

Experimental formation of Pb, Sn, Ge and Sb sulfides, selenides and chlorides in the presence of sal ammoniac: A contribution to the understanding of the mineral formation processes in coal wastes self-burning

František Laufek (1), František Veselovsky (1), Milan Drábek (1), Bohdan Křibek (1), and Mariana Klementová (2)

(1) Czech Geological Survey, Klárov 3, 118 21 Prague, Czech Republic, (2) Institute of Inorganic Chemistry of the AV CR, v.v.i., 250 68 Řež, Czech Republic

The formation of sulfides, selenides and chlorides was experimentally studied at 800 or 900°C in the presence of sal ammoniac in a sealed silica glass tube. Synthetic PbS, PbSe, SnS, GeS, SnGeS₂, PbSnS₃, SnS and Sb₂S₃ or natural uraninite were used as a starting charge. Depending on the chemical composition of the sulfide/selenide charge, galena, unnamed SnGeS₃ phase, herzenbergite, berndite, ottemannite, stibnite and unnamed SnSb₂S₄ and Sn₂Sb₃S₆ phases were identified in sublimates, together with cotunnite and an unnamed (NH₄)₂SnCl₆ phase. When natural uraninite in a mixture with sal ammoniac was used as a charge, the reaction product comprised abundant cotunnite and minor chalcocolloite due to volatilization of radiogenic lead. When sulfur was introduced to the charge with uraninite and sal ammoniac, galena was found in reaction products. The results of our experiments revealed that if sulfide or selenide phases and NH₄Cl are placed in a thermal gradient, it is possible to accelerate their mobility through a process of hydrogen chloride vapor transport. Within the transport process, new solid products are either isochemical or non-isochemical. The isochemical composition of resulting phases with charge probably represents simple sublimation of the original solid phase in form of self-vapor. The non-isochemical phases are probably formed due to combination of sublimation and condensation of various gas components including gaseous HCl. The valency change of metals (e.g. Sn²⁺ to Sn³⁺) in several reaction products indicates redox reactions in the gas mixture or during the solidification of resulting products.

The role of ammoniac is not clear; however, formation of unnamed (NH₄)₂SnCl₆ compound identified in one of our experiment, indicate possible formation of ammonium complexes.

In contrast to experiments where sulfides or selenides were used as a part of charge, mobility of uraninite was not proved under experimental conditions employed. It is consistent with an absence of uranium minerals in products of self-burning. The product of uraninite thermal decomposition was predominantly lead chloride (cotunnite) resulting from the release of radiogenic lead from uraninite structure. However, when sulfur was added to the charge, skeletal crystals of galena were found in the reaction products.

Acknowledgments: This study was carried out within the Czech Science Foundation grant project “A model of mobilization and geochemical cycles of potentially hazardous elements and organic compounds in burnt coal heaps” (GACR 15-11674S panel P210).