

Original papers

OCHRE PRECIPITATES AND ACID MINE DRAINAGE IN A MINE ENVIRONMENT

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This paper is focused to characterize the ochre precipitates and the mine water effluents of some old mine adits and settling pits after mining of polymetallic ores in Slovakia. It was shown that the mine water effluents from two different types of deposits (adits; settling pits) have similar composition and represent slightly acidic sulphate water (pH in range 5.60-6.05, sulphate concentration from 1160 to 1905 g.dm⁻³). The ochreous precipitates were characterized by methods of X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and B.E.T. method for measuring the specific surface area and porosity. The dominant phases were ferrihydrite with goethite or goethite with lepidocrocite.

INTRODUCTION

Historical and current mining of coal, gold, polymetallic ores, left in the world a lot of dumps of waste material, tailings, abandoned mines, shafts, adits, etc. Sulphide minerals in these deposits by aerobic conditions (air and water) are liable to microbio-chemical biodegradation by acidophilic chemotrophic microorganisms (namely genera *Acidithiobacillus* and *Archaea*) and as a result are acid mine drainage (AMD) [1-5]. AMD is strongly acidic sulphate water (pH 1-3) and it contains, except of primary products of the pyrite oxidation (H₂SO₄, Fe), also other solubilised metals (Cu, Pb, Zn, Al, etc.) depending on the composition of deposited waste rock.

Depending on the conditions (pH, sulphate concentration, time, etc.) various precipitates are formed of solid phases of ferric oxyhydroxides (ochre precipitates) from AMD, like jarosite precipitate [(NaKH₃O⁺)Fe₃(SO₄)₂(OH)₆], ferrihydrite (Fe₅HO₈.4H₂O), goethite (α -FeOOH), schwertmanite [Fe₈O₈(OH)₆SO₄] or usually mixtures of these [6-10]. Mixtures of different minerals are often observed, partly due to transformation processes to thermodynamically more stable minerals [11].

Ferric oxyhydroxides can be precipitated in the natural conditions, e.g. after mixing, or diluting AMD with fresh surface water, in the drainage channels, in other places of mine water discharge (adits, settling pits, etc.). Mineralogical and geochemical evidence of both

the ochre precipitated and the water collected from the surroundings of seven closed sulphide mines in Finland showed that in the spring, after the snowmelt, the acid mine sludge formed was predominantly schwertmannite, which was partly transformed during warm summer months to goethite [12]. The upper portion of the sediment column within a compost wetland, constructed for AMD treatment in Athens Country, Ohio, contained predominantly schwertmanite but there have been signs of transformation phase to goethite observed, the goethite amount increased in proportion with the depth [13]. Although schwertmanite is metastable with respect of goethite, experiments at the abandoned As mine in Nishimoka, showed that transformation of schwertmanite to goethite may be retarded by the presence of absorbed As⁵⁺ in the structure [14]. Schwertmanite (in acidic field) and ferrihydrite (in neutral pH), containing of As and Sb, were identified in the ochreous sediments from four abandoned Sb deposits in Slovakia. In older sediments ferrihydrite transforms to more stable goethite [15]. Ochre precipitates from the AMD sites around coalfield of Assam (India) mainly consist of goethite, schwertmanite, ferrihydrite and jarosite. Formation of ferrihydrite was favoured at high organic carbon content in the water effluent. Role of bacteria for the formation of minerals were also observed [16]. Ochre precipitates deposited water draining of sulphide-rich lignite in abandoned mine Sokolov basin (Czech Republic), showed marked variation in colour and mineralogy as a function

of effluent pH [17]. Under acidic condition (pH 3.7) orange precipitate with dominated schwertmanite was formed. The reddish-brown ferrihydrite was observed in the alkaline effluent (pH 7.3) that has not been affected by mine drainage. Colour variation could be served as indicators of genetic environments under which the minerals were formed.

Iron oxides can be precipitated also extracellularly by various organisms [18]. Precipitation is frequently a by-product of metabolic process involving iron (Fe^{2+}) as an energy resource and has important significance for the circulation of iron [19]. Iron precipitating bacteria such as *Gallionella*, *Leptotrix* and *Siderocapsa* require lower pH and Eh than for abiotic precipitation. Various forms and unique shape of *Gallionella ferruginea* and other bacterium – like cocci or spheres and rods or cylindrical organism were revealed by SEM photographs of ochreous precipitates. The cell wall of *Gallionella* species in the ochreous precipitate was incrustated with Fe together with minor Si, Ca, Al, S. These bacteria are capable of promoting the absorption and crystallization of Fe and other elements [20]. The special-shaped microgoethite revealed in the sediment from Fushi Reservoir probably originated from biological activity, not from the weathering of siderite [21]. Ferric bacteria *Gallionella sp.* oxidize Fe^{2+} to Fe^{3+} and excrete formed $\text{Fe}(\text{OH})_3$ outside of cell as hydrosol that is gradually changed to weakly crystalline goethite. After the bacteria die, helicoid-shaped is retained by the goethite. Well-preserved cocoid *Archaea* and rod-shaped microbes were founded in the As-rich hydrous ferric, mainly goethite, but not in the lepidocrocite or jarosite from acid hot springs in the Waitape geothermal area, New Zealand [22]. Microbes probably mediated rapid oxidation of Fe^{2+} to Fe^{3+} , which was then rapidly co-precipitated with as a weakly crystalline goethite and such promoted mineralization and preservation of the microbes. Lack of microbes in the lepidocrocite and jarosite may reflect ecological controls that precluded microbe mineralization or reflect different precipitation rates.

This work is focused on the characterization of mine waters and ochre precipitates forming in the old mines - old adits and tailings for the extraction and processing of polymetallic ores in some mining regions of Slovakia.

MATERIALS AND METHODS

The samples were taken from the area after the old mining and metallurgical activity in the Banská Štiavnica and Hodruša-Vyhne ore field [23] and in the Slovenské Rudohorie – Smolník [24].

Locality and sample SM: settling pit is situated near Smolnícka Huta north-east of deposit of Cu-ore [24]. Mining and quarrying was finished in 1989. Waste dump and flotation refinement were displaced on this settling pit from 15th century to 1990 [25].

Locality and sample SE: settling pit Sedem Žien is situated among Banská Štiavnica and Banská Belá [26]. There were displaced flotation refinements of polymetallic ores processing of the plant Nová šachta from 1975 to 1994. Its reconstruction was completed in 1995 – 1997. Drainage water and Fe-sludges/ochre precipitates were removed from the body of a pond system of drainage channels.

Localities and samples V, H: are from the old adits near water reservoirs Belianská vodná nádrž and Dolnohodrušská vodná nádrž areas, recorded in mining maps from the 19th century, today there are only fragments.

Composition of mine water and Fe-sludge/ochre precipitates were determined at the Acme Analytical Laboratories (Vancouver), Ltd. by method ICP-ES/ICP-MS, group water analysis 2CA (2009), 2C (2010) and soil analyse (group analyses 1E) by 4 acid digestion analysis ICP-ES (www.acmelab.com). Content of sulphate was determinate by titration method using $\text{Pb}(\text{NO}_3)_2$ [27].

Diffraction patterns were collected with a PANalytical X'PertPRO diffractometer equipped with a conventional X-ray tube ($\text{Co}_{K\alpha}$ radiation, 40 kV, 30 mA, line focus) and a multichannel detector X'Celerator with an anti-scatter shield. X-ray patterns were measured in the range of 10 to 95° 2 Θ with step of 0.0167° and 1050 s counting per step. In this case we used conventional Bragg-Brentano geometry with 0.04 rad Soller slit, 0.5° divergence slit, 1° anti-scatter slit, 15 mm mask and Fe beta-filter in the incident beam, 5.5 mm anti-scatter slit and 0.05 rad Soller slit in the diffracted beam.

Qualitative analysis was performed with the HighScorePlus software package (PANalytical, The Netherlands, version 3.0d) and JCPDS PDF-2 database [28]. Structural morphology of the samples was revealed by SEM (Scanning Electron Microscopy). A Philips XL30CP microscope equipped with EDX (Energy Dispersive X-ray), Robinson, SE (Secondary Electron) and BSE (Back-Scattered Electron) detectors and a Jeol JSM-6510LV microscope equipped with an EDX and a WDX (Wavelength Dispersive X-ray) were used. For the observations in SE electrons the samples were coated with thin conductive Au-10 % Pd alloy layer. The EDX information is correct to about ± 3 %.

Specific surface area was determined by the B.E.T. (Brunauer-Emmett-Teller) method [29] from nitrogen adsorption-desorption isotherm acquired at liquid-nitrogen temperature using a NOVA 4200e instrument. A 12 h outgas at 80 °C was used before measurement.

RESULTS AND DISCUSSION

Mine water/AMD from described settling pits and old mine adits are slightly acidic water with dissolved sulphate salts of Ca, K, Na, Mg, Si (concentration range

in mg dm^{-3}). Minor compounds (concentration in mg l^{-1}) are represented by Fe, Al, Mn, Li, Co, Zn, Cu, As, Cr and others, as shown in Table 1. The concentration of ingredients may vary, slightly depending on the season of the year (in the summer are more concentrated than in the spring and autumn rainfall makes them more diluted). Mild acid value of water and solubilised sulphates could be the result of the biooxidation process (by the chemolithotrophic bacteria, mainly the genera *Acidithiobacillus*, and *Archaea*) of pyrite [30-32]. This microflora can be either a natural part of sulphide rocks, or has been passed through these rocks in the settling pit construction, as it was the case of the settling pit Sedem Žien. On the other hand, buffer capacity of other matrix is sufficient to neutralize the sulphuric acid formed by the bioprocess and the hydrolysis of ferric ion minerals. The occurrence of Si in the waters may be associated with the decomposition of quartz and aluminosilicates (the main component of settling pits) by inorganic and organic acid formed by bioprocessing [26].

These water effluents do not comply with the legislative criteria for the quality of surface waters (Gov. Reg. SR Nr. 269/2010 Coll.) in several parameters e.g. conductivity, content of sulphates and content of Mn, Fe, Al and Zn. However, these effluents do not contain

Table 1. Composition of acid mine drainage of settling pits and old mine adits (sample collected during summer season).

Locality - sample	Settling pit		Old mine adit	
	H	V	SE	SM
Parameters				
pH	5.60	5.90	6.05	5.75
Conductivity λ ($\mu\text{S cm}^{-1}$)	1035	1740	1667	1730
Sulphate concentration (mg dm^{-3})	1160	1840	1890	1905
Element concentration (mg dm^{-3})				
Ca	214	410	318	214
Mg	17.7	57.4	40.2	154
K	4.2	3.6	30.8	24.4
Na	7.7	14.6	15.4	11.3
Si	11.5	9.7	4.6	7.7
Element concentration ($\mu\text{g dm}^{-3}$)				
Fe	< 10	3020	43	< 10
Mn	810	4900	3200	31.7
Al	1170	594	6	5
Zn	62	50	1240	44.3
Cu	5.3	4.2	4.2	7
As	1.8	< 0.5	1.4	0.7
Cd	0.24	0.32	3.92	0.51
Cr	< 0.5	< 0.5	< 0.5	0.60
Ni	7	4.7	8.2	63.5
Co	120	200	30	96.3

Note: content of other elements (ppb. Pb: 1.0-1.4; P: 20-58; Se, W, Sb, Mo < 1).

heavy metals like As, Cr. Water effluents flow out from the adits and enter the water reservoirs (Belianská and Dolnohodušská vodná nádrž). Their flow is low and thus the impact on water quality in reservoirs is negligible (volumes of water in reservoirs represent several million m^3). Another situation is in the waters of settling pits. These drainage ditches channelled to the nearest streams, which can not only affect the quality and stream ecology, but also consequently the groundwater and soil. The solution could be microbial remediation, acid reduction microorganisms using the sediment sulphate reducing bacteria genera *Desulfovibrio*. Resulting in a formation of hydrogen sulfide (H_2S) and subsequent in a formation of metal sulphide precipitates [33-36]. Thus we can effectively reduce the levels of sulphates and metals. This principle has been tested in the case of AMD from the flooded mine and abandoned mine in Smolník area, Slovakia [37]. Negative impacts on the ecology of streams, could have fine Fe-sludge/ochre precipitate, which in these places occur and are drifted to the waters. Acid mine drainage are responsible for physical, chemical, and biological degradation of stream habitat. Iron hydroxides and oxyhydroxides may physically cover the surface of stream sediments and streambeds destroying habitat, diminishing availability of clean gravels used for spawning, and reducing benthic macro-invertebrates [38]. The AMD and iron precipitate discharge not only affected the total number of phytoplankton, but also affected negatively their group and species composition [39].

Creation of various forms of ferric oxyhydroxides is the result of complex abiotic and biotic processes occurring in ore and waste containing sulphide minerals. Element composition of the sludge samples were determined by ICP-ES method (determination of 22 elements) and semi-quantified by SEM-EDX. The results of elemental analysis show that the composition of the precipitates is similar and corresponds to a relatively pure ferric oxyhydroxides containing Fe in range of 42-46 %. The content of Mn, Ca, Al, and Zn is in the range of 0.1 to 1.5 %. Other elements are only the minor components of sludge (concentration below 0.01 %; Table 2). The presence of quartz was discovered by EDX

Table 2. Composition of ochre precipitate by method 4 acid digestion analysis ICP-ES (group analyses 1E, Acme Analytical Laboratories Ltd., Vancouver).

Fe- ochre precipitate element (%)	Samples			
	H	V	SE	SM
Fe	46	42.3	42.5	43.2
Al	0.58	0.9	0.12	0.56
Ca	0.72	0.86	1.42	1.05
S	0.70	0.11	0.32	0.51
Mn	0.15	2.1	0.41	0.48
Zn	0.03	0.04	0.67	0.80

Note: This method does not allow determination of Si.

analyses and X-ray diffraction analyses. This component is probably a result of contamination during sampling of the natural environment. Quartz particles (4-6 %) were partially covered with fine precipitate and could not be separated by sieving. Representation of other components by EDX is insignificant Al (1%), Ca (1-2 %), Cu (0.9-1.4 %), Zn (0.5-0.6 %), Mn (0.7 %).

Powder X-ray diffraction (XRD) was used for determining the phase composition of the collected samples. The results of the phase composition are presented in Table 3.

Table 3. Phase composition of natural ochreous precipitates from old mine adits and settling pits.

Sample	Phase composition
H	Gt, Ft, Sch, Ak, quartz
V	Gt, Ft, quartz
SE	Gt, Ft, quartz, Cu-Zn-Fe-oxides
SM	Gt, Le, mica (muscovite), chlorite

Note: Gt - goethite; Ft - ferrihydrite; Sch - schwertmannite; Le - lepidocrocite; Ak - akaganéite (β -FeOOH).

Weakly crystalline goethite was observed in all 4 samples collected in mixture with ferrihydrite (sample H, V, SE) and with lepidokrocide (sample SM). Schwertmanite and akagenéite were found only in the sludge of old mine adit H. Schwertmannite is thermodynamically unstable with respect to jarosite or goethite [40], but its formation from soluble oligomers requires less structural rearrangements and thus, the phase composition is influenced by kinetic factors. In the case of sample H, which is present in 4 phases of the Fe-oxyhydroxides, it can be assumed that the goethite was also indirectly transforming the previously precipitated schwertmannite and akagenéite, like in acidic sulphate-rich soils [41]. The occurrence of iron bacteria *Gallionella ochracea* and *Leptotrix ferruginea* in water over sediment, particularly in the area of V, supports the hypothesis of biologically induced precipitation of ferric oxyhydroxides [42]. In case of synthetic Fe-oxyhydroxides obtained at laboratory recovery from typical AMD by homogenous precipitation using urea and fractional precipitation using NaOH, the schwertmanite with goethite was observed [43, 44] and the process of their formation is probably affected by the pH value (pH 2-3) [7, 8]. While described natural Fe-products with main phases goethite and ferrihydrite were created in weak acid environment at low concentration of sulphates (pH 5.6-6.0; Table 1).

The results of specific surface area and porosity measurements of the sample from old settling pit SE is shown in Figure 1. All other samples (from old mine adits H, V and old settling pit SM) have almost the same curves. The observed hysteresis loops matched well to the H3 type hysteresis, which is usually found on solids with

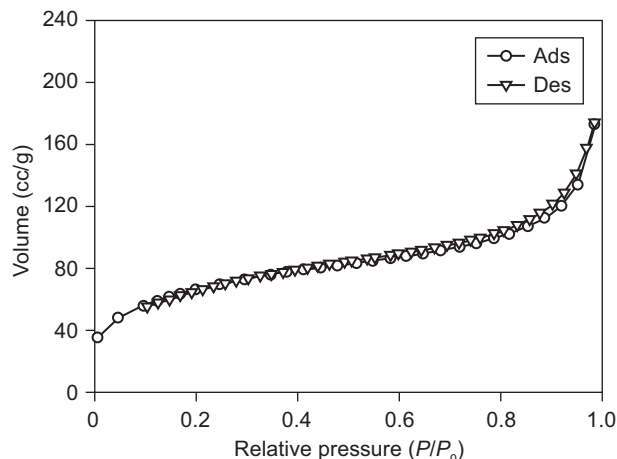


Figure 1. Nitrogen adsorption - desorption isotherm of sample SE

wide distribution of pore size (observed with aggregates of plate-like particles giving rise to slit-shaped pores) [45]. The surface area data are strongly correlated with the mesopore volume. Observed isotherms corresponds to isotherm type II, which is characteristic of the non-porous or macroporous (pore size > 50 nm) solids. The character of the hysteresis loops remained the same for all four samples corresponding to H3 hysteresis loop type. The hysteresis loops are very narrow, the adsorption and desorption branches being almost vertical and nearly parallel above 0.9 relative pressures, confirming the presence of a significant outer surface. The results of specific surface area and of porosity measurements are given in Table 4. The sample from settling pit SE had one of the lowest average pore size and higher specific surface area in comparison to the sample from old mine adit H which had the highest average pore size and the lowest specific surface area. It corresponds with micrographs from scanning electron microscope (Figure 2). The ochre precipitates are agglomerated in few mm aggregates. The samples have quite large surface area (in the range 150-250 m² g⁻¹) and they could be cheap and good adsorbents for removal of some pollutants from water environment [46-48].

Table 4. Specific surface area and porosity of samples found in old mine adits and settling pits.

Parameter	Samples			
	H	V	SE	SM
SA specific surface area (BET) (m ² g ⁻¹)	170	254	221	169
V _m monolayer volume (cm ³ g ⁻¹)	48.7	73.0	63.6	48.4
Total pore volume (cm ³ g ⁻¹)	0.323	0.323	0.268	0.246
Average pore size (nm)	7.72	5.17	4.86	5.84

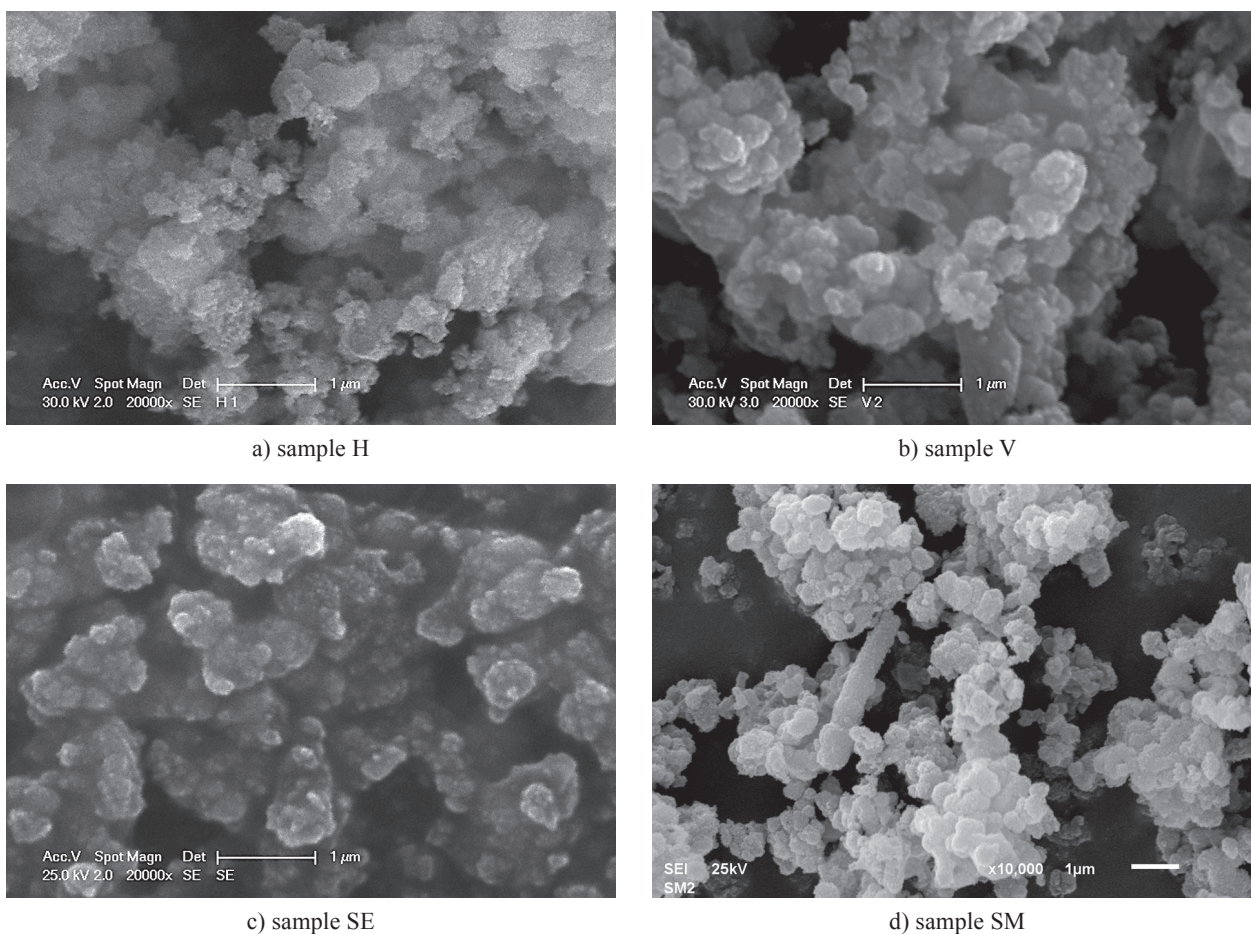


Figure 2. SEM micrographs of natural ochre precipitates: V and H - samples from old mine adits; SE and SM - samples from settling pits.

CONCLUSIONS

Tested acid mine drainage from old mine adits and settling pits do not introduce with their composition serious environmental risks of contamination of surface water and underground water and soil. Formation of ochre precipitate in natural conditions in controlled old mine adits and settling pits is the result of combination of various factors which leads to sub-microscopic Fe-particles production with quite high specific surface area (in range 157 – 254 m².g⁻¹). From the observed hysteresis loops which are usually found on solids with wide distribution of pore size it is visible that natural ochre materials have combination of mesopores and macropores and due to this property they could be potentially used like sorbents. The study of sorption properties of these natural ferric products and possibility of their application in the pollutant removal (like As, F, Cr, Pb, phosphates etc.) will be the aim of further experimental study.

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