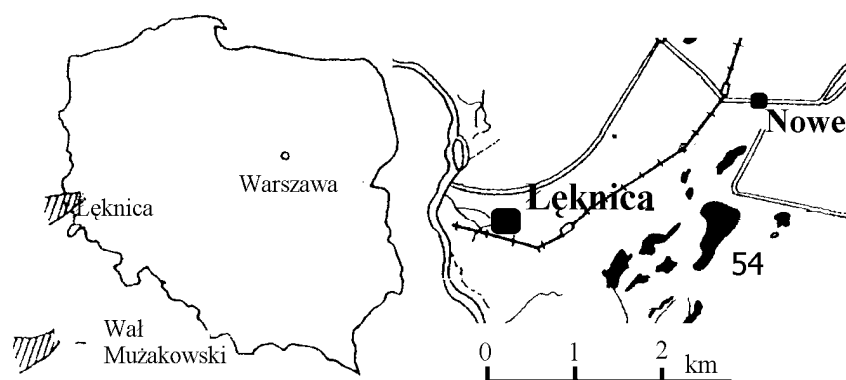


Fig. 1. The area of study

Table 1. Morphometry of the reservoir no 54

water level	surface area	max length.	max width.	extension coefficient	max depth.	shoreline length	shoreline development
[m above s.l]	[ha]	[m]	[m]		[m]	[m]	[m]
132,0	20,2	896	468	1,91	21,5	2625	1,65

The water balance for this reservoir consists from the following components: inflow - underground tributary and precipitation and outflow - underground outflow and evaporation. The reservoir has no connections with surface water like streams or other lakes. It results in the fact, that the chemical composition of its waters depends mainly on the composition of ground water, precipitation and reactions within water body. On the base of more than 30 years of monitoring, one can notice, that the acidification of its waters is still becoming larger. Although the pH value increased from 2.5 in the mixolimnion to above 4 in monimolimnion, the values of the neutralization potential (Schoepke, 1999) increased from about -13 (surface water) to above -56

mmol/dm<sup>3</sup> (water close to the bottom). The concentration of iron, calcium and sulphate in water profile varied respectively from 129, 78 and 1123 (surface) to more than 1500, 400 and 4200 (21 m deep) mg/dm<sup>3</sup>. The aluminum amount decreased with the depth from 35,2 (surface) to 18,3 mg/dm<sup>3</sup> (close to the bottom).

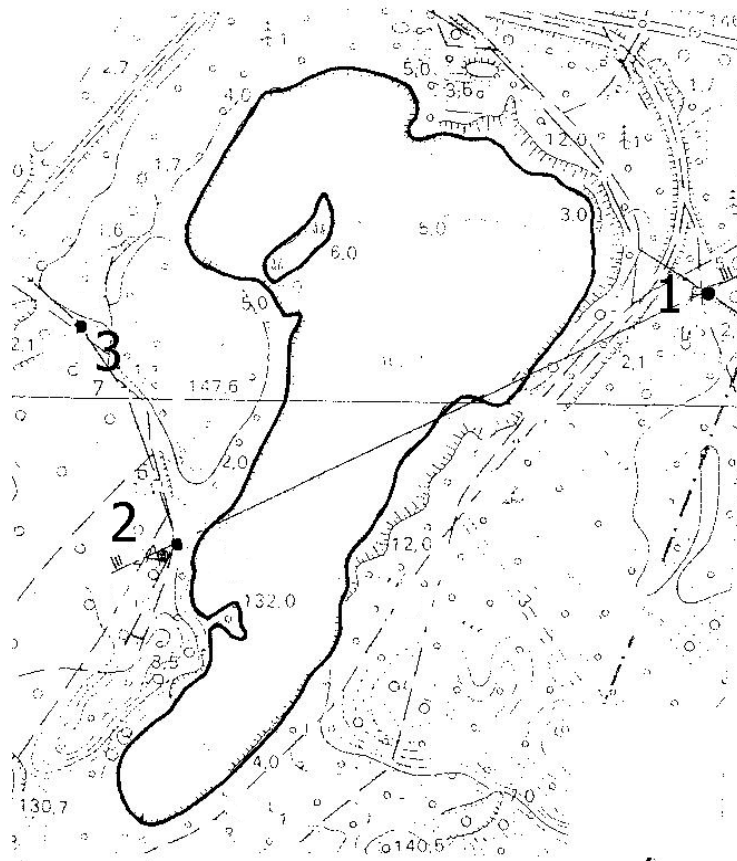


Fig. 2. Location of the piezometers

Piezometer 1 was located on the ornate high heap of excavation. Terrain level is there 10 m higher than lake watertable. Piezometers 2 and 3 were bored on the opposite side of the lake. They are located 4 and 7 m higher than lake surface. All piezometers had confined watertable located from 0,46 to 7,12 m H<sub>2</sub>O below lake water level. Unconfined watertable was almost on the same level as the water surface in the reservoir (tab. 2). Groundwater flows in direction EW from piezometer 1 to piezometers 2 and 3.

Table 2. Watertable location, m below sea level

Location	Lake surface	Piez. 1	Piez. 2	Piez. 3
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confined	-	132,37	124,63	124,55
unconfined	132,0	132,73	131,13	130,67

Water, which flowed into the lake (piezometer 1) had low mineralization, pH value about 4,4 and low concentration of other ions. Ground water composition in piezometers 2 and 3 was strongly influenced by monimolimnion lake water (Kołodziejczyk, Jachimko, 2008). Although piezometers 2 and 3 were located closed to each other, groundwater composition differed extremely. High mineralization level pointed on the monimolimnion influence on water composition. Water in piezometer 2 was very acid with pH value 2,51, contained high amounts of iron, aluminum and calcium. Water in piezometer 3 had the highest pH value and calcium concentration but aluminum amounts stayed on the comparable level as in piezometer 1. The main parameters of groundwater composition are listed in the table 3.

Table 3. Composition of groundwater (Jachimko, unpublished)

Parameter	Unit	Piez. 1	Piez. 2	Piez.3
pH	-	4,38	2,51	5,82
conductivity	mS/cm	0,104	2,60	1,33
iron total	mg/dm <sup>3</sup>	7.44	95,5	65,4
aluminum	mg/dm <sup>3</sup>	0,081	63.52	0,041
calcium	mg/dm <sup>3</sup>	11	104	116

#### 4. METHODS

Soil samples were taken from three, the 25 m deep, bore holes located round the lake (fig. 2.). Samples were taken approximately every 1 m of the depth. Aluminum, iron and calcium concentrations were measured using Atomic Adsorption Spectroscopy (Spectrometer Varian type AAS 10) after digestion of dry samples in a mixture of 3 parts of HCl and 1 part of HNO<sub>3</sub>. Total organic carbon was calculated as the difference between total carbon (TC) and total inorganic carbon (TIC). TC and TIC were analysed by TOC Analyzer Shimadzu SSM after drying in 105°C.

#### 5. RESULTS

Chemical composition of soils under discussion varied with geological structure (fig. 3) and groundwater conditions. In the piezometer 1 four, thin brow-coal horizons were found: three of them in aeration zone on depths 0,9-1,4, 4,2-5,7

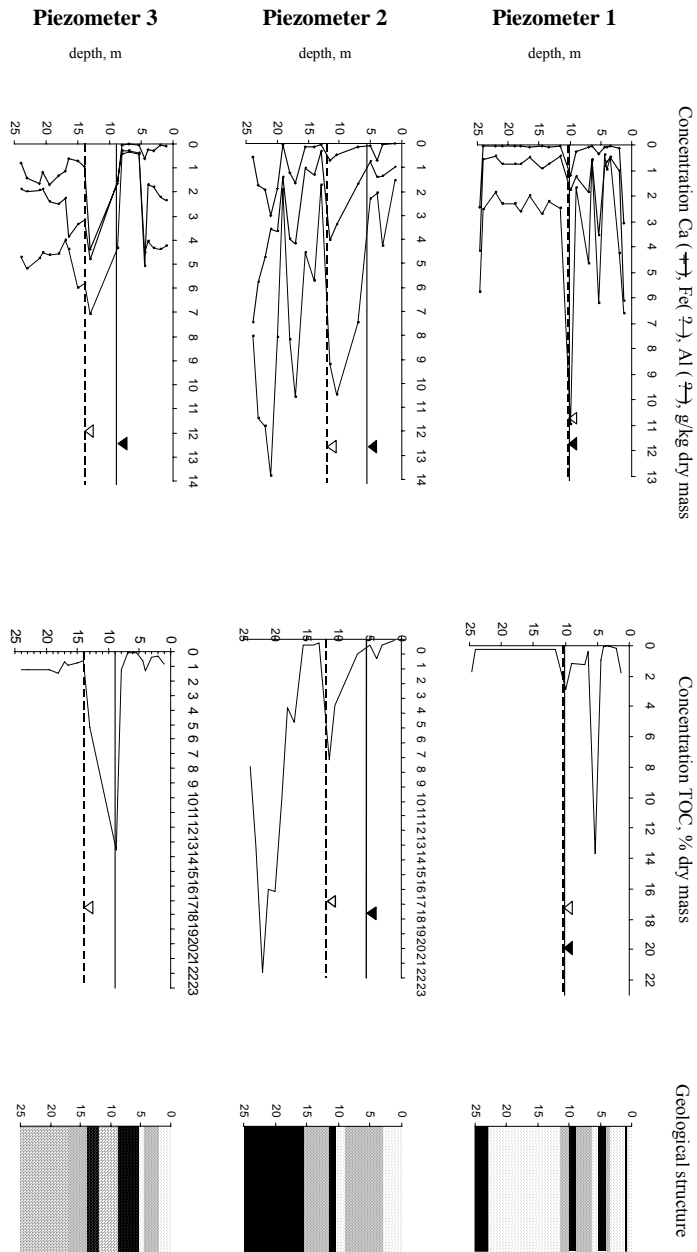


Fig. 3. Chemical composition of soil

and 9,5-10,5 m and one in saturation zone on depth 24,0-2,4,5 m. The highest amount of TOC (13,71% dry mass) was stated on the depth 5,4 m in the second coal strata. The concentration of carbon in the others coal-layer samples was low and didn't exceed 3% dry mass. The concentration of TOC in another, sand and sand with humus stratum were even lower. In the aerated sand with humus strata TOC varied from 0,11 to 1,21% dry mass. In the saturated sand layer, between 10,5 – 24,5 m depth, concentration of TOC didn't exceed 0,25 % dry mass. In the piezometer 2 there were two coal horizons, separated by sand with humus strata, located on the depth 10,5-12,0 m and below 15,7 m. Both coal stratum stayed within saturated zone. Aerated zone consisted of two sand stratum separated by sand with humus layer. Concentration of carbon increased with the depth from surface to the watertable, decreased in the sand layer between 14-15,5 m (where the concentration of carbon was below 0,5 % dry mass), and then increased again in the deepest coal strata. The highest amount of TOC (22.65 % dry mass) was found on the depth 22 m. In the piezometer 3 there was only one, very thin (0,3 m) coal-layer located on 8,6-8,9 m depth, between sand-coal stratum. The concentration of carbon in this sample equaled 13,58 % dry mass. The impurities of coal was found also in the clay layer, between 9,0 and 14,0 m depth. Above and below it, within sand and ash layers, the concentration of TOC doesn't exceed 1,5 % dry mass.

The relationships between iron, aluminum and calcium concentrations had the similar pattern independently on sample geological structure. In every sample the highest concentration of iron, then aluminum and the lowest amounts of calcium were found. The amounts of iron and aluminum stayed in the range respectively from 0,002 to 13,58 and 0,33 to 7,08 g/kg dry mass. In the piezometer 1 iron concentration varied from 0,42 to 10,94 g/kg dry mass in the aeration zone and changed in a very narrow range, between 1,85 to 2,64 g/kg dry mass, in subsoil below groundwater table. Aluminum concentration in the top soil was almost equal to the iron amount and varied from 0,49 to 6,11 g/kg dry mass. In the saturation zones, on 10,5-24 m depth, aluminum amount didn't exceed 1 g/kg dry mass. The soils contained very low concentration of calcium, which varied from 0,02 to 4,37 g/kg dry mass. The lowest amounts of calcium were found in sand stratum, especially below water level, where calcium concentration didn't exceed 0,1 g/kg dry mass. Higher amounts, more than 1 g/kg dry mass, were stated in clay and coal stratum. In the piezometer 1 below water level the plots showing the concentration of calcium, aluminum and iron were almost parallel. In piezometer 2 concentrations of calcium, aluminum and iron varied with depth and no pattern of changes can be found. The lowest concentration of cations were found at upper layers from terrain surface to 5 m depth and at depths 13 and 19 m. The highest amounts were detected in brown coal strata at depth 10-11,5, 17 and 21 m (with exclusion of aluminum

concentration, the highest concentration 7,45% dry mass, were detected at 24 m depth). The concentration of iron, aluminum and calcium in soils from piezometer 3 varied in narrower range than in piezometer 2 although geological structure seemed to be much more complicated. In the upper sand and sand with humus stratum the amounts of cations are similar. Highest amounts were found at 5 m depth and then decreased to the lowest values in this place. Between 9 and 13 m depth cation concentrations increased significantly and reached the highest values at depth 13 m. Below it the concentration of cations varied in a narrow range.

## 6. DISCUSSION OF RESULTS

The geological structure of the boreholes under research was very complicated and consisted of many, often very thin, stratum, mainly sand, coal or sand with humus, clay or ash impurities. Groundwater recharge were located within fine and silty sand layer of the thickness from 3 to 14 m. Aquifers were separated from precipitation by impermeable brown-coal strata in the piezometers 1 i 2 and by clay with coal in piezometer 3. Chemical composition of soils was very differential. The concentration of calcium in aeration zone in each location was very low, which excluded calcium buffering. In addition high amounts of aluminum and iron accumulated there were natural reservoir of acidity. Shallowly covering coal strata had contact with oxygen in the presence of iron compounds. It created conditions for pyrite weathering and enriched soil water in protons and sulphate ions. Peaks of concentration on the border between aeration and saturation zones can be explained by precipitation of secondary minerals due to water table variation. Chemical composition of soil in saturated zone stayed under strong influence of groundwater. The most stable chemical composition was found in saturation sand zone in piezometer 1. Groundwater in piezometer 1 is saturated with aluminum (alunite  $KAl_3(SO_4)_2(OH)_6$ , gibbsite  $Al(OH)_3$ ) and ferrous (goethite  $FeOOH$ ) compounds and unsaturated with respect to calcium. It gives conditions, in which the coating of sand grains by iron and aluminum oxides is possible (Sucha at al., 2002). Small amounts of TOC and calcium made impossible neutralization water acidity by cation exchange (Bache B.W., 1984) or biochemical sulphate reduction. In piezometer 3 groundwater was saturated with aluminum ( $Al(OH)_{3am}$ ), ferrous ( $Fe(OH)_{3am}$  and siderite  $FeCO_3$ ) and calcium (gypsum  $CaSO_4 \cdot 2H_2O$ ). The amounts of calcium, iron and aluminum were bigger than in piezometer 1 sand layer due to smaller grain size and greater surface area in ash layer. Soils in piezometer 2 had the most complicated chemical composition and the biggest amount of iron. It may be the results of interaction with groundwater of high mineralization (adsorption equilibrium) and the presence of pyrite within coal layer.



## 7. CONCLUSIONS

1. Concentration of calcium, aluminum and iron in analysed soils depended on geology and aquifer conditions (contact with AMD).
2. All analysed soils contained high amounts of iron and very low amounts of calcium
3. High amounts of aluminum and iron accumulated in soils are natural reservoir of acidity.
4. Chemical composition of geological structure in the area of the reservoir 54 favored acidification due to exposure of pyrite coal layer on oxygen in aeration zone, high contamination of iron and aluminum compounds and lack of calcium salts.

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