SUMMARY

The mineralogy and the chemistry of slags from medieval Pb-Ag smelting were studied. The archaeological site at Bohutín dating from 14-15th century is located in the historical mining/smelting district of Příbram in the Czech Republic. The aim of this work was to determine the general chemical and mineralogical composition of slags, mineralogy of phases, bulk metal and metalloid contents and finally their binding in the individual phases through a combination of the following analytical methods: (X-ray diffraction analysis, optical and scanning electron microscopy, electron microprobe, Raman spectroscopy). On the basis of these results we tried to restore the historical conditions of ore smelting and processing.

The slags are mainly composed of Fe- or Mn-Fe silicates (olivine-type phases), clinopyroxenes and rare oxide phases (magnetite). The commonest phase is a silicate glass enriched in Pb (up to 49 wt. % PbO). The grains of quartz and feldspars form the residual phase, which is derived from the unmelted gangue. Metals are mainly bound in sulphides and intermetallic compounds forming droplets or inclusions (< 1 μm to tens of μm in size) trapped within the silicate glass. The following sulphide and metallic phases were identified: galena (PbS), wurtzite (ZnS), pyrrhotite ($Fe_{1-x}S$), covellite (CuS), chalkocite (Cu_2S), chalcopyrite ($CuFeS_2$), other Cu-Fe sulphides and complex intermetallic compounds of Sb, Sn, Ni, Cu, As and Fe. The relics of organic matter (charcoal) identified by Raman spectroscopy were observed in one sample of slag.

The slag melt crystallization and solidification proceeded in a very short time. The textures of olivine (dendrites) show that the cooling regime of the slag melt was extremely rapid (in some cases up to 1450 °C/h). The melting temperature of slags was established about 900 – 1200 °C. The bulk chemistry of the slags show that they are relatively poor in Ca (only up to 3.7 wt. % CaO) indicating that no calcite flux was added during the medieval smelting. However, high Fe content (up to 20 wt. % Fe_2O_3) corresponds to application of Fe fluxes in the furnace charge. Extremely high concentrations of Pb were observed (up to 34.4 wt. % PbO) indicating a relatively low efficiency of Pb recovery.

This investigation show that both chemical and mineralogical compositions of historical slags are strongly influenced by ores and gangue compositions, fluxes added, charcoal and wood ashes, processing and cooling conditions.

Key-words: slags, Pb-Ag ores, medieval smelting, metallurgy, mineralogy.