



August 20, 1985

Dr. Malcom Knapp  
U.S. NRC  
623-SS  
Washington, D. C. 20555

Dear Dr. Knapp:

Thank you for your response to the YIN comments on the "Technical Position on the Determination of Radionuclide Solubility in Groundwater for Assessment of High Level Radionuclide Waste Isolation, NRC Technical Position" dated November 1984.

There is however, still some concern on the behalf of the YIN contractors regarding the NRC response to point 4.2 having to do with the control of pH.

We are enclosing our comments in this regard for your consideration.

Sincerely,

Russell Jim, Manager  
Nuclear Waste Program

enclosures

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AUG 09 1985

FROM: D.A. Crerar, V.V. Nguyen, and J. Ryan/EWA, Inc.

SUBJECT: Response to Comments made by Malcolm R. Knapp (NRC) to Russell Jim (Yakima Indian Nation) dated July 3, 1985 concerning EWA Comments on the "Technical Position on the Determination of Radionuclide Solubility in Groundwater for Assessment of High Level Radionuclide Waste Isolation, NRC Technical Position", Dated November 1984.

DATE: August 1, 1985

This note addresses the NRC response to point 4.2, specifically the paragraph: "It is not true that pH conditions are difficult to control precisely in experiments above 100°C. At the pressures expected in a HLW repository, boiling will occur at temperatures greater than 100°C. Buffering of hydrothermal solutions is a well-established method of controlling pH conditions."

This is an important point, and misunderstanding here by the NRC could create overconfidence in experimentally derived thermodynamic properties. The solubilities, stabilities and aqueous speciation of many compounds are pH-dependent. It is essential that the pH be accurately known in experiments which derive such pH-dependent properties; this is particularly true in cases where these thermodynamic properties are used to compute behavior in systems, such as HLW repositories, which differ significantly from the experimental conditions.

Many pH-buffering techniques have been developed to date for experimental hydrothermal systems (see reviews by Barnes, 1981; and Crerar et al., 1985). Typically these procedures do not provide highly accurate estimates of true pH under experimental conditions. It is important that the NRC be aware of the limitations in current

hydrothermal buffering techniques, since these limitations are frequently a major source of error in experimentally derived thermodynamic data.

Commonly used hydrothermal pH buffers include: combinations of salts and acids or bases -- for example,  $\text{NaHS} + \text{H}_2\text{S}$  or  $\text{NaHCO}_3 + \text{H}_2\text{CO}_3$  (e.g., Barnes, 1981; Crerar and Barnes, 1976); gas phase buffers such as  $\text{CO}_2$  (e.g., Crerar et al., 1978); silicate mineral pairs such as potassium feldspar + muscovite + quartz (e.g., Montoya and Hemley, 1975);  $\text{AgCl} + \text{Ag} + \text{HCl}$  combined pH and hydrogen fugacity buffer (Eugster, 1977); and flowing  $\text{H}_2$ -electrode EMF cells (e.g., Sweeton et al., 1973; Patterson et al., 1984). While high-temperature-pressure pH electrodes are currently in the developmental state (Niedrach et al., 1980), these are not yet suitable for work with complex hydrothermal systems because a useful, stable response cannot be maintained over sufficiently long periods of time, and because the electrode is readily fouled by dissolved electrolytes.

The flowing EMF cell has been successfully applied to the determination of acid ionization constants under hydrothermal conditions. However, it is of limited usefulness in experiments with simulated HLW both because of the flow configuration of the cell and because hydrogen fugacity is necessarily fixed at highly reducing values. The  $\text{AgCl}$  buffers function reliably only above  $400^\circ\text{C}$ , and the silicate buffers are very sluggish below  $350^\circ\text{C}$  (Uzdowski and Barnes, 1972).

The central problem in estimating true pH for the buffers summarized above is the dearth of thermodynamic data on hydrothermal systems in general. Taking the  $\text{CO}_2$  gas-phase pH buffer as an example, rough estimates of pH can be obtained from measured excess  $\text{CO}_2$

pressure and simple equilibrium calculations such as described by Crerar et al. (1978) for the system  $\text{CO}_2\text{-H}_2\text{O-NaCl}$ . However, truly accurate calculation of pH requires a complete equilibrium computation including all significant solution species; for multi-component chemical systems this becomes increasingly tenuous because fully reliable, experimentally-derived thermodynamic data are not yet available for most solution species (see discussion by Wood, 1985, for example). This problem applies to all pH control procedures where one or more solution components are used to buffer experimental pH. The problem becomes even more complex with silicate buffers such as K-mica + K-feldspar where the thermodynamic properties of the solid phases can vary significantly with the substitution of cations other than potassium; the thermodynamic properties of such systems have been measured experimentally only for the pure end-member phases, and even in these cases, the problem with computing true pH and chemical equilibrium for all solution species remains. In many applications, the solution species themselves are not well known or have been inadequately characterized -- this is in addition to the general lack of thermodynamic data for high-temperature aqueous species. Finally, activity coefficients have been measured experimentally for only a few simple salts under the anticipated hydrothermal conditions (Wood, 1984; Crerar et al., 1984); the activities and related thermodynamic properties of mixed electrolytes and species in multi-component hydrothermal systems are not yet available, and this imposes serious error on the calculation of pH in such systems.

While most such buffers cannot yet provide exact pH values at run conditions, they do permit general estimates of pH and they are useful

in maintaining a fixed, internally consistent pH. Unfortunately, the general acceptance of these buffers and their routine use in the experimental literature has lead to the widespread misconception that they do, in fact, give exact pH values. Most hydrothermal experimentalists are well aware of these limitations, but the problem may not always be apparent to those applying the experimentalists' data. The true pH at run conditions may differ by one or more units from estimated pH (based on estimated errors in typical data for high-temperature solution species); these discrepancies can produce considerable error in estimated thermodynamic properties such as the equilibrium constants of solubility reactions.

If the NRC knows of any on-going works that challenge these comments, we request that all specific information be made available to us for examination. This includes information on how to acquire direct access to observation of the experiments.

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