

VAPOR-LIQUID PARTITIONING OF PHOSPHORIC ACID AND SODIUM PHOSPHATES

Mirosław S. Gruszkiewicz, Donald A. Palmer, and John M. Simonson
Aqueous Chemistry and Geochemistry Group, Chemical Sciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee, 37831

The volatility of phosphoric acid and sodium phosphates in aqueous solutions at temperatures reaching 350 °C is of interest to electric power utilities running water/steam cycles with various forms of phosphate treatment of boiler water. Sodium phosphates provide an adjustable alkaline environment and a buffer protecting from pH changes that can severely damage the boiler in a short time in case of impurity in-leakage in the feedwater. However, at high temperature the vaporous carryover of phosphate and sodium to the turbine and other parts of the cycle can be significant and contribute to solid deposits and corrosion.

Orthophosphoric acid is a relatively weak acid with very low vapor pressure over aqueous solutions at room temperature. Both the association and relative volatility of the acid increase as the dielectric constant of water decreases with increasing temperature. In alkaline solutions the concentration of the volatile neutral species is low, but the high concentration of sodium could still cause a significant carryover of sodium phosphates to the steam. In order to develop a quantitative model of sodium phosphate volatility in a wide range of temperatures and Na/PO₄ ratios, measurements of liquid and vapor compositions in a static equilibrium cell were conducted at ORNL between 150 °C and 350 °C. Vapor-liquid partitioning constants were determined using a general thermodynamic model of phosphoric acid and activity coefficients of sodium phosphates based on earlier high-temperature isopiestic measurements and the Pitzer ion-interaction equations. After a review of the available literature on speciation of phosphate solutions, only the four principal mononuclear species were included in the model.

The results indicate that the volatility of sodium dihydrogen phosphate causes a residual transfer of phosphate to steam that cannot be decreased by increasing pH. However, only at the highest temperatures where phosphate treatment is not recommended, would increasing pH cause an increase of phosphate carryover. Other phosphate species (HPO₄²⁻ and PO₄³⁻) can be considered practically nonvolatile. The thermodynamic model of vapor-liquid partitioning of impurities developed at ORNL suggests that the amount of vaporous carryover derived from pH-independent measurements may have been previously overestimated. The total vaporous carryover of phosphates is overwhelmed by the mechanical carryover of droplets of liquid with the steam. It could only be significant if more efficient steam separators were used in the future, or at extremely high temperature.

Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-00OR22725, Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.