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MICROBIOLOGY OF ACID WATERS ANS FERRUGINOUS PRECIPITATES FORMATION IN THE POLISH PART OF THE MUSKAU ARCH – PRELIMINARY RAPORT

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Summary: This work presents preliminary results of mineralogical, geochemical and microbiological investigations carried out in the Polish part of the Muskau Arch. As a result of sulphide oxidation in this abandoned mining area, highly acidified Fe-rich waters have been formed. Ferruginous precipitates composed mainly of schwertmannite, goethite, jarosite and gypsum accompany them. Both the water chemistry and the rate of the sediments formation vary significantly due to seasonal weather changes and microbiological activity.

Key words: AMD environment, pyrite oxidation, the Muskau Arch, schwertmannite, goethite, jarosite, microbiological variability

1. INTRODUCTION

The Muskau Arc is a large glacitectonic belt formed mainly during Saale glaciation. This horseshoe-shaped structure is open to the north and crosses the Polish-German border (from Brandenburg, via Saxony to the Lubuskie voivodeship in Poland). Intense glacitectonic disturbances lifted Miocene lignite beds (as well as co-occurring sands and clays) towards the Earth's surface. These deposits were exploited in numerous open-cast mines, from the late 18th to the late 20th century. Both the operation and abandoning of the mines were moving from the north (from Tuplice region). The last active lignite mine pit "Babina" (located on the south east of Łęknica) was closed in the early 1970-ties. The abandoned mine areas have been filled with water forming so-called "anthropogenic lakeland". Sulphuric acid forms as a result of oxidation of sulphide minerals (mainly pyrite) of coal beds, resulting in water acidification and creation of the Acid Mine Drainage (AMD) type environment. Released iron and sulphate precipitate as ochreous accumulations. Both water and the accompanied precipitates are the object of interest in this study.

2. MATERIALS & METHODS

During the field works, started in November 2005, about 65 water and precipitate samples ware collected (Fig. 1 – long arrow). Temperature, electrolitic conductivity and pH of the water were measured *in situ*. Then the samples were filtered using 5 μm filters and stabilized with HNO_3. The cation concentrations ware estimated using ICP-MS (Ca, Mg, Mn, Al, As) and FES (Na, K). Talat Fe as well as selected anions (NO_2^-, NO_3^-, SO_4^{2-}) were measured by VIS spectrometry and Cl^- by titration with $AgNO_3$.
The mineral composition of freeze-dried precipitates was evaluated using X-ray diffraction (XRD), thermal analyses (DTA) and scanning electron microscopy (SEM-EDS).
The paper presents also preliminary results of water microbiological investigations near Łęknica (Fig 1 – short arrow). They started in September 2009 and completion of research is planned in August 2010. Monthly collected samples at five selected localities are subject to both microbiological and chemical analyses. Chosen groups of microorganisms have been incubated on Petri dishes or in tubes and then characterized qualitatively and quantitatively after specific time of incubation. The optimal incubation time and the temperature are different for diferent types of microorganisms. These parameters are: 24 hours and 37°C for mesophilic bacteria, 72 hours and room temperature for psychrophilic bacteria, about 10 days and 28°C for heterotrophic ferric bacteria, *Acidothiobacillus ferrooxidans*, filamentous bacteria of the genus *Leptothrix* and fungi. Also a growth medium must be specific to particular types of microorganisms. Psychro- and mesophilic bacteria are incubated on MPA medium, heterotrophic ferric bacteria on the medium based on Winogradski receipt, *A. ferrooxidans* on 9K medium, fungi on the Czapek-Dox medium [Olańczuk-Heyman 1998].

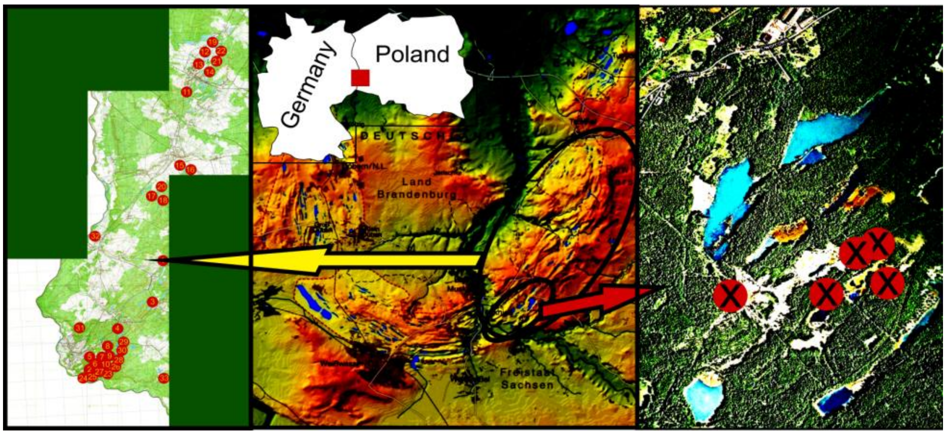

Fig. 1. Map of study area with sampling points for mineralogical-hydrogeochemical (long arrow) and microbiological (short arrow) investigations (sources: Kupetz 2009, Google Maps satellite image)

3. RESULTS

A distinctly low pH value (2.49-7.42; median 3.24) and high electrolytic conductivity (250-3100 μS/cm, median 1399 μS/cm) are typical of the analyzed water samples. High concentrations of Fe, Ca and SO_4 (up to 530, 376 and 2987 mg/l, respectively) have been found (Fig. 2). On the other hand, sodium and potassium levels are relatively low (up to 14 and 20 mg/l, respectively). Seasonal changes in concentration of major ions and physico-chemical parameters have also been observed (data not presented here). This variability is related mainly, but probably not solely, to the changing weather conditions.

The precipitates are reddish-brown and orange. They are highly porous and contain numerous organic remnants (for example tree leaves). In many cases, especially during a low humidity season, white, yellowish or transparent, large gypsum crystals (up to 1-2 mm in size) cover the sediment surface.

Mineralogical investigations have shown that, apart from gypsum, the main constituents of the precipitates are goethite α-FeOOH, schwertmannite $Fe_{16}O_{16}(OH)_{12}(SO_4)_2 \cdot nH_2O$ and jarosite $KFe_3(OH)_6(SO_4)_2$. According to the XRD patterns, goethite can either be well or poorly crystalline, depending probably on the formation conditions, mainly water chemistry. Schwertmannite, on the contrary, is always poorly ordered (Fig. 3 a) and usually forms typical of this hydroxysulphate, hedgehog-like aggregates of small (< 2 μm long), needle-shaped crystallites (Fig. 3 b, c).

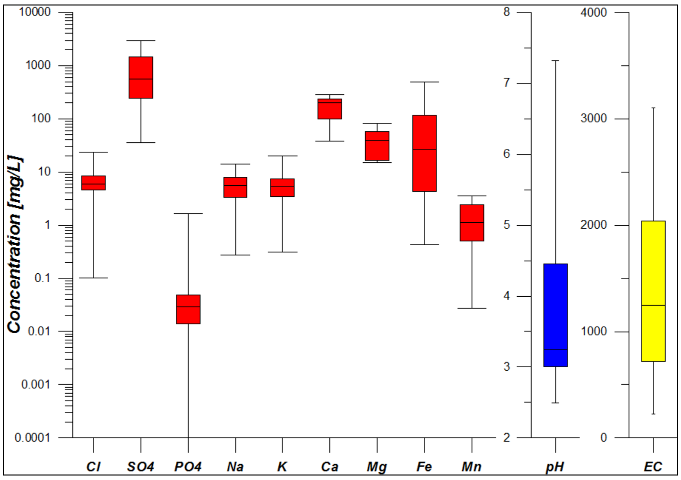

Fig. 2. Variability of water composition from the Łękinca area

Table 1. Comparison of water microbial communities in autumn and winter (data for one sampling point)

	Month	
	October 2009	***February 2010***
The average number of bacterial cells in a 1 cm^3		
Psychrophilic	76	2
Mesophilic bacterias	307	2
Leptothrix sp.	10	4
The average number of fungal colonies in a 1 cm^3		
Fungi	5	0
The average titer value found for each group of bacteria in 1 cm^3		
Acidithiobacillus ferrooxidans	$1*10^{-1}$	0
Heterotrophic ferric bacteria	$1*10^{-3}$	$1*10^{-1}$

Surface morphology of schwertmannite may indicate that it has been formed as a result of mircobiological activity (biotic path). Jarosite, in contrast, occurs usually in the form of well-crystalline bipyramids (Fig. 3 h, i) a few μm in size. Both the shape and the size of the jarosite crystallites suggest that it the mineral precipitated abiotically.

Preliminary microbiological investigations have revealed relatively low amount of psychro- and mesophilic bacteria and fungi in the water samples studied (Table 1). However, *Acidithiobacillus ferrooxidans* and heterotrophic ferric bacteria are relatively numerous. A very clear variability in their number depending on the ambient temperature (season) has been observed, in particular for the fungal population and colonies of *A. ferrooxidans*.

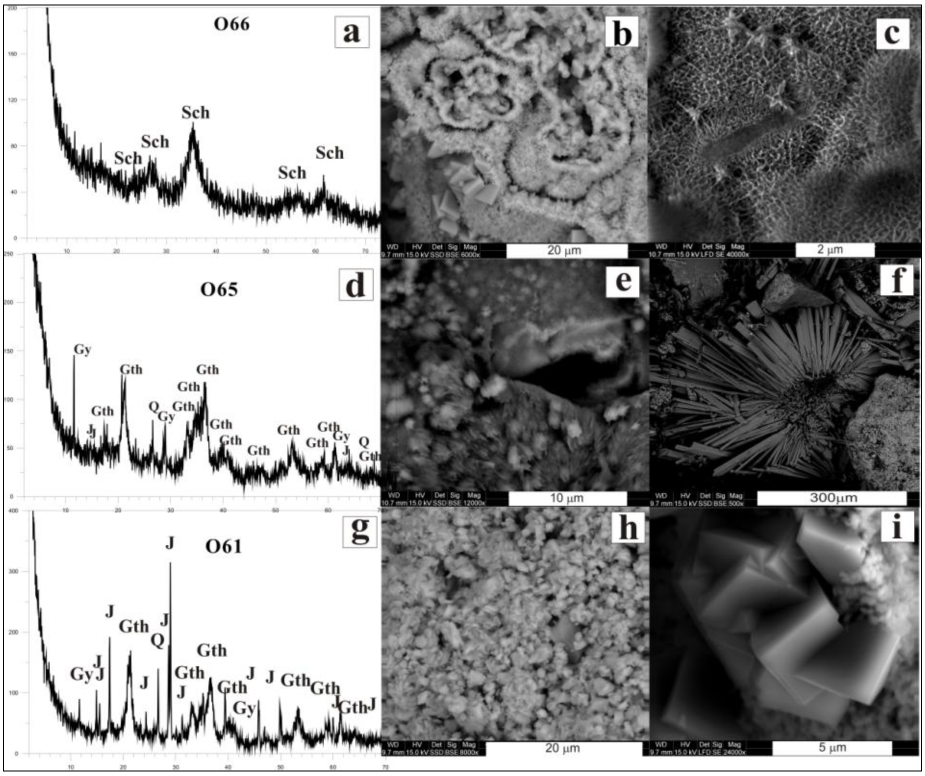

Fig. 3. XRD patterns and SEM micrographs of the precipitates. (a)(b) (c) schwertmannite, (d)(e) goethite (f) gypsum, (g)(h)(i) jarosite. Explanation of symbols: Sch – schwertmannite, Gth – goethite, J – jarosite, Gy – gypsum, Q –quartz

4. DISCUSION

The formation of ferric oxyhydroxides and hydroxysulphates is a result of iron oxidation and hydrolysis. Ferrous ion oxidation is, however, very slow in an acidic environment, so in autors opinion microbial communities play an important role in the process. The pH value and concentration of sulphate determine which ferrugineous phase precipitated. At the lowest pH (<3) and highest (SO_4^{2-}), jarosite is preferentially formed. When the pH value increases (3–4) and sulphate concentration decreases, schwertmannite precipitates instated of jarosite [Bingham 2000, Schwertmann 1995]. Such a mineral association is rather typical of AMD environments. It is noteworthy, however, that schwertmannite, which was first recorded in 1994 in Finland [Schwertmann 1995], has not been well known so far, especially in Poland, where it has been found only twice [Parafiniuk, Siuda 2007].

5. ACKNOWLEDGEMENTS

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MIKROBIOLOGIA KWAŚNYCH WÓD A TWORZENIE SIĘ ŻELAZISTYCH OSADÓW W POLSKIEJ CZĘSCI ŁUKU MUŻAKOWA – WSTĘPNE WYNIKI

S t r e s z c z e n i e

W pracy przedstawiono wstępne wyniki badań mineralogicznych, geochemicznych i mikrobiologicznych wykonywanych w polskiej części Łuku Mużakowa. W wyniku utleniania siarczków w tym opuszczonym obszarze górnictwa tworzą się wody bardzo zakwaszone oraz bogate w żelazo. Osady żelaziste składają się głównie z schwertmannitu, goethytu, jarosytu oraz gipsu. Zarówno chemia wody oraz tempo powstawania osadów różnią się znacząco ze względu na sezonowy warunki pogodowe i aktywność mikrobiologiczną.