Testing and Applications of a Thermodynamic Database for the Hydrogeochemical Modelling of Acid Mine Brines

/ *PATRICIA ACERO SALAZAR (1,*), CARLOS AYORA IBÁÑEZ (2), LUIS FRANCISCO AUQUÉ SANZ (1), MARIA PILAR ASTA ANDRÉS (1), MARIA JOSÉ GIMENO SERRANO (1), JAVIER GÓMEZ JIMÉNEZ (1), JUAN M.A.MANDADO COLLADO (1), MARIA PILAR LAPUENTE MERCADAL (1)*

(1) Petrology and Geochemistry Area, Earth Sciences Department, University of Zaragoza, C/Pedro Cerbuna 12. 50009, Zaragoza (Spain)
(2) Institut for Environmental Diagnosis and Water Studies, IDAEA- CSIC, C/Jordi Girona, 18. 08028, Barcelona (Spain)

INTRODUCTION.

Acid brines are frequently generated in the pore spaces of mine tailings due to the oxidation of sulphide minerals and to the dissolution of other accompanying mineral phases. This situation is especially accused in abandoned mine tailings exposed to weathering in areas with arid or sub-arid climate, in which amounts of dissolved solids of several hundreds of grams have been frequently measured (Moncur *et al*., 2005; Acero *et al*., 2008). These extremely high concentrations represent a major difficulty during the geochemical modelling of these acid waters, since they prevent from using the usual Ion Association models for the calculation of the activity coefficients of dissolved species.

A usual strategy in this situation is using the Pitzer ion interaction model (Pitzer, 1973), which requires the previous estimation of ion interaction coefficients among the target elements in the modelled case. Unfortunately, many of the most important ion-ion interactions in hypersaline acid waters, involving Fe^{2+}, Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+}, SO_4^{2-} and other ions, are poorly included in the hydrogeochemical databases.

In this study, a thermodynamic database for the hydrogeochemical modelling of acid mine brines using the Pitzer ion interaction approach was compiled and a test of its thermodynamic consistency was carried out.

METHODOLOGY.

The extensive set of data on ion interaction coefficients compiled by Tosca *et al.* (2005) for the hydrogeochemical modelling of Martian brines was used as a starting point, and the interaction coefficients for iron, aluminium, copper and zinc (Reardon and Beckie, 1987; Reardon, 1988) were added. For the equilibrium constants of mineral phases, the thermodynamic database WATEQ4f.dat (Ball and Nordstrom, 1991) was used as the main data source and it was expanded to include several hydrated and non-hydrated sulphates and oxy-hydroxy-sulphate mineral phases.

Apart from the gathering of literature data for the thermodynamic database, a compilation of calculated and experimental solubility values for several single and binary salt systems was carried out. Especial emphasis was put on including relevant data for the most usual mineral phases in acid mine environments, such as melanterite, halotrichite, alunogen, chalcantite, pickeringite, jarosite or epsomite. The aim of this compilation is to serve as a base for checking the apparent thermodynamic consistency of the resulting thermodynamic database. These testing exercised were carried out using the PHREEQC geochemical code (Parkhurst and Appelo, 1999).

RESULTS AND DISCUSSION.

As depicted in Fig. 1 for some of the test cases run, the performance of the

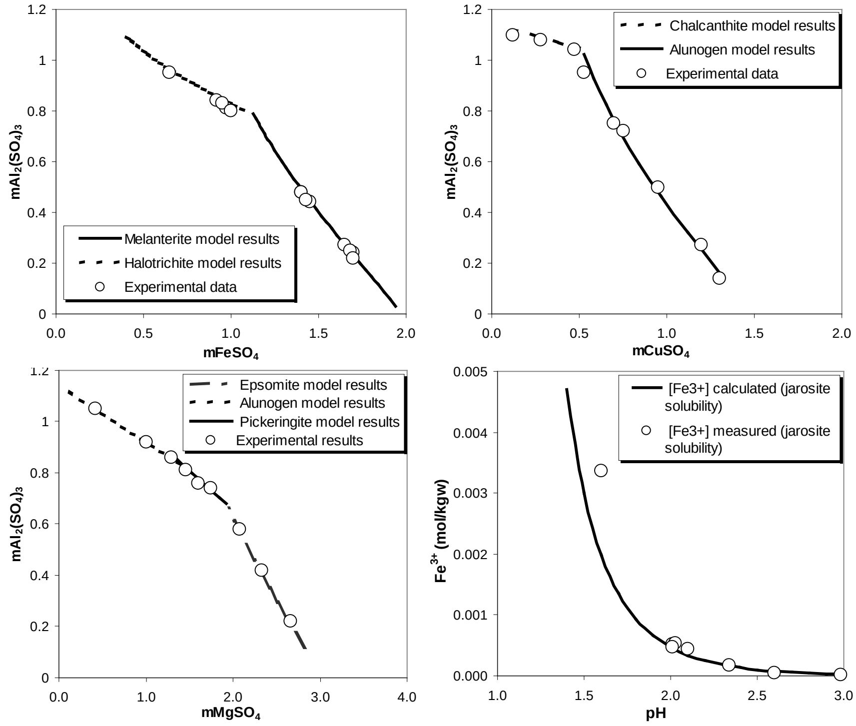

fig 1. *Comparison of some of the experimental and simulated results of mineral solubility using the thermodynamic database for specific ion interactions in acid mine brines, used as a check for the apparent thermodynamic consistency of the whole set of compiled data.*

palabras clave: Drenaje Ácido de Mina, Modelización Termodinámica, Salmuera, Pitzer.

key words: Acid Mine Drainage, Thermodynamic Modeling, Brine, Pitzer.

* corresponding author: **patriace@unizar.es**

resulting thermodynamic database for reproducing the experimental and calculated solubility data for several single and binary mineral systems found in the literature was very good. As a general trend, simulated solubilities matched almost perfectly the corresponding data obtained in experiments, which indicates that the database developed in this study is apparently thermodynamically consistent.

Real-Case Application of the Developec Database.

Once the thermodynamic database was compiled and its apparent consistency tested, it was used to reproduce the main geochemical features and processes observed during several column experiments carried out using mine tailings. For these experiments, ten columns were filled with fresh and water-saturated mine waste from a tailings impoundment. Each column was placed under an infrared bulb, which acted as a constant heat source throughout the 125-day experiment. The crust formed on top of the columns was sampled and studied at different stages of increasing dryness and ionic strength of the pore water solutions. Pore water compositions obtained by squeezing of portions of columns at different depths and at different stages of evaporation

Speciation-solubility calculations carried out with the enhanced database and with the assistance of the PHREEQC code provided with results fully consistent with the mineralogical and hydrochemical evolution observed during the column experiments. Furthermore, a reactive transport model using the database and the RETRASO-CODE_BRIGHT code (Saaltink *et al*., 2004) reproduced the same mineral association and the time sequence of minerals precipitating on top of the columns throughout the experiment, as well as the evolution of pore water compositions at different column depths and times.

CONCLUSIONS.

The database for specific ion interactions developed in this study has been proven to be thermodynamically sound and to adequately reproduce by numerical simulations not only the experimental data obtained for many binary and ternary systems in earlier works but also the data obtained in evaporative column experiments specifically designed to study the behaviour of acid mine brines (Ionic Strength even above 15 m).

The enhanced database will allov simulating hypersaline and complex acic water systems and to account for man water-mineral interactions not taken intc consideration in earlier scientific anc technical studies.

AKNOWLEDGEMENTS.

The work has been partially supported by the Spanish National R+D Project CTM2007-66724-C02-01/TECNO. Patricia Acero is supported by a Contract of the Program “Juan de la Cierva” of the Spanish Government.

REFERENCES.

Acero, P., Ayora, C., Carrera, J. (2007): Coupled thermal, hydraulic and geochemical evolution of pyritic tailings in unsaturated column experiments Geochimica et Cosmochimica Acta, ***71****, 5325-5338.*

Ball, J. & Nordstrom, D.K. (1991): User’s manual for WATEQ4f with revised thermodynamic database and test cases for calculating speciation of major, trace and redox elements in natural waters. U.S. Geological Survey Water-Resources Investigation Report 91-183.

Moncur, M., Ptacek, C., Blowes, D., Jambor, J. (2005): Release, transport and attenuation of metals from an old tailings impoundment. Appl. Geochem., ***20****(3), 639–659.*

Reardon, E.J. (1988): Ion interaction parameters for AlSO4 and application to the prediction of metal sulfate solubility in binary salt systems. J. Phys. Chem., ***92****(22), 6426–6431.*

Reardon, E.J., Beckie, R.D. (1987): Modelling chemical-equilibria of acid-mine drainage - the FeSO4-H2SO4-H2O system. Geochim. et Cosmochim. Acta, ***51*** *(9), 2355–2368.*

Parkhurst, D. L. & Appelo, C.A.J. (1999): User's Guide to PHREEQC (Version 2), a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water Resources Research Investigations Report 99-4259, 312 p.

Pitzer, K.S. (1973): Thermodynamics of electrolytes. 1. Theoretical basis and general equations. J. Phys. Chem., ***77****(2), 268–277.*

Saaltink, M.W., Batlle, F., Ayora, C., Olivella, S., (2004): RETRASO, a code for modelling reactive transport in saturated and unsaturated porous media. Geol. Acta, ***2****(3), 235–251.*

Tosca, N.J., McLennan, S.M., Clark, B.C., Grotzinger, J.P., Hurowitz, J.A., Knoll, A.H., Schroder, C., Squyres, S.W. (2005): Geochemical modeling of evaporation processes on Mars: Insight from the sedimentary record at Meridiani Planum. Earth. Planet. Sci. Lett., ***240****(1), 122–148.*