

Abstract

The presented dissertation attempts to contribute to the current knowledge on the arsenic (As) mineralogical speciation in diverse types of solid materials, such as contaminated soils and mine wastes.

Introductory part of the dissertation provides a general introduction to As chemical and physical characteristics and to the behavior in the environment, with the main emphasis on As solid phase speciation in soils and mine wastes.

Next part of the dissertation summarizes and briefly evaluates mineralogical methods to the study of primary and secondary As-bearing phases. The main aim is to help with better orientation in the application of these methods. The literature review showed that although a rank of modern methods have been developed in last years (HAADF-STEM, AFM, BFM, PIXE, XAS techniques, ND, etc.), there remain several established methods (XRD, SEM, etc.) as a starting step for mineralogical research. Some other group of methods has been found as possible useful for the study of As solid phase speciation (e.g., RS, DTA, TGA, Vis DRS, VMP).

The main part of the dissertation is presented as a set of three papers on similar subjects published in scientific journals - Environmental Geology, Science of the Total Environment and Geoderma.

The following geochemical and mineralogical methods and approaches were used to achieve the particular aims (summarized collectively): soil samples were characterized by its pH, chemical composition (by X-ray fluorescence, XRF), carbonate, humus, exchangeable cations and H⁺, and oxalate extractable Fe contents. Mineralogical and chemical speciation of the As was studied by mineralogical methods and sequential extraction: the As-bearing minerals were concentrated by several ways (panning, heavy fluids) and determined using X-ray diffraction analysis (XRD), the Debye-Scherrer powder method, scanning electron microscopy equipped with an energy-dispersive microanalysis (SEM-EDX), electron microprobe analysis (EMPA) and Raman spectroscopy.

The first published paper titled "Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ)" describes research of the soil, mine tailing, and waste dump profiles above three mesothermal gold deposits in the Bohemian Massif with different anthropogenic histories. The amorphous hydrous ferric oxides, As-bearing goethite, K-Ba- or Ca-Fe- and Fe- arsenates pharmacosiderite, arsenosiderite, and scorodite, and sulphate-arsenate pitticite were determined as products of arsenopyrite or arsenian pyrite oxidation. The As behaviour in the profiles studied differs in dependence on the surface morphology, chemical and mineralogical composition of the soil, mine wastes, oxidation conditions, pH, presence of (or distance from) primary As-mineralisation in the bedrock, and duration of the weathering effect. Although the primary As-mineralisation and the bedrock chemical composition are roughly similar, there are distinct differences in the As behaviour amongst the Mokrsko, Roudný and Kašperské Hory deposits.

The aims of the second paper titled "Oxidation of the arsenic-rich concentrate at the Přebuz abandoned mine (Erzgebirge Mts., CZ): mineralogical evolution" were: I) To study the oxidation of two most common primary As minerals, arsenopyrite and löllingite, stored in a unique anthropogenic deposit; and II) To evaluate As contamination in the close surroundings of this deposit. The studied concentrate (ore concentrate with up to 65 wt.% of As) contains very small proportion (<5 vol.%) of gangue minerals such as quartz and feldspars; the oxidation of arsenopyrite and löllingite (and accessory pyrite) is thus practically not complicated by interference with additional minerals and elements. Arsenolite, scorodite, kaatialaite and native sulphur were found to be the main secondary phases originating by dissolution of arsenopyrite and löllingite. New secondary phases precipitate on the surface of the ore-concentrate body but also form cement among the grains of finely milled material. The following succession of secondary minerals was determined: arsenolite, scorodite + native sulphur and kaatialaite. Significant As migration into the proximal environment was revealed: 2580 and 13,622 mg.kg⁻¹ were the highest arsenic concentrations in two sections excavated at distances of 0.5 and 1.5 m from the concentrate body.

The third paper titled "Mineralogical speciation of arsenic in soils above the Mokrsko-west gold deposit, Czech Republic" was aimed at the natural soil profiles contaminated by As at the Mokrsko gold deposit. The aims of the paper were: I) To determine mineralogical speciation of As throughout the whole soil profiles. II) To verify a possible relationship among some selected pedological parameters and As-bearing secondary minerals. III) To test a representative sample of sequential extractions developed for soils contaminated by As and compare the obtained data with knowledge accomplished during the mineralogical studies. Results were compared and discussed regarding the two different types of soil environment: I) soil developed above the flat unforested granodiorite bedrock and II) soil developed above the volcanosedimentary bedrock in a sloping forested area. Iron (III) oxyhydroxides; K(-Ba) pharmacosiderite, arseniosiderite, scorodite, and jarosite were identified as products of arsenopyrite. Arsenates of varying chemical compositions dominate the soil above the granodiorite, while goethite, minor hematite and other indistinguishable FOHs are observed in the soil above the volcanosediments. The diversity and stability of the As secondary minerals in the studied soils are influenced partly by variation in the bedrock composition and mainly by the presence/absence of vegetation cover which mirrors in various contents of exchangeable Ca^{2+} , content of Fe oxalate, and pH. The results of the sequential extraction show an average to high As retention by these soils, when As was extracted during the third and fourth extraction steps (NH_4 -oxalate buffer, ascorbic acid) in most samples. This finding indicates that As is more mobile in soils where arsenates dominate over well crystallized Iron (III) oxyhydroxides.

Key words: soil, mine wastes, applied mineralogy and geochemistry, arsenic (As), As solid phase speciation, secondary As minerals

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