

## **Ionization of H<sub>2</sub>O – saturated CO<sub>2</sub> at PT conditions relevant to CCS**

RYAN M. CAPOBIANCO<sup>1\*</sup>, MIROSLAW S. GRUSZKIEWICZ<sup>2</sup>,  
ROBERT J. BODNAR<sup>1</sup>, J. DONALD RIMSTIDT<sup>1</sup>

<sup>1</sup>Department of Geosciences, Virginia Tech, Blacksburg, USA,  
rcapobi@vt.edu (\* presenting author)

<sup>2</sup>Oak Ridge National Laboratory, Oak Ridge, USA,  
gruszkiewicz@ornl.gov

Recent studies have shown that mineral carbonation reactions proceed rapidly in the presence of CO<sub>2</sub> – rich (“supercritical”) H<sub>2</sub>O – CO<sub>2</sub> fluids at temperatures and pressures relevant to Carbon Capture and Storage (CCS) [1][2]. These earlier studies suggest that reactions are occurring on the mineral surface (or in a thin film of aqueous fluid), rather than as dissolution – precipitation mediated by the bulk fluid, as is the case in aqueous geochemistry. This has important implications for CCS in saline aquifers, as the CO<sub>2</sub> – rich phase is positively buoyant with respect to existing brine and will be the fluid in contact with cap rock. Reactions between the CO<sub>2</sub> – rich phase and the cap rock can enhance storage security (if carbonate minerals form) or degrade security (if the fluid corrodes the cap rock). It is well known that in aqueous solutions, H<sub>2</sub>O and CO<sub>2</sub> react to form H<sub>2</sub>CO<sub>3</sub> which ionizes and promotes dissolution – precipitation reactions. If significant ionization occurs in CO<sub>2</sub> – rich fluids under geologically relevant conditions, understanding reactions between H<sub>2</sub>O – saturated CO<sub>2</sub> and mineral phases present in the aquifer will be important when assessing risk associated with CCS.

When ionization occurs in a fluid, such as due to dissociation of H<sub>2</sub>CO<sub>3</sub>, it allows the fluid to conduct electricity. The conductivity of the fluid is related to the concentration of ions, their charge, solvation, and the physical properties of the fluid. In this study we measure the conductivity of H<sub>2</sub>O – saturated CO<sub>2</sub> solutions from 25 to 200°C and 7.39 to 20 MPa using a flow-through conductivity cell. Flow conductivity experiments reduce error associated with sorption to the walls of the cell and accumulation of impurities. Combined with a low cell constant (0.03/cm) we are able to detect conductivity on the order of pS to nS/cm.

In this study we show that conductivity of H<sub>2</sub>O – saturated CO<sub>2</sub> does not exceed 3nS/cm from 25-200°C and 7.39 to 20MPa. These conductivity values are comparable to “dry” CO<sub>2</sub> (< 3ppmw H<sub>2</sub>O), and indicate that little or no ionization is occurring. In addition, we show that there is no detectable relationship between H<sub>2</sub>O content and conductivity from < 1ppmw H<sub>2</sub>O to saturation. We conclude that at these conditions “wet” CO<sub>2</sub> has no significant ability to ionize.

[1] Schaef et al. (2011) *Geochimica et Cosmochimica Acta* **75**, 7458-7471. [2] Kwak et al. (2010) *J. Phys. Chem. C* **114**, 4126-4134.

## **Seasonal and inter-annual variations in emerging groundwater mine pollution: Essential background information for acid mine drainage management and remediation**

MANUEL A. CARABALLO<sup>1,2\*</sup>, FRANCISCO MACÍAS<sup>2</sup>,  
JOSÉ MIGUEL NIETO<sup>2</sup>, CARLOS AYORA<sup>3</sup> AND  
MICHAEL F. HOHELLA, JR.<sup>1</sup>

<sup>1</sup> Department of Geosciences, Virginia Tech, Blacksburg, VA  
24061, U.S.A., [manuelac@vt.edu](mailto:manuelac@vt.edu) (\*presenting author)

<sup>2</sup> Geology Department, University of Huelva, Campus “El Carmen”,  
E-21071 Huelva, Spain.

<sup>3</sup> Institute of Environmental Assessment and Water Research, CSIC,  
Jordi Girona 18, E-08034 Barcelona, Spain.

Design and development of water resources management and restoration strategies requires a deep understanding not only of the specific characteristic of the pollution affecting the water environment but specially of the possible short and long term cycles affecting the intensity of the pollution. The acid mine drainage (AMD) emerging from the adit of Mina Esperanza (Iberian Pyrite Belt, SW Spain) was selected as a typical AMD groundwater effluent from a sulfide mining district influenced by a dry (Mediterranean) climate. This point AMD discharge was monitored for more than four years to reveal the effect of seasonal and inter-annual weather changes in the water flow rate and pollutant concentration. Three well differentiated polluting stages were observed corresponding to: 1) stable low flow rate and high metals concentration, 2) increasing-decreasing cycle of both high to extreme metals concentration and flow rate, and 3) increasing-decreasing cycle of flow rate but steady high metals concentration. The specific processes and mechanism involved in the generation of these three stages (pyrite dissolution, evaporitic salts precipitation-redissolution and pluviometric inter-annual fluctuations) can be understood on the basis of the water chemistry and statistical analyses performed. Despite the almost negligible seasonal variations observed in the AMD pollution, the important variability observed in the inter-annual periods strongly recommends long-period AMD monitoring as essential background information for water resources management. This knowledge is being shown to be critical to efficiently perform environmental impact studies in these specific areas (sulfide mining and dry climates) and subsequently to design efficacious remediation strategies.