In-situ measurement of pH and dissolved gases in NaCl-bearing fluid at high temperatures and pressures

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The in-situ monitoring of aqueous solution chemistry at elevated temperatures and pressures is a major challenge in geochemistry. The direct and accurate pH measurement of aqueous systems is difficult to achieve above 100 °C, and hence is not made on a routine basis. Using an innovative methodology coupling in-situ Raman spectroscopy and potentiometry we measured simultaneously CO_2 dissolved concentration and pH in the H_2O-CO_2-NaCl system at temperature up to 280 °C, pressure up to 150 bar and salinity up to 1.4 molal [1]. The continuous in-situ pH monitoring is based on an oxygen-ion conducting ceramics sensor coupled to an external pressure balanced Ag/AgCl reference electrode. The pH sensor is composed of an yttria-stabilized zirconia ceramics tubing containing a dry Cu–Cu_2O internal reference element. We report for the first time in situ pH values for the H_2O-CO_2-NaCl system under hydrothermal conditions. A Pitzer specific-ion-interaction aqueous model based on carefully revised Pitzer coefficients valid at temperature up to 250 °C was further developed. The revised Pitzer parameters for the H_2O-CO_2-NaCl system are formatted for pitzer.dat thermodynamic database working with Phreeqc geochemical software and available for the scientific community. This model confirmed the accuracy and consistency of the measurements. The combination of in situ Raman spectroscopy and in situ pH measurement opens up new perspectives for the study of geological fluids and for the monitoring of high temperature, high pressure industrial processes (e.g. cooling circuits in nuclear power plant, CO_2-H_2S sequestration, ore processing). The method we described is of primary interest for quantification of gas mixtures (e.g. CO_2 + H_2S, CO_2 + SO_2) dissolved in hydrothermal fluids with a high degree of accuracy, without sampling and quenching the reaction fluid. The probes (pH and Raman) tested here can be applied for the continuous in situ monitoring of geothermal boreholes and oil/gas wells.

[1] Truche *et al*. (2016) GCA 177, 238-253.