



Brief Characterisation of Ochre from the Marta Adit (Nižná Slaná, Spiš-Gemer Ore Mts., Eastern Slovakia)

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Abstract

The contribution deals with the study on composition of ochre sample from the Marta adit at Nižná Slaná. Three samples were prepared from ochre by hand picking and screening, which were subjected to GA, AAS, XRF and XRD. Salts precipitated on surface at drying contain 17.7 % S (53 % as SO₄), 16.5 % MgO, 13.6 % Fe₂O₃, 3.54 % CaO and 1 % MnO. As to mineral composition, sulphates such as gypsum, starkeyite and rozenite are dominant. The fraction of grain size under 250 micron contains 30 % Fe₂O₃, 28.6 % SiO₂, 8 % Al₂O₃, 6.6 % CaO, 2.9 % MgO and 1.95 % S. Notable is content of arsenic in this fraction, which attain as high as 1.84 %. Quartz and gypsum occur as dominant crystalline phases. As to coarser fraction, i.e. under 150 microns, 44.5 % SiO₂, 16.8 % Fe₂O₃, 11.3 % Al₂O₃, 6.9 % CaO, 2.4 % MgO a 2.3 % C were assayed. Dominant quartz is accompanied by mica, plagioclase, ankerite and dolomite. It was shown that arsenic is bonded in finer grain size fraction.

Keywords: mineralogical composition, ochre, Nižná Slaná, Slovakia

Introduction

An occurrence of ochre in abandoned mining workings in Slovakia is fact known for narrow special-interest group. The formation of ochre is caused by weathering mainly by iron-containing minerals and problems of acid mine drainage (AMD) is connected with this process.

The most of problems with acid mine drainage are connected with oxidation of iron sulphidic minerals, that results in environment acidity increasing, release sulphates and metals. Although formation of acids and lixiviation of metals are usually connected with oxidative dissolving of sulphidic minerals, also other mineral groups, such as sulphates, carbonates, oxides and aluminosilicates can be source of metals in AMD. But just pyrite / marcasite (FeS₂), pyrrhotite (Fe_{1-x}S, (x = 0–0.17, IMA: Fe₇S₈)) and chalcopyrite (CuFeS₂) as the most common sulphides are at weathering also the most common source of acid mine drainage. The often contain isomorphous admixtures of trace elements and this fact results in contamination of AMD by high concentration of elements such as As, Cd, Cu, Mo, Ni, Pb, and Zn [1–3].

In Slovakia, the quality of mining waters, refuse heaps and settling pits drainages, quality of sediments / ochres in mining workings and an influence of effluents on quality of water and sediments in rivers is monitored in the areas of abandoned mines. Moreover, mechanism of sulphides weathering, contribution of microorganisms to their weathering processes, also influence of pH and temperature, climate on formation of secondary minerals, i.e. mainly ochres, as well as function of ochres at mobility of toxic elements in soils and water, and at toxic elements removing from waters are studied naturally not only in Slovakia [1, 4–8]. The

Smolník abandoned mine (eastern Slovakia) is studied in particular detail [9–12], but an attention is paid to localities such as Pezinok (western Slovakia) [9, 13], Banská Štiavnica (central Slovakia) [9, 14] and Poproč (eastern Slovakia) [15, 16]. So, the study on composition of ochre from Nižná Slaná may contribute to new knowledge and understanding about this issue.

Materials and Methods

The sample of ochre was taken from the Marta adit at Nižná Slaná (súradnice??). It was dried in laboratory drier MMM Venticell (Czech Republic) at temperature 105 °C. Then, white thin crust of precipitated salts was carefully removed (Fig. 1). A rest of sample, practically own ochre was subjected to sieving using vibratory sizer TE-III (Czech Republic) equipped by the screen of mesh size 250 µm. So, in such way, three samples were prepared, which were analysed by GA, AAS, XRF and XRD.

SiO₂ content was assayed gravimetrically (GA). Major elements, i.e. Fe, Al, Mg, Ca, Mn, K, Na and As have been analyzed by atomic absorption spectroscopy using the device VARIAN with accessories: Fast Sequential AAS AA240FS, Zeeman AAS AA240Z with Programmable Sample Dispenser PSD120, Graphite Tube Atomizer GTA120 and Vapor Generation Accessory VGA-77 (Australia).

Minor elements such as Ti, V, Cr, Co, Ni, Cu, Zn, Sb, Hg and Pb were determined using a SPECTRO XEPOS X-ray fluorescence spectrometer model XEPO3, range of elements: ¹¹Na–⁹²U, scattering targets: Mo, Co, Al₂O₃, Pd, HOPG-crystal, X-ray lamp (type VF50): Pd with Be window, resolution: 145 keV on line K α Mn. The sample for XRF analysis was dried and sieved to below 100 µm, then 5 g of sample were homogenized with 1 g of Clariant micro powder C (CEREOX BM-0002-1) and then pressed under 15 t to a pellet with a 32 mm diameter.

Carbon, hydrogen, nitrogen and sulfur were determined using a CHNS Vario MACRO Cube analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) equipped with a thermal conductivity detector. Helium (purity 99.995 %, intake pressure 2 bar) was chosen as a carrier gas in all analyses. The purity of oxygen for combustion was 99.995 % with intake pressure of 2 bar. The combustion tube was set at 1150°C, the reduction tube at 850°C. The sulfanilamide (C = 41.81 %, N = 16.26 %, H = 4.65 %, S = 18.62 %) was used as the CHNS standard.

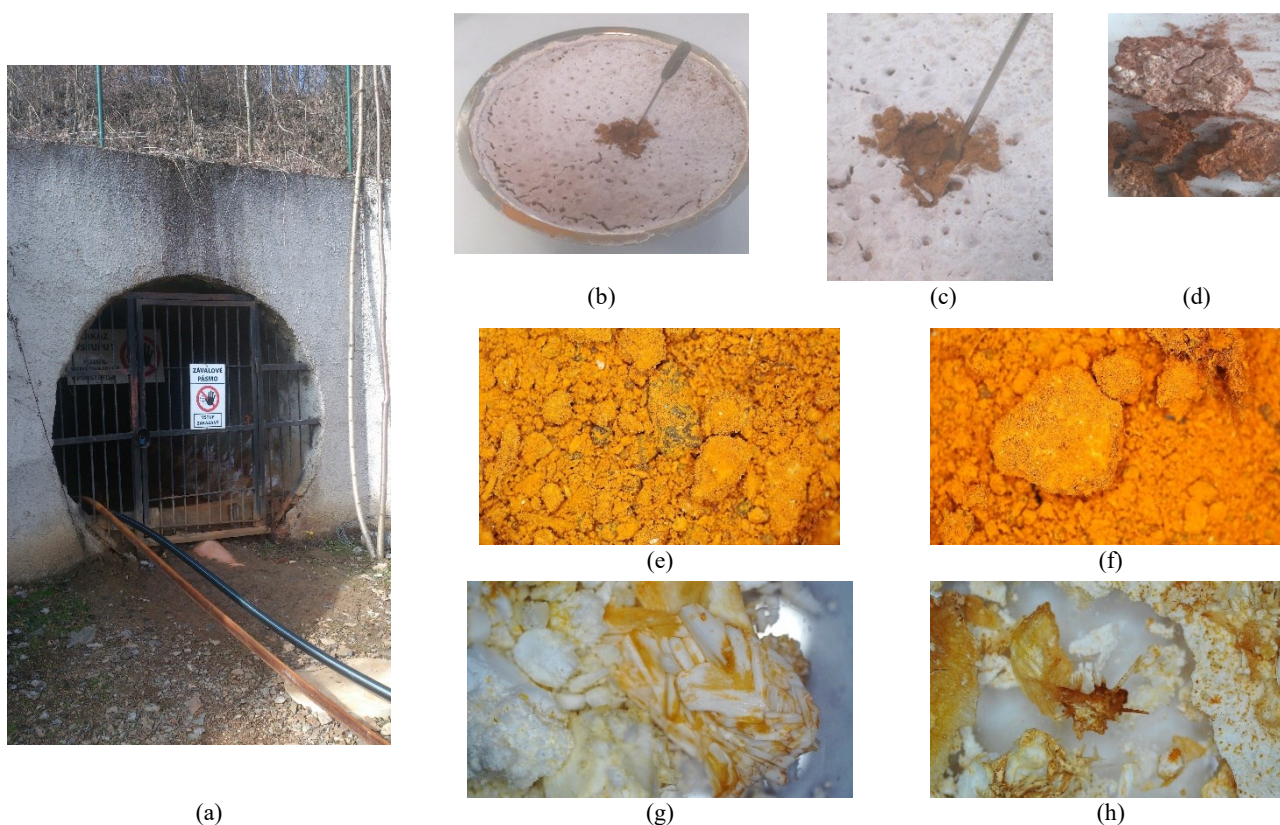


Fig. 1. Precipitated sulphates.

- (a) – the Marta adit, (b) – dried sample of ochre with crust formed from precipitated sulphate salts on surface, bowl diameter 25 cm, (c) – detail of (b), (d) – a piece of dried ochre with crust (upper piece width 4 cm), (e) and (f) ochre (mag. 25x) coarser grains coated by red (oxy)hydroxides (g) piece of crust obtained by air drying (mag. 15x), (e) piece of crust obtained by air drying (mag. 30x)

X-ray powder diffraction study was performed using D8 Advance diffractometer (Bruker, Germany), working with Cu K α radiation at voltage 30 kV and current 40 mA. The data were collected over the angular range $5^\circ < 2\theta < 80^\circ$ with measuring steps 0.03° and a counting time 5s. Measured diffractograms were processed using programs Diffracplus Basic and Excel. The databases such as webmineral, handbookofmineralogy and the Arizona bookcase were also used at mineral phases identification [17–19]. Abbreviations of minerals were used after [20].

Documentation of ochre sample was performed by mobile phone Sony Xperia. Optical observations were performed by monocular microscope Levenhuk (magnification max. 30x).

Results and Discussion

The results of chemical analyses are introduced in Tabs 1–2. XRD patterns are illustrated in Figs. 2–4.

Tab. 1. Composition of ochre fractions and salts precipitated during sample drying in %.

sample	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	MnO	As	C	H	N	S
sulphate salts	0.4	13.6	0.1	3.54	16.5	0.33	0.18	1.03	0.20	0.350	2.405	0.250	17.699
ochre -250 μm	28.6	30.1	8.2	6.58	2.9	0.93	0.76	0.26	1.84	1.755	1.240	0.305	1.949
ochre +250 μm	44.5	16.8	11.3	6.90	2.4	1.59	1.48	0.23	0.78	2.300	0.504	0.285	0.456

Tab. 2. Selected minor elements in ochre in ppm.

Column	Ti	V	Cr	Co	Ni	Cu	Zn	Sb	Hg	Pb
ochre	1385	51	< 1	89	282	37	481	220	< 1	1010

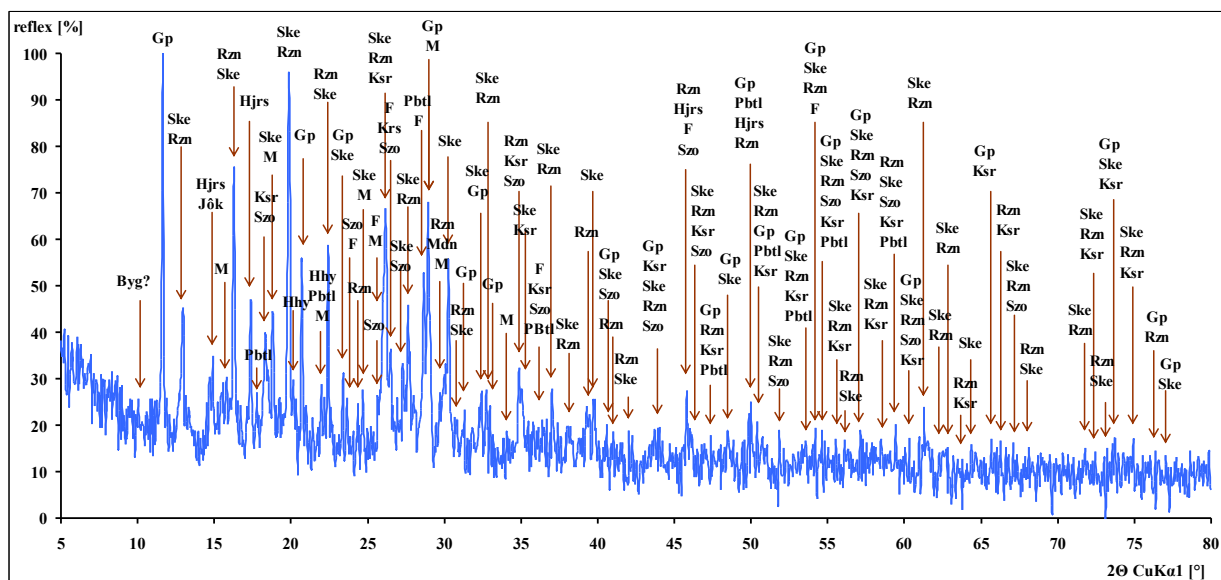


Fig. 2. XRD pattern of precipitated salts - interpretation.

Gp – gypsum – CaSO₄ • 2H₂O, Ske – starkeyite – MgSO₄ • 4H₂O, Rzn – rozenite – Fe²⁺SO₄ • 4H₂O, Szoz – szomolnokite – Fe²⁺SO₄ • H₂O, Ksr – kieserite – MgSO₄ • H₂O, Pbtl – parabutlerite – Fe³⁺(SO₄)(OH) • 2H₂O, Hhy – hexahydrate – MgSO₄ • 6H₂O, Hjrs – hydroniumjarosite – (H₃O)Fe³⁺₃(SO₄)₂(OH)₆, F – Iron Sulphate Hydrate - diiron(II) bis(sulphate(VI)) dihydrate – Fe₂(SO₄)₂ • (H₂O)₂ (card 01-085-5307), M – Magnesium Sulphate Hydrate - magnesium sulphate(VI) 2.5-hydrate Mg(SO₄) • (H₂O)_{2.5}, (card 01-077-9800), Byg – botryogen – MgFe³⁺(SO₄)₂(OH) • 7H₂O, Jök – jökokuite – Mn²⁺(SO₄) • 5(H₂O)

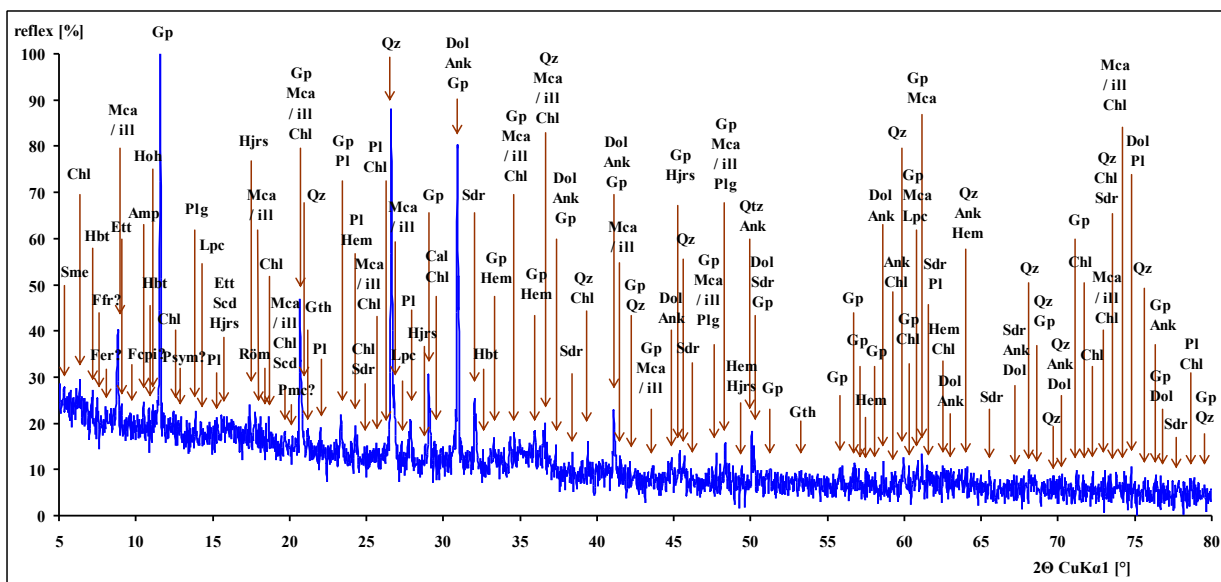


Fig. 3. XRD pattern of ochre fraction -250 micron - interpretation.

Gp – gypsum – CaSO₄ • 2H₂O, Qz – quartz – alpha-SiO₂, Mca/ill – mica/illite, most probably muscovite/sericite – KAl₂(AlSi₃O₁₀)(OH)₂, Hbt – hydrobiotite – K(Mg,Fe²⁺)₆(Si,Al)₈O₂₀(OH)₄ • nH₂O, Pl – plagioclase, most probably albite – NaAlSi₃O₈, Chl – chlorite (probably clinocllore), Sme – smectite, Dol – dolomite – CaMg(CO₃)₂, Ank – ankerite – Ca(Fe²⁺,Mg)(CO₃)₂, Sdr – siderite – Fe²⁺CO₃, Cal – calcite – CaCO₃, Gth – goethite – alpha-FeOOH, Lpc – lepidocrocite – gamma-FeOOH, Amp – amphibole, Hem – hematite – alpha-Fe₂O₃, Hjrs – hydroniumjarosite – (H₃O)Fe³⁺₃(SO₄)₂(OH)₆, Hoh – hohmannite – Fe³⁺₂(SO₄)₂O • 8H₂O, Röm – roemerite – Fe²⁺Fe³⁺₂(SO₄)₄ • 14H₂O, Ett – ettringite – Ca₆Al₂(SO₄)₃(OH)₁₂ • 26H₂O, Fcpi – ferricopiapite – Fe³⁺_{0.67}Fe³⁺₄(SO₄)₆(OH)₂ • 20H₂O, Scd – scorodite – Fe³⁺(AsO₄) • 2H₂O, Pmc – pharmacolite – Ca(AsO₃OH) • 2H₂O, Psym – parasymplesite – Fe³⁺₃(AsO₄)₂ • 8H₂O, Fer – ferrarisite – Ca₅(AsO₃OH)₂(AsO₄)₂ • 9H₂O, Ffr – fibroferrite – Fe³⁺(SO₄)(OH) • 5H₂O

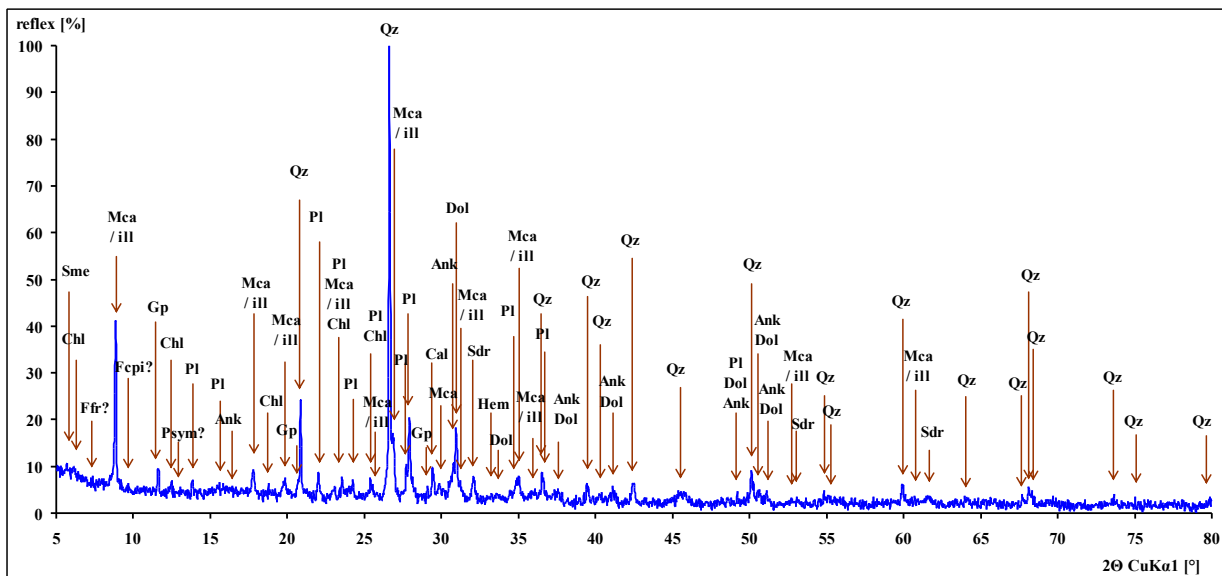


Fig. 4. XRD pattern of ochre fraction +250 micron - interpretation.

Qz – quartz – α - SiO_2 , Mca/ill – mica/illite, most probably muscovite/sericite – $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$,
 Pl – plagioclase, most probably albite – $\text{NaAlSi}_3\text{O}_8$, Gp – gypsum – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$,
 Chl – chlorite (probably clinocllore), Sme – smectite, Dol – dolomite – $\text{CaMg}(\text{CO}_3)_2$, Ank – ankerite – $\text{Ca}(\text{Fe}^{2+}, \text{Mg})(\text{CO}_3)_2$,
 Sdr – siderite – $\text{Fe}^{2+}\text{CO}_3$, Cal – calcite – CaCO_3 , Psym – parasymplesite – $\text{Fe}^{2+}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$,
 Fepi – ferricopiapite – $\text{Fe}^{3+}_{0.67}\text{Fe}^{2+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$, Ffr – fibroferrite – $\text{Fe}^{3+}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$

Chemical and mineralogical composition of precipitated salts depends on amount and quality of water, with which ochre is saturated. Thus during drying, saturated water elevated to the surface and evaporated and in such way calciferous, magnesium and iron sulphates precipitated.

The precipitated salts (Fig. 2) are dominantly represented by gypsum, starkeyite and rozenite. As accompanying minerals occur two unnamed phases iron sulfate hydrate or diiron(II) bis(sulfate(VI)) dehydrate, and magnesium sulfate hydrate or magnesium sulfate(VI) 2.5-hydrate, and also szomolnokite and kieserite. All other phases can be considered as accessories or their presence is questionable.

As to ochre fraction –250 microns (Fig. 3) gypsum and quartz are dominant. Accompanying minerals are represented by mica, plagioclase (albite), dolomite, and ankerite. Peaks of siderite and calcite are also well observable. On the other hand the peaks of goethite and lepidocrocite are low/weak. Significant amount of iron is bonded in amorphous $\text{Fe}(\text{OH})_3$. Other minerals occur as accessories or their presence is not sure, often only their main peak is recognisable.

Concerning ochre fraction +250 microns (Fig. 4) quartz is dominant mineral and it is accompanied by mica, plagioclase, ankerite and dolomite. Also peaks of siderite, gypsum chlorite are visible well. An occurrence of other phase they can be considered as accessories or their occurrence is questionable. Goethite and lepidocrocite were not identified.

So ochre from Nižná Slaná is formed mainly from primary barren minerals of this deposit, gypsum and also from only one valuable mineral, i.e. siderite [21]. Basic association is similar to Smolník (quartz, feldspar, mica, chlorite), but ochre from Nižná Slaná does not contain schwertmannite, and instead of jarosite in Smolník, most probably hydroniumjarosite occurs in Nižná Slaná. But the most difference is abundance of carbonates in ochre from Nižná Slaná.

Concerning arsenic as the most toxic mineral of this deposit it seems that it concentrates in finer fraction and can form individual mineral phases most probably scorodite – $\text{Fe}^{3+}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$, further pharmacolite – $\text{Ca}(\text{AsO}_3\text{OH}) \cdot 2\text{H}_2\text{O}$, parasymplesite – $\text{Fe}^{2+}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ and ferrarisite – $\text{Ca}_5(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2 \cdot 9\text{H}_2\text{O}$. From above mentioned implies that ochre limits arsenic mobility. Moreover there are huge amount of research works dealing with application of ochres or better said iron (oxy)hydroxides in arsenic removal from waters, or for this purpose synthetic iron (oxy)hydroxides are prepared. Besides above mentioned goethite and lepidocrocite, akaganite beta- FeOOH is known by its high affinity especially to arsenic [22].

Conclusion

Ochre from Nižná Slaná is formed mainly by primary minerals of deposits, such as quartz, mica, albite, chlorite, dolomite, ankerite, calcite, siderite and gypsum. Goethite and lepidocrocite occur only in finer grain size fraction of ochre. Chemical analysis showed that just finer fraction of ochre contain much more arsenic and iron (1.84 % As, 30.1 % Fe_2O_3), then coarser one (0.78 % As, 16.8 % Fe_2O_3). So it points to the fact that Fe (oxy)hydroxides limits of arsenic mobility at this locality.

Acknowledgments

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