MINERALOGY OF WEATHERING PRODUCTS OF MINE WASTES AT SELECTED DEPOSITS IN SLOVAKIA

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In this study, we have investigated secondary minerals forming in the environment of mine tailings at the localities Slovinky, Rudňany-Markušovce and Čučma. Siderite-barite-sulphide deposit Rudňany and siderite-sulphide deposit Slovinky were intensively mined for Cu and Fe ores. Sulphide minerals include mainly chalcopyrite, tetrahedrite, pyrite and arsenopyrite. Sulphides at Sb-Au deposit Čučma are represented mainly by stibnite, pyrite and arsenopyrite.

Samples were collected from mine tailing impoundments from several boreholes and dug wells. Samples were separated into light and heavy fraction by panning in water or in ethanol. Several greenish and reddish grains were separated from all tailing material with binocular loupe from locality Slovinky. Selected heavy-grain concentrates were prepared for further study in the form of standard thin and polished grain mounts, for inspection in transmitted and reflected polarized light, respectively. Chemical composition of the individual grains and oxidation rims were determined with a Cameca SX100 electron microprobe (ŠGÚDŠ, Bratislava) in wavelength dispersive mode under the operation conditions of 15 kV, 20 nA. Samples of interest were later prepared for μ-X-ray diffraction experiments. The μ-XRD data were collected at the beamline of the Synchrotron Radiation Laboratory for Environment Studies (SUL-X, Angströmquelle, Karlsruhe, Germany) in the synchrotron radiation source ANKA. All the μ-XRD patterns were preliminary evaluated by the DIFRAC^{plus}EVA software using PDF4 database. The 1D XRD patterns were then used for the Rietveld refinement with the programs GSAS and TOPAS.

The most common sulphides in flotation wastes at Markušovce and Slovinky are pyrite and chalcopyrite, tetrahedrite occurs rarely. At Čučma, pyrite is the most abundant sulphide; arsenopyrite and stibnite are less common. Primary oxides in tailing impoundments are represented by hematite (Markušovce), and valentinite (Čučma). Oxidation products can be divided into two groups: oxidation rims on primary sulphides and individual grains of secondary oxides. Oxidation rims on pyrite grains are composed of Fe oxides/hydroxides with enhanced amounts of elements such as Mg, Mn, Ca, Si, As, Cu and Sb. These oxides were mostly identified as a mixture of poorly crystalline goethite with amorphous Fe oxy-hydroxides. Rims on chalcopyrite grains are depleted in Cu, compared to primary sulphide and conversely enriched in As, Sb and Ca (Slovinky). Rims on arsenopyrite grains are often depleted in As compared to primary arsenopyrite and enriched in Ca, Si, Cu, Pb (Slovinky, Markušovce) and Sb (Čučma).

Goethite is the most frequent secondary mineral at all studied sites, hematite is also common. Goethite grains from Markušovce and Slovinky are often enriched in Cu (up to 1.29 at%), Si (2.91 at%), Mg (2.1 at%), Mn (2.14 at%), Sb (0.38 at%) and As (0.46 at%). Cell parameter *a* is in the range from 4.5599(7) Å to 4.69(9) Å, *b* from 9.88(2) Å to 10.02(2) Å and *c* from 3.00(10) Å to 3.056(9) Å, cell volume is in the range from 136.46 Å^3 to 141.25 Å^3. A significant positive correlation was observed between cell parameter *b* and Cu content (R = 0.94), which can indicate substitution of Cu for Fe in the structure of goethite. Goethite grains from Čučma have following cell parameters: *a* is in the range from 4.55(8) Å to 4.7(2) Å, *b* from 9.9(4) Å to 10.05(1) Å, *c* from 2.98(4) Å to 3.06(4) Å and cell volume is in the range from 136.6(4) Å^3 to 140.4(2) Å^3. Differences in cell parameters are caused probably by enhanced amounts of elements such as Sb, As, Cu, from which at least a part is probably incorporated directly into the structure of the mineral. At Slovinky, secondary Cu minerals occur also frequently and were identified as cuprite, malachite and azurite, or their mixture. Secondary mineral covellite was observed in few samples at Slovinky and Markušovce. Products of tetrahedrite oxidation (Markušovce, Slovinky) are represented by Fe oxy-hydroxides with remains of Cu, Sb, As, Hg and S (from primary ore), and enhanced amounts of Ca and Mg (adsorbed from pore solutions). At Čučma, where the content of Sb is high in the tailing impoundment minerals from roméite group (pyrochlore supergroup) and tripuhyite were also identified.

Acknowledgement. This study was supported by the Slovak Research and Development Agency under the contract No. APVV-0663-10 and APVV-VMSP-P-0115-09.