

# Vertical Changes of Iron and Manganese Concentration in Water from Abandoned “Zakrzówek” Limestone Quarry near Cracow (South Poland)

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## Abstract

The “Zakrzówek” quarry is located in the south-western suburb of Cracow, about 600-900 m to the east of the Vistula riverbed. Exploitation of the Upper Jurassic limestone reached about 30 m below the static water level. Flooding process was started in 1992 after the mine abandoning and finished in the summer 1997 after extremely flood event. As a result of the high relative depth of the pit lake the stratification of the water column is observed. The deepest part of the “Zakrzówek” reservoir contain water with highest TDS and also the anoxic zone is present on a depth of 20 m. Iron and manganese concentrations within water body are strongly influenced by varying redox potential.

**Key words:** Zakrzówek quarry, Upper Jurassic limestones, pit lake, aquatic chemistry, iron, manganese

## Introduction

The abandoned “Zakrzówek” quarry is situated in a southern suburb of Cracow in a small horst structure formed by Upper Jurassic limestones. The limestones were mined from 1953 to 1991 to provide raw material for soda produced by Solvay’s method. The deepest limestone quarrying was at a depth of about 60 m below the surface, or about 30 m below the water level of Vistula River, which flows only 600 – 900 m away from the quarry (Fig. 1). The Vistula River is highly polluted mostly by brines originating from dewatering of coal mines in Upper Silesian Coal Basin. Agriculture, sewage and industrial wastes also provide significant contaminant loadings.

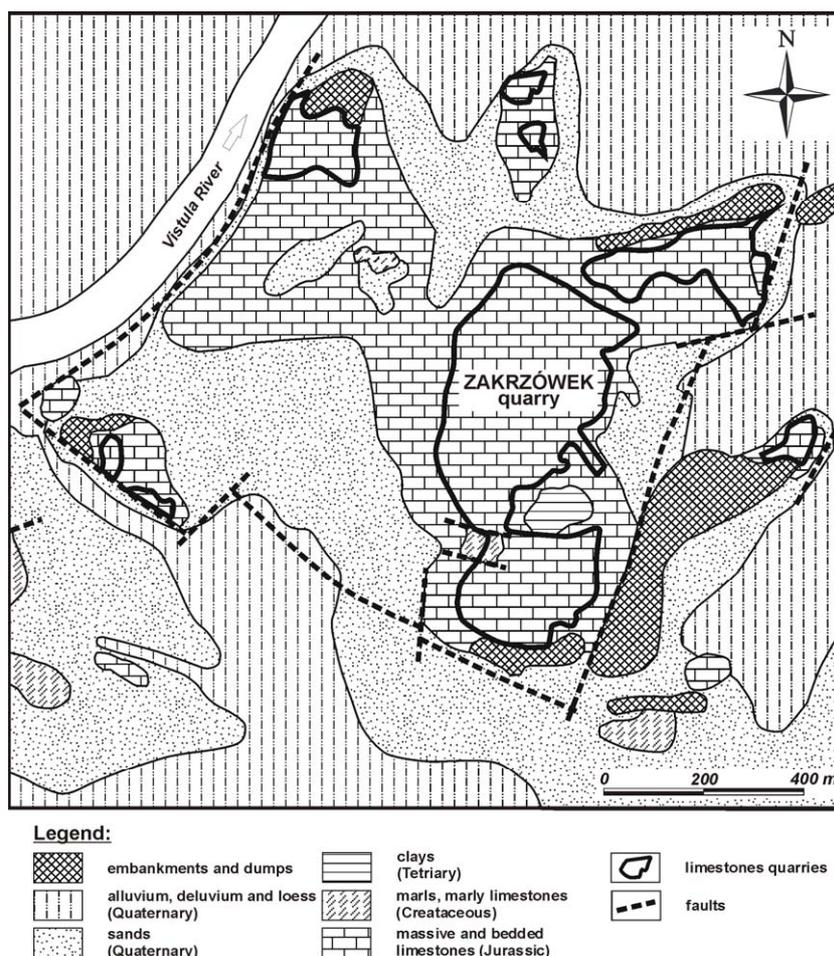
Main aquifer in the Zakrzówek horst is formed by fractured and karstified Upper Jurassic limestones. However, fractures and bedding planes are the main conduits of underground flow. Wide fractures especially favorable for water flow occur in weathered parts of the horst and in tectonic zones (Kulma et al., 1991). High-angle fractures (70 – 90°) dominate and have two principal directions: NE – SW and NW – SE. In limestones many various karst cavities and conduits can be observed. Hydraulic conductivity of Upper Jurassic karst-fissured limestones, determined by a three-step pumping test in a single well is equal  $k = 3.54 \times 10^{-5}$  m/s. Upper Jurassic limestones are surrounded by Quaternary sediments (Fig. 1), mainly water-bearing alluvial sands and gravels. The sediments in western part of the horst are directly connected with the Vistula River. Average hydraulic conductivity of the Quaternary sands and gravels is  $k = 2,8 \times 10^{-4}$  m/s. Along the eastern part and southern margins of the Zakrzówek horst, Quaternary sands are thin and dry.

In 1991 exploitation of limestone in Zakrzówek quarry was stopped and in November 1992 the process of flooding was started. The finishing of this process was accelerated by extremely flood event in a July 1997.

According to Motyka & Postawa (2000) main sources of water inflow to the quarry are as follow: (1) direct recharge by precipitation, (2) infiltration of water from Vistula River, (3) infiltration of meteoric water through the Zakrzówek horst.

Chemical composition of precipitation deposited on the area on Zakrzówek horst was measured in the period of 1996 – 2007. Dominant ions in precipitation’s water are Ca, HCO<sub>3</sub> and SO<sub>4</sub>. In the water from Vistula River, polluted by brines, the Cl and Na ions are dominant. Average concentration of Cl ion in Vistula River water during the Zakrzówek quarry flooding (1992 – 1997) reached the value of 1028.7 mg/L. However, content of this ion range from 48.2 mg/L to 2004.9 mg/L (Motyka, Czop, 2004). The chemical composition of the groundwater within Jurassic limestone aquifer is weakly explored. As a consequence of the precipitation water interaction with carbonates the Ca and HCO<sub>3</sub> are the dominant ions. Diversified proportions of the salty Vistula River water admixtures are responsible for formation of groundwater with complex hydrochemical types.

**Figure 1** Geology of the “Zakrzówek” quarry area



### Hydrochemistry of water in the “Zakrzówek” pit lake

Chemical composition of water gathered within “Zakrzówek” pit lake is monitored continuously from the moment of the starting the quarry flooding. The water samples are collected every week from the surface of the water body. The range of the hydrochemical research of the water from surface layer of “Zakrzówek” pit lake is diversified, all samples are examined for concentration of chlorides and for selected samples the complete chemical analysis is taken. For better understanding the processes influenced on the chemical composition of water within described reservoir the 5 series (1996, 2001, 2003, 2004, 2005) of the hydrochemical logging were made. The last 3 series from the period 2003-2005 were made precisely and include all important parameters and constituents.

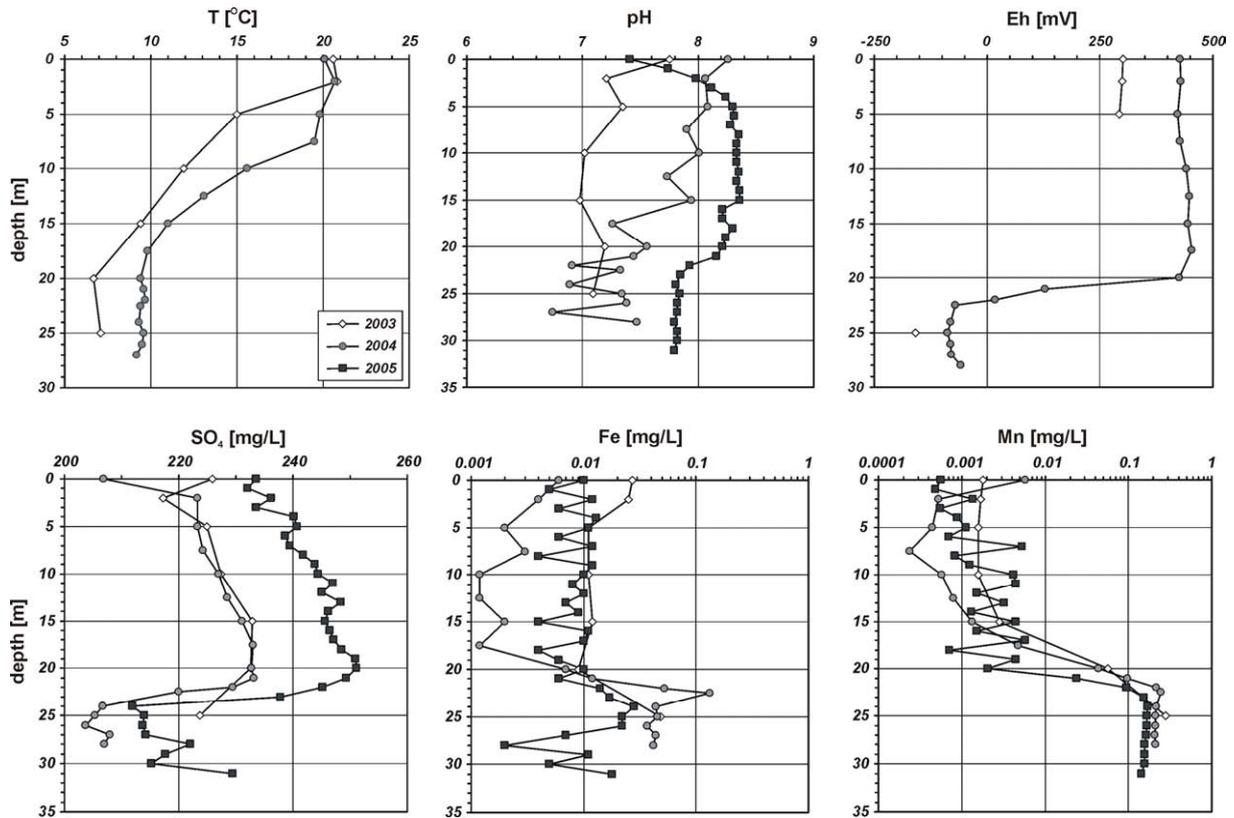
Temperature of water in the quarry was measured in May 2003 and September 2004. Upper zone of the water body to the depth of 5-7,5 m had temperatures of about 15-21°C. Temperature of water decreased gradually and in the deepest part typically range from 7 °C to 11°C (Fig. 2).

Changes of the water pH versus depth were insignificant but some trend of decreasing of pH with depth is observed (Fig. 2). In the upper part of the pit lake the pH usually ranges from 7.4 to 8.3 and in the deeper part from 6.7 to 8.3.

Redox potential (Eh) was measured “in situ” only in September 2004. Until 20 m Eh of water range from +422 to +454 mV. On the depth of 21 m the value of +129 mV was registered, below this depth the value of Eh decreasing rapidly. Measured redox potential on the depth of 22 m is +18 mV and between 22,5 m and 28 m range from -58 mV to -87 mV.

It's evident that from the depth of about 21-22 m to the bottom of pit lake the reduction conditions are present. In this zone hydrogen sulfide (H<sub>2</sub>S) was detected in 09.2004: on the depth of 21 m in concentration of 0.34 mg/L, on 22 m - 1.28 mg/L and between 22.5-28 m ranged from 53 to 62 mg/L. A large majority of the dissolved constituent concentrations in the “Zakrzówek” pit lake water column varies significantly in vertical profile.

**Figure 2** Selected hydrochemical profiles for the “Zakrzówek” pit lake



### Iron and manganese in water of the “Zakrzówek” pit lake

Among different microelements detected in water from Zakrzówek pit lake changes of iron and manganese concentrations are spectacular.

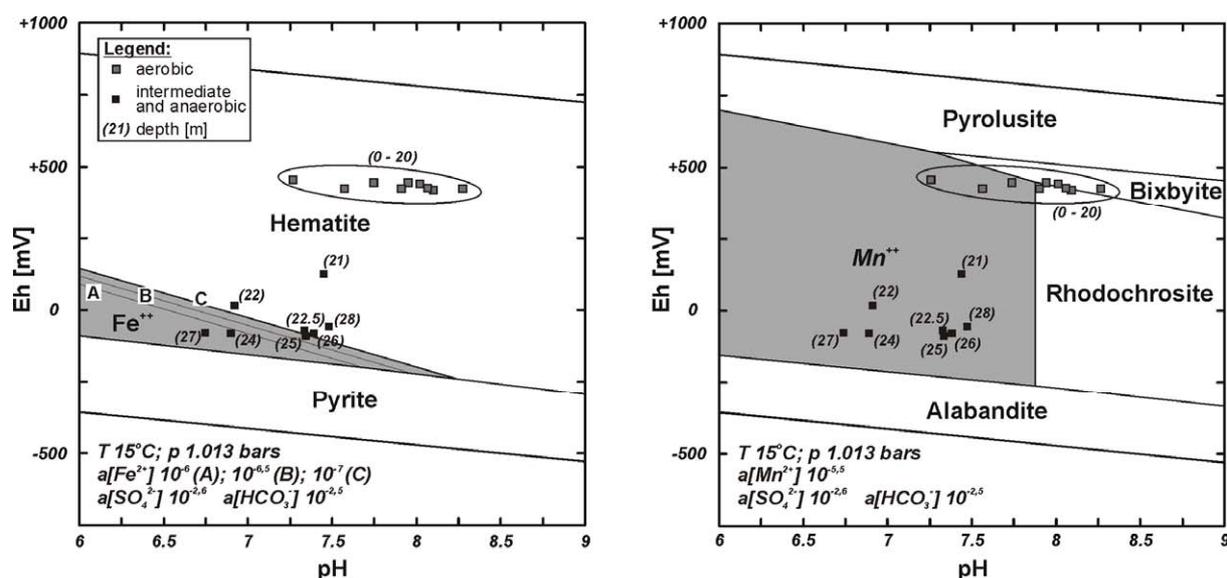
Concentration of iron was analyzed in spring (May 2003 and May 2005) and autumn (September 2004). The pattern of the concentration changes with depth for the iron is similar for all series of hydrochemical research (Fig. 2). Iron concentrations in water column between the reservoir’s surface and depth of about 20 m were similar. For example in 2003 concentration of iron in all samples was independent to the depth and ranged from 0.009 to 0.048 mg/L the same situation was observed also in 2004 and 2005. It’s also interesting that concentrations of the iron for spring series in 2003 and 2005 are similar but significantly higher than for the hydrochemical measurements from September 2004.

The deepest part of the “Zakrzówek” pit lake with anaerobic condition is characterized by enrichment of the iron in the water samples. For all measurement series the significant increase of the iron concentration was observed for the zone located on the depths between 20 m and 23 m.

Described phenomenon is particularly clear for the data from hydrochemical research of the “Zakrzówek” reservoir from September 2004. Concentrations of iron in water until 21 m of depth were very low and ranged from 0.001 to 0.012 mg/L. In the deeper part of the pit lake below the depth of 21 m the iron concentration were between 0.037 and 0.13 mg/L. This is also typical for “Zakrzówek” pit lake that below the zone of the peak content the iron concentration decreasing.

Concentration of manganese in water generally is growing slightly with depth of the Zakrzówek pit lake (Fig. 2). Similarly like in a case of iron the manganese concentrations in the reservoir’s profile are splitting to two sections. The upper parts of the water body are characterized by relatively low manganese concentration range from 0,0002 mg/L to 0,005 mg/L. The enrichment of manganese in water samples is beginning on the depth of about 20 m. The concentrations of this element increasing significantly and range from 0,02 mg/L to 0,28 mg/L. The difference in comparison with the pattern of iron changes with depth is also observed for manganese concentration in the deepest parts of the “Zakrzówek” pit lake. Water column between the depths of 22 m and 31 m contain practically the same quantities of the manganese.

Figure 3 Redox-pH diagrams for iron and manganese



## Conclusions

Concentration of iron and manganese in the vertical profile of water column in abandoned Zakrzówek quarry strictly depends on redox condition.

The upper part of the “Zakrzówek” pit lake from the water body surface to the depth of about 20 m is in the aerobic condition, with the values of the redox potential about +400 mV. According to the standard redox-pH diagram in oxidizing environment the low-soluble speciations of ferric iron ( $\text{Fe}^{3+}$ ) are dominant (eg. hematite or ferrihydrite) (Hem, 1992; Bethke, 2004).

The deeper part of the “Zakrzówek” pit lake from the depth of about 21-22 m is in the anaerobic conditions. The redox potential (Eh) in this zone tends to the negative values and range from +18 mV to about -80 mV. The thermodynamic equilibrium is shifting to ferrous iron form ( $\text{Fe}^{2+}$ ) with relatively higher solubility in water. As a consequence the increase of the iron concentration in the intermediate zone of “Zakrzówek” pit lake (between the depths of 21-23 m). Decrease in iron concentrations in the deepest part of water reservoir is connected with possible lowering of the redox potential and formation insoluble ferric sulfides (pyrite). The next possible scenario for water layer close to the pit lake bottom is the decreasing of the redox potential and thermodynamic equilibrium shifting to the hematite form of iron.

For the manganese in the upper oxidized zone of “Zakrzówek” pit lake relatively higher values of pH promote the formation of the rhodochrosite ( $\text{MnCO}_3$ ) or bixbyite ( $(\text{Mn,Fe})_2\text{O}_3$ ). In the deeper part of the described artificial reservoir in the anaerobic condition the bivalent manganese ions are dominant speciation. Formation of the low-soluble manganese sulfides (eg. alabandit –  $\text{MnS}$ ) is also possible in this zone in scenario of further decrease in redox potential.

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