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Arsenate uptake by gypsum: a neutron diffraction study

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Gypsum $CaSO_4 2H_2O$ is one of the more common minerals in sedimentary environments. It is a major rock forming mineral that produces massive beds, usually from precipitation out of highly saline waters. Gypsum is also a common industrial by-product from a number of processes involving neutralization of sulphuric acid. Most by-product gypsum is disposed of in landfill sites, although an estimated 20% is used as a construction material and in agriculture (.....Miller, 1995). Its agronomic uses include the improvement of soil structure in saline and sodic soils (...............Shainberg et al., 1989) and alleviation of soil acidity (........Oates and Caldwell, 1985). However, industrial by-products can contain heavy metals, As, salts and other possible contaminants and their use as soil amendments may be constrained by a lack of knowledge about their potential environmental effects. Arsenic contamination of drinking water supplies is a word-wide problem of increasing concern. Last years, increased attention has focused on the occurrence, origin and mobility of arsenic in natural waters. This attention has been motivated by concern over the human heath effects of arsenic long term low level exposure (.....Smedley and Kinniburgh, 2002; ....Harvey et al., 2002]).The presence of arsenic in metallurgical and mining circuits increased the production cost, interferes with metal extractions, deteriorated the product purity, presents environmental hazards and creates disposal problems (........Piret and Melin, 1989). Hydrometallurgical processes produce mostly soluble arsenic compounds, which are usually eliminated by precipitation and impoundment. The problems associated with the present practices of arsenic disposal are the generation of large volumes of ferric oxyhydroxide and gypsum sludges upon neutralization of arsenic rich acidic solutions and the long term stability of those sludges.

The reactions developed during As (V) uptake by gypsum from aqueous solution were characterized by Neutron Diffraction structural studies. Gypsum was synthesized under three different pH conditions (4, 7.5 and 9) by addition of Na_2SO_4 and $CaCl_2$ solutions doped with As(V).These samples were studied using a two-axis diffractometer (D20) located at the High Flux Reactor of Institut Laue Langevin, Grenoble, France. This instrument has a large position sensitive detector in a banana-like configuration, allowing whole spectra to be collected at once. A monochromatic neutron beam (1.3 Å) is diffracted by powdered samples placed in cylindrical vanadium containers and neutrons are registered as function of scattering angle with an angular range of 120º. The neutron diffraction patterns were processed with the full-pattern analysis Rietveld method to refine the crystal structure. For each sample lattice constants of unit cell were determined; I2/c space group was assumed for gypsum structure. Under the hypothesis of replacement of sulfates by arsenates, the variation of the unit cell volume was simulated by using the software VASP (Vienna Ab-initio Simulation Package).

Our results show that incorporation of As in gypsum produces the expansion and deformation of the unit cell, as it is demonstrated by the different evolution of three lattice constants. Neutron powder diffraction experiments show changes in the volume cell which are in good agreement with the thermodynamical data taken from the literature: the biggest expansion of the unit cell is found at pH 9, where it exists the highest concentration of the specie AsO_4^{-3}. Our experimental results were constrasted against those obtained from numerical simulations of the interatomic potentials, which allow a quantitative estimate of the As(V) in the gypsum lattice.

The evolution and stability of this solid solution have a great relevance in environmental chemistry because it is a possible mechanism for the immobilization of As in natural environments.

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