

Dr. MANUEL A. CARABALLO SHORT-TERM VISIT FIMIN REPORT

Calculation of the "field" solubility constant range for schwertmannite: an essential tool for the geochemical modeling and environmental characterization of AMD affected systems.

After previous field works done by myself in collaboration with Professor Dr. José Miguel Nieto's group in the Iberian Pyrite Belt (SW Spain), we found some interesting results concerning the link between AMD water hydrochemistry, schwertmannite bulk chemistry and the solubility constant (Ks) of this mineral. However, some additional field samples and laboratory work are needed to efficiently cover this topic. The aim of the present project is to calculate a "field" Ks for schwertmannite using the wide range of AMD water chemistries that can be found in the Odiel and Tinto Basins.

The calculation of schwertmannite's Ks is an issue that has been faced from laboratory to field studies during the last two decades and it has been observed that this mineral is better defined by a range of Ks rather than using a single value. The reliable determination of this Ks range using field conditions will have a significant impact on the hydrochemistry of AMD systems and specially on the use of geochemical models in AMD environments because schwertmannite can be considered the main Fe mineral phase controlling the hydrochemistry and mineralogy of the system. The findings of this study are not restricted to AMD polluted streams; in addition they can be employed in other systems dominated by Fe where the precipitation of schwertmannite plays a key role (e.g., acidic soils).

1. DESCRIPTION OF THE WORK CARRIED OUT DURING THE VISIT

As previously mention, the main aim of this short-term visit was to obtain new water and solid samples to complement an existing work.

To obtain the needed information several steps were required: first of all a field sampling campaign was performed to get the solid and water samples of this study. Secondly, the solid samples were conditioned before finally studying them and the water samples by the use of different analytical techniques.

1.1. Field Sampling:

For a sampling point to be considered valid, schwertmannite has to be the only Fe mineral phase comprising the precipitates. This approach implies that it is impossible to know (apart from a guessing based on the experience of the researcher taking the sample) if a sample is going to be valid until a XRD study or other mineralogical technique is employed to know the mineralogy of the sample.

During this field campaign 4 valid and 2 invalid samples were obtained. The reduced number of samples obtained is explained because only some specific sampling points used in a previous campaign were selected in the current campaign. This sampling strategy responded to the need of study the effects that the hydrochemical seasonal variations have on the mineralogy of the precipitates.

1.1.1 Water Sampling:

Water samples in direct contact with the precipitates were sampled. Those samples were filtered immediately after collection through 0.1 μ m Millipore filters on Millipore syringe filter holders, acidified in the field to pH < 1 with suprapur HNO₃ and stored at 4 °C in 60 mL sterile polypropylene containers until analyzed.

Temperature and electrical conductivity were measured in the field using a portable CM35 meter (Crison®) with 3 points calibration (147 and 1413 μ S·cm⁻¹ and 12.88 mS·cm⁻¹). The pH and redox potential (Eh) were measured using a PH25 meter (Crison®) with Crison electrodes. Eh and pH were controlled and calibrated using 2 points (240–470 mV) and 3 points (pH 4.01–7.00–9.21), respectively, with Crison standard solutions. Dissolved O₂ was measured with an auto-calibrating Hanna® portable meter.

1.1.2. Solid Sampling:

Solid samples were collected from the water courses using filtering technique or directly recollecting the most superficial precipitates from the streambed depending on each sampling points conditions. The samples were air dried at room temperature in the laboratory and were ground to powder using a tungsten-carbide mill.

1.2. Laboratory analyses:

Concentrations of dissolved Al, As, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, Pb, S, Si, Sr and Zn in water samples and in solid samples after being submitted to pseudo-total digestion procedure using HNO₃ were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES Jobin-Yvon Ultima2).

Multi-element standard solutions prepared from single certified standards supplied by SCP SCIENCE were used for calibration. They were run at the beginning and at the end of each analytical series. Certified Reference Material SRM-1640 NIST freshwater- type and inter-laboratory standard IRMM-N3 wastewater test materials (European Commission Institute for Reference Materials and Measurements) were also analyzed. No significant differences were found between the certified values and the experimental concentrations measured. Detection limits were calculated by average and standard deviations from 10 blanks. Detection limits were: 200 μ g l⁻¹ for Al, Fe, Mn, Mg, Na, Si and S; 500 μ g l⁻¹ for Ca; 50 μ g l⁻¹ for Zn; 5 μ g l⁻¹ for Cu; 2

$\mu\text{g l}^{-1}$ for As and $1 \mu\text{g l}^{-1}$ for the other trace elements.

The X-ray diffraction (XRD) study of randomly oriented powder samples was performed using a Bruker D5005 X-ray Diffractometer with Cu $K\alpha$ radiation at the CRSUH. Diffractometer settings were: 40 kV, 30 mA and a scan range of $2-65^\circ 2\theta$, $0.01^\circ 2\theta$ step size and 12-s counting time per step.

2. DESCRIPTION OF THE MAIN RESULTS OBTAINED

At the time of writing this report, the mineralogical and chemical characterization of the seven solid samples obtained was accomplished as well as the study of the water chemistry of the seven sampling points. These results shown than only two of the seven sampling points were invalid for this study purpose due to the presence of jarosite and goethite in addition to schwertmannite.

The obtained results complement the existing database that will be used to calculate the solubility constant range for schwertmannite.

Thanks to the increase in the previous database by the inclusion of these new data, not only a more reliable and extent calculation of schwertmannite's solubility constant will be obtain but also correlations between parental water chemistry and precipitated schwertmannite bulk chemistry is going to be address by the use of statistical analyses.

3. PROJECTED PUBLICATIONS / ARTICLES RESULTING OR TO RESULT FROM THE GRANT

In the following three months the database, finally completed after this sampling campaign, will be studied and the results obtained employed to write a paper in a journal included in the science citation index. The high quality of the data obtained as well as the relevance of the information suggested at this point by these results will certainly place this research in a top journal in the areas of Geochemistry, Mineralogy, Water Resources or Environmental Sciences.