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Department of Nuclear Energy

November 30, 1983 WM Record File

WM Project 10/11/16

A-3167

Docket No. _____

Mr. Everett A. Wick
High Level Waste Licensing Management Branch
Division of Waste Management
Mail Stop 965 SS
U. S. Nuclear Regulatory Commission
Washington, D. C., 20555

Distribution:

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MR	DB	
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FOR JL, N.S.

Dear Mr. Wick:

We have read the review of our letter report on uncertainties in basalt reactions. The version of the report that was reviewed was written under restrictive conditions on both the content and the time allotted. The report was written as an informal critique of the BWIP SCR not as a scientific publication. We have already explained that originally we were asked not to include geological references. This letter was restricted to the waste package and near field problems not to geologic aspects of far field. The letter deals with basic concepts of thermodynamics. We are not aware of any argument that negates these concepts for geochemical systems. We are familiar with the discussion of errors by Anderson given by the reviewer. The original letter report addressed problems with the treatment of these reactions by DOE in the BWIP SCR. We do not believe the NRC or its contractors should, in the absence of supporting evidence, assume minimal uncertainties for the DOE assumptions. Our position was, and still is, that if the DOE quotes thermodynamic values without explaining how they were derived, the assumption that the errors can be random is not unreasonable. It is the responsibility of the authors of the SCR to defend arguments for minimal uncertainties. An expanded discussion on how the NBS and Kubaschewski treat uncertainties was included in the version of the report for the NRC research meeting.

Although Table 1 is no longer included in the new version of our report, we do not agree with the reviewer's comments on the inconsistency in the JANAF table. The statement quoted from our report is rigorously correct. If equilibrium occurs between Fe and FeO, FeO and Fe₃O₄ and Fe₃O₄ and Fe₂O₃, the O₂ fugacity must show the behavior we noted. The well known fact that the Fe-FeO equilibrium does not occur at low temperatures does not invalidate this. The reviewer is not distinguishing between consistency and validity. On occasion when a solid is known to be metastable or unstable, equilibrium reactions can be used to calculate approximate values. In those

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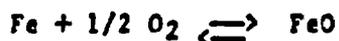
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cases the activity used for the metastable solid in the calculations must be greater than unity (i.e., the metastable form of the solid by definition has a higher value of the free energy than the stable form). Table 1 can only be made consistent by using activities of FeO that are less than unity. Thermodynamic tables are constructed to be internally consistent first and correct when possible. In discussing errors and new data, the NBS (NBS Tables of Chemical Thermodynamic Properties - J. Phys. Chem. Ref. Data Vol. II, Suppl. 2, 1982) notes,

"Newer measurements on some species have become available after their property values were fixed and used in subsequent calculations. It is not possible to incorporate all of these newer measurements into the tables without a detailed analysis of the effect of the changes on interrelated selections. Unless great care is used, relatively significant errors in the calculated values of $\Delta_f H^\circ$, $\Delta_f G^\circ$, or ΔS° for specific processes may result from the introduction of such data. The user is advised not to make these substitutions. They can be made only after careful examination of the measurement network. As an example, when the enthalpy of formation of $Al_2O_3 \cdot 3H_2O$, gibbsite, was changed recently, 45 other values had to be adjusted to maintain optimum relationships.

"The danger is that 'improving' one value for a property of one substance may distort calculated values for chemical processes. There may be compounds of the same element or distantly related substances for which the value in question was used as an auxiliary datum."

The point of Table 1 was that thermodynamic tables such as the JANAF tables list values for the equilibrium constant for reactions such as



even when such equilibria do not occur. The uncertainty treatments that the reviewer is quoting deal with data at temperatures where the reactions occur. The extrapolation of these uncertainties to other temperatures where these reactions may or may not occur is complex. It is our opinion that such tenuous extrapolations are not the responsibility of the regulatory agency or its contractors. Most of the reviewer's comments on his page 4 deal with second and third order effects that have little bearing on our paper. His ΔG test for consistency and his introduction of non-available Eh and pH values for estimating H_2 overpressures when H_2O appreciably decomposes, are the responsibility of the DOE, if they are necessary at all for these qualitative arguments.

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The discussion by the reviewer of dissolved oxygen in equilibrium with an f_{O_2} of 10^{-30} completely misses the point in our report that at low temperatures dissolved O_2 in water is generally not in equilibrium with the oxygen fugacity determined from the dissociation of water but is associated with whatever gas is above the water.

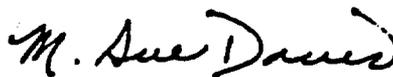
We are also aware of the fact that magnetite exists in nature. The experiments quoted in the original letter report (not in the revised version) deal with very high surface area powders of magnetite. We have been able to use such powders below $200^{\circ}C$ to separate H_2 to H_2O conversions from CO to CO_2 conversions because of kinetic effects. The experiments can be used to obtain upper bounds on the kinetics of magnetite-hematite conversions in high surface area powders relative to basalt. These limits are useful since the DOE in the SCR assume magnetite-hematite equilibria over long times at low temperatures. However, since they are being run in a non-waste management program, they are no longer mentioned in the revised version of this paper. The revised version also includes the references requested.

Finally, we find the reviewer's comment "there is no basis to state that radiolysis will be a major factor in waste package behavior..." unreasonable. Even the DOE recognizes that small changes in the aqueous environment induced by radiolysis can change the corrosion rates of canisters and the ion exchange properties of backfills. In the case of salt, radiation effects to the salt and radiolysis of the brine cause large chemical changes that affect the integrity of many candidate materials.

Sincerely,



Donald G. Schweitzer, Associate Chairman
Head, Nuclear Waste Management Division



M. Sue Davis, Deputy Division Head
Nuclear Waste Management Division

DGS:MSD:gfs
cc: D. Alexander, NRC